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Activated Persulfate and Hydrogen Peroxide Treatment of Highly Contaminated Water Matrices: A Comparative Study

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***Abstract*—The efficacy of Fe^{2+}-activated persulfate (PS) and hydrogen peroxide (HP) treatment in total organic load and selected organic pollutants removal from different highly polluted industrial effluents was evaluated and compared. The studied wastewater samples involved a paint production wastewater (S1), phenolic wastewater (S2) and mature landfill leachate (S3). The coagulation proved an effective technique to pre-treat S1, and thus to reduce substantially the amount of chemicals required in the subsequent oxidation step. The Fenton treatment (HP/Fe^{2+}) proved more effective S1 post-treatment technology than the PS/Fe^{2+} process and resulted in substantial COD and DOC removal as well as in considerable the BOD_7/COD ratio increase. In the case of S2 and S3, the application of Fenton process also demonstrated higher total organic load removal efficacy than the PS/Fe^{2+} system. Conversely, the HP/Fe^{2+} oxidation was characterized by a temperature increase and excessive foam formation. The findings of this study provide valuable information for further full-scale applications of Fe^{2+}-activated HP and PS based processes for the treatment of highly contaminated wastewater with the most effective concentrations of reagents used.**

***Index Terms*—Activated persulfate oxidation, Fenton process, organic contaminants, wastewater treatment.**

I. INTRODUCTION

The application of hydroxyl radical-based advanced oxidation technologies ($HO^{\bullet}$-AOTs) proved to be highly effective in degradation of persistent and bio-recalcitrant organic pollutants presented in various industrial effluents. The $HO^{\bullet}$ can be formed by the activation of hydrogen peroxide (HP, H_2O_2) and/or O_3 by transition metals, semiconductors, ultraviolet (UV)/visible and ultrasound (US) irradiation. The main benefits of $HO^{\bullet}$-AOTs include high reaction rates and non-selective oxidation due to hydroxyl radicals, which result in effective degradation of different pollutants and potential reduction of toxicity in the treated water and wastewater [1]-[7]. Among $HO^{\bullet}$-AOTs, the Fenton process is a widely studied and applied technique for wastewater treatment based on the generation of $HO^{\bullet}$ from HP activated by Fe^{2+} at preferably acidic pH ~3 [6], [8]-[10]. The commonly accepted mechanism of the Fenton process consists of the sequence of reactions, where $HO^{\bullet}$ are produced through Eq. (1) and the activator is regenerated via Eq. (2), or from reaction of Fe^{3+} with organic radicals [2], [3]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2)$$

Recently, the innovative treatment technique based on the persulfate (PS, $S_2O_8^{2-}$) oxidation has been studied as an alternative to $HO^{\bullet}$-AOTs for water matrices treatment [11]-[16]. The persulfate is a strong oxidant that after activation produce even stronger sulfate radical ($SO_4^{\bullet-}$) [13]. The main methods used for $SO_4^{\bullet-}$ generation are heat (Eq. (3)), UV or US irradiation (Eq. (4)) activation, transition metal ion (Eq. (5)) activation, alkaline activation, strong oxidant activation [13], [17].

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\bullet-} \quad (3)$$

$$S_2O_8^{2-} + \text{radiation} \rightarrow 2SO_4^{\bullet-} \quad (4)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{\bullet-} + SO_4^{2-} \quad (5)$$

The oxidation by $SO_4^{\bullet-}$ has several advantages over $HO^{\bullet}$-AOTs. Namely, different from $HO^{\bullet}$, $SO_4^{\bullet-}$ is more stable and selective for oxidizing unsaturated double and triple bonds as well as aromatic constituents [17]. Moreover, the SO_4^{2-}, which is the main product of PS decomposition, is innocuous for the environment. Therefore, the application of activated PS is usually suggested as a feasible selection for the advanced chemical oxidation of a wide range of contaminants. Furthermore, the structure of PS is a symmetrically substituted derivative of HP [18] and among different transition metals used in persulfate activation, Fe^{2+} is the most frequently applied metal. As a consequence, the oxidation by ferrous ion-activated PS has substantial degree of similarity with the HP/Fe^{2+} system, and the efficacy of both processes could be simply compared. Notably, during the ferrous ion-activated HP or PS treatment of industrial effluents, the oxidation and coagulation of ferric oxyhydroxides both contribute to the removal of the organic load. Conversely, practical application of these AOTs could be limited because of the large amount of ferric sludge generated during coagulation step unless the complete reuse of ferric oxyhydroxide sludge as an iron source in the following Fenton-based treatment is undertaken [19].

Therefore, the main purpose of this study was to evaluate and compare the potential of the HP/Fe^{2+} and PS/Fe^{2+} process in organic load and selected target compounds removal from

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three different highly polluted industrial effluents: a paint production wastewater, phenolic wastewater, and mature landfill leachate. It was proposed, that the results obtained within this study could help to expand the knowledge of ferrous ion-activated hydrogen peroxide and persulfate applicability to treat real high-strength industrial effluents.

II. MATERIALS AND METHODS

A. Chemicals and Materials

Hydrogen peroxide (PERDROGEN™, ≥30%), sodium persulfate ($Na_2S_2O_8$, ≥99%) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, ≥99%) were purchased from Sigma-Aldrich. All of the other chemicals were of reagent grade and used without further purification. Ultrapure water (Millipore Simplicity® UV System) was used to prepare the stock solutions. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) aqueous solutions were used to adjust the pH.

The studied real wastewater samples were comprised of: i) Sample 1 (S1) – a paint production wastewater consisting mainly of equipment wash water and residues of water-based multi-color paints, ii) Sample 2 (S2) – a phenolic wastewater formed during condensation of vapor from an oil shale thermal process, and iii) Sample 3 (S3) – a mature municipal landfill leachate. The collected effluents were stored at 4 ℃. The main properties of wastewater samples are presented in Table I.

TABLE I: THE MAIN PARAMETERS OF STUDIED WASTEWATER SAMPLES

Parameter (unit)	S1	S2	S3
COD (g/L)	42.3	40.1	9.8
DOC (g/L)	2.6	9	2.75
BOD_7 (g/L)	0.25	5.6	2.5
BOD_7/COD	0.006	0.14	0.26
TPC (g/L)	n/a	0.75	0.025
pH	7.75	8.9	7.85
TSS (g/L)	1.6	n/a	3.4
TS (g/L)	66.7	0.45	14
TFS (g/L)	8	0.34	9.4

n/a – not analyzed

B. Experimental Procedure

The coagulation with commercial ferric sulfate coagulant was performed in a jar test apparatus (Kemira). The sample S1 volume in each jar was 0.6 L. The coagulant doses varied in the range of 100-1000 mgFe/L. The operating conditions were as follows: 1 min of fast mixing at 400 rpm, 30 min of slow mixing at 40 rpm, and ~20 h of sedimentation.

All of the Fenton and PS/Fe^{2+} treatment trials were performed in batch mode and in non-buffered solutions at ambient room temperature (22 ±1 ℃). Effluent samples (0.5 L) were treated in a 1 L cylindrical glass reactor with a constant agitation speed (~300 rpm) for a period of 24 h. First, the activator ($FeSO_4 \cdot 7H_2O$) was added, and after its complete dissolution, the HP/Fe^{2+} or PS/Fe^{2+} oxidation was initiated by immediately adding oxidant. The initial pH (pH_0) of the wastewater samples was adjusted to 3 in the subsequent treatment, unless otherwise specified. The oxidation was terminated by addition of NaOH (2 or 10 M) to adjust the pH of the treated samples to ~8. This process was followed by a settling period of ~20 h. Finally, the supernatant was collected for further analysis. The wastewater oxidation experiments with non-activated HP and PS were conducted in identical reactors under the same treatment conditions for the respective activated oxidation trials.

All experiments were duplicated and the results of the analyses are presented as the mean with a standard deviation of at least three parallel replicates

C. Analytical Methods

The total solids (TS, 105 ℃), total suspended solids (TSS, 105 ℃), total fixed solids (TFS, 600 ℃), and the 7-day biochemical oxygen demand (BOD_7) were determined according to APHA [20]. The activated sludge used as a seed source in the BOD_7 test was obtained from a municipal wastewater treatment plant in Tallinn, Estonia, and was not acclimated before BOD_7 measurements. The chemical oxygen demand (COD) was determined using a closed reflux colorimetric method [20]. The correction for the hydrogen peroxide interference of the COD test was performed using the correlation equation reported by Kang et al. [21]. The pH was measured using a digital pH meter (Schott CG-840). The total iron concentration in the initial and treated samples was measured using an *o*-phenanthroline method [20]. The residual PS concentration in the treated samples was measured spectrophotometrically at λ=352 nm by a potassium iodide reaction with PS towards the formation of I_2 [22]. The residual HP concentration in the treated samples was measured spectrophotometrically at λ = 410 nm with titanium sulfate by a hydrogen peroxide-Ti^{4+} complex formation [23]. The total phenolic content (TPC) was measured spectrophotometrically with aminoantipyrine according to ISO 6439 [24]. The dissolved organic carbon (DOC) was measured in filtered (0.45 μm, CA membrane) wastewater samples using a TOC analyzer multi N/C® 3100 (Analytik Jena).

III. RESULTS AND DISCUSSION

A. Paint Manufacturing Wastewater Treatment

Coagulation with ferric sulfate was utilized to remove suspended organic and inorganic compounds from the highly loaded S1 (Table I) and to provide a pre-treatment step before subsequent advanced chemical oxidation. As a result, 96 and 85% of COD and DOC, respectively, were removed from the S1 wastewater at a coagulant dosage of 200 mgFe/L, mainly because of a considerable decrease in the TS (≥95%) and TSS (≥50%) concentration. Besides, more than a 10-fold increase in a BOD_7/COD ratio was observed in the pre-coagulated S1 (cS1), indicating effective bio-recalcitrant compounds removal during the coagulation step but still inadequate to ensure no inhibitory effect on the microbial activity of biomass. Therefore, the subsequent HP/Fe^{2+} and PS/Fe^{2+} experiments were conducted only with cS1 (COD = 1.17 g/L, DOC = 0.300 g/L) and the data presented in Figs. 1 and 2 indicates a purification efficacy of the oxidation process only.

The results of the Fenton treatment of cS1 at different COD/HP weight ratios after oxidation step (pH_0 3) and sedimentation phase (pH ~8) are shown in Fig. 1. The effect of HP concentration was studied for the Fenton treatment of cS1 at the fixed HP/Fe^{2+} weight ratio of 5/1, which is optimal for highly loaded wastewater treatment [8]. An increase in the applied Fenton reagent dose led to an improvement in wastewater treatment efficacy. Irrespective of HP concentration, the DOC removal was lower than COD reduction. It should be noted that at a $COD/HP/Fe^{2+}$ weight ratio of 1/1/0.2 the mineralization was twice less effective than COD removal. For higher oxidant doses ($COD/HP/Fe^{2+}$ weight ratio of 1/2/0.4 and 1/3/0.6) the extent of DOC removal was more comparable with reduction in COD. In the Fenton treated cS1, irrespective of HP concentration used, no traces of residual oxidant were detected.

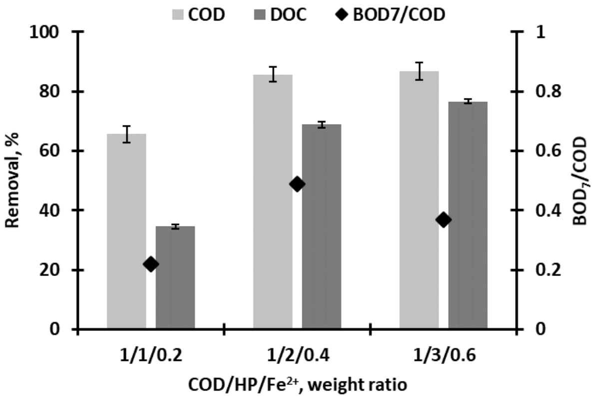

Fig. 1. COD and DOC removal and the BOD_7/COD ratio as a function of the $COD/HP/Fe^{2+}$ weight ratio in the HP/Fe^{2+} treatment of cS1 wastewater.

The most effective $COD/HP/Fe^{2+}$ weight ratio for the pre-coagulated S1 proved to be 1/2/0.4 resulting in 14 and 31% of residual COD and DOC, respectively. Additionally, the BOD_7/COD ratio increase was the highest at the same weight ratio and reached a final value of 0.49, which means more than a 6-fold and 81-fold increase compared to the pre-coagulated and initial S1, respectively.

The oxidative potential of non-activated HP was studied as well. The results of the oxidation at a COD/HP weight ratio of 1/2 indicated a negligible COD removal and more than 50% of unused HP in cS1 after 24 h of oxidation.

The ferrous ion-activated activated PS treatment experiments were also performed with a 24-h oxidation (pH_0 3) and ~20-h sedimentation step (pH ~8) to ensure the complete dissociation of PS and to simplify the comparison of the studied systems. Accordingly, the COD removal remained nearly identical in trials with a $COD/PS/Fe^{2+}$ weight ratio of 1/1/0.2, 1/2/0.4 and 1/3/0.6 and did not exceed 35% as presented in Fig. 2. The DOC removal was similar as well in all the ferrous ion-activated PS trials. In general, the mineralization was less effective than COD reduction and comprised no more than 7%. The residual PS was detected in all treated cS1 samples, but comprised less than 10%. Similar to the other studied parameters, the BOD_7/COD ratio was steady after the PS/Fe^{2+} treatment and nearly identical to the value obtained for the initial cS1.

The observed lower cS1 treatment efficacy by the PS/Fe^{2+} process as compared to the Fenton treatment can be explained by the absence of simultaneous ferrous ions oxidation and ferric ions reduction in the PS/Fe^{2+} system as presented in Eq. (2) for the Fenton process. The possible mechanism of PS ferrous ion activation may be described as follows [14]:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet -} + SO_4^{2-} \qquad (6)$$

$$SO_4^{\bullet -} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \qquad (7)$$

Accordingly, the reaction between PS and Fe^{2+} via Eq. (6) results in fast formation of $SO_4^{\bullet -}$. However, the $SO_4^{\bullet -}$ also reacts with Fe^{2+} and rapidly converts it to Fe^{3+} through Eq. (7). Consequently, the oxidation of Fe^{2+} to Fe^{3+} occurs not only in the generation of $SO_4^{\bullet -}$, but also in the conversion of $SO_4^{\bullet -}$ to SO_4^{2-}. The newly generated $SO_4^{\bullet -}$ reacts immediately though the competitive reactions with organic pollutants and excess Fe^{2+} resulting in lower degradation efficiency of the organic contaminants. In order to control the reaction presented in Eq. (7), the adjustment of activator dose could be done. Accordingly, three different $COD/PS/Fe^{2+}$ weight ratios of 1/1/0.1, 1/1/0.2, and 1/1/0.4 were used to treat the pre-coagulated S1 as presented in Fig. 2. The increase in COD and DOC removal was negligible with increase in the activator concentration. On the other hand, the dissociation of persulfate proved dependent on activator dose, and thus the residual PS concentration comprised 10, 7, and 1% at a $COD/PS/Fe^{2+}$ weight ratio of 1/1/0.1, 1/1/0.2, and 1/1/0.4, respectively.

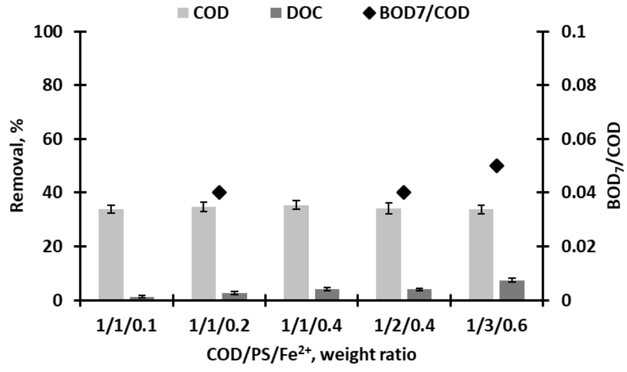

Fig. 2. COD and DOC removal and the BOD_7/COD ratio as a function of the $COD/PS/Fe^{2+}$ weight ratio in the PS/Fe^{2+} treatment of cS1 wastewater.

The results of the non-activated PS treatment at a COD/PS weight ratio of 1/2 indicated no changes in COD and DOC values and more than 93% of unused persulfate in cS1 after 24 h of oxidation.

In general, the application of the ferrous ion-activated PS process for the treatment of pre-coagulated paint production wastewater was less effective as compared to the Fenton process. The highest obtained overall COD and DOC removal was 99.5/96.5% and 98/89% for the pre-coagulation combined with HP/Fe^{2+} and PS/Fe^{2+} system, respectively.

B. Phenolic Wastewater Treatment

The results of S2 treatment by the Fenton system at different $COD/HP/Fe^{2+}$ weight ratios are presented in Fig. 3. Similar to the cS1 trials, the weight ratio of HP/Fe^{2+} was maintained at 5/1. As it was expected, an increase in the applied oxidant concentration led to an enhancement in the organic load removal (COD, DOC) and biodegradability (BOD_7/COD) of the treated S2 samples. In general, the mineralization was lower than the COD removal; e.g. at a COD/HP/Fe^{2+} weight ratio of 1/0.4/0.08, the DOC removal was two times less effective (29%) than the reduction in COD (58%). No traces of residual HP were detected in the treated S2 samples, indicating the complete dissociation of oxidant under the studied treatment conditions. The non-activated HP oxidation at a COD/HP weight ratio of 1/0.4 resulted in negligible organic contaminants degradation and more than 85% of unused HP after 24 h of treatment.

In the case of Fenton treatment trials without pH_0 adjustment, a fast drop in the pH of the reaction mixture was observed at the beginning of the oxidation most likely due to the acidity of the added Fenton reagents and the formation of acidic intermediates. Accordingly, the final pH (pH_f) values were lower than 2.7 in all the Fenton systems except for the treatment at a COD/HP/Fe^{2+} weight ratio of 1/0.4/0.08, which resulted in a pH_f of 4.22. Notably, the adjustment of the pH_0 to 3 prior to the addition of the reagents in the Fenton treatment at a COD/HP/Fe^{2+} weight ratio of 1/0.4/0.08 resulted in COD and DOC removal enhancement up to 11 and 5%, respectively.

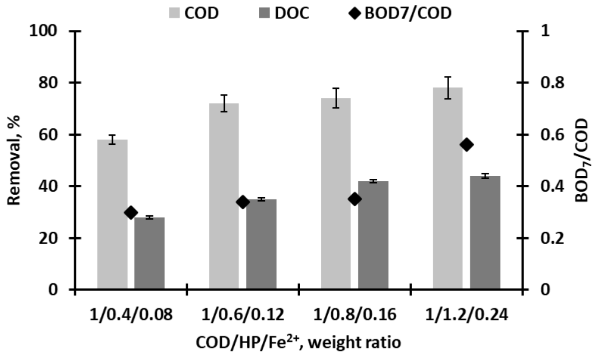

Fig. 3. COD and DOC removal and the BOD_7/COD ratio as a function of the COD/HP/Fe^{2+} weight ratio in the HP/Fe^{2+} treatment of S2 wastewater.

The temperature increase (T↑) and excessive foam formation immediately after activation of hydrogen peroxide belong to the main challenges in the full-scale application of the Fenton process for industrial wastewater treatment. In the present study, a moderate T↑ of 10 ℃ and foam formation of as much as 25% of the initial S2 sample volume were observed during treatment at a COD/HP/Fe^{2+} weight ratio of 1/0.4/0.08. However, the application of Fenton oxidation at a COD/HP/Fe^{2+} weight ratio of 1/1.2/0.24 resulted in a substantial T↑ of more than 50 ℃ and more aggressive foam formation as large as 300% of the initial sample volume. Accordingly, the addition of an anti-foaming agent as well as temperature monitoring may be required to control the foam production and exothermic reaction. To overcome these limitations, ferrous ion-activated persulfate was studied as an alternative process to treat the high-strength S2.

The application of PS/Fe^{2+} system resulted in lower organic load removal and biodegradability improvement than the Fenton process (Figs. 3 and 4). On the other hand, only negligible T↑ (2-4 ℃) and the complete exclusion of foam formation observed during the PS/Fe^{2+} oxidation makes this advanced method a viable solution for the treatment of S2.

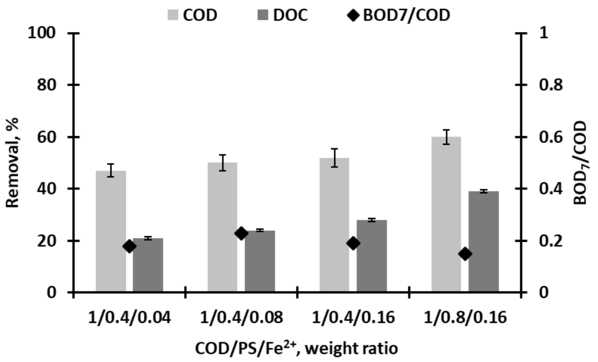

Fig. 4. COD and DOC removal and the BOD_7/COD ratio as a function of the COD/PS/Fe^{2+} weight ratio in the PS/Fe^{2+} treatment of S2 wastewater.

To assess the efficacy of the ferrous ion-activated persulfate oxidation, the effect of different oxidant and activator concentrations (Fig. 4) along with pH_0 adjustment to 3 was studied. The COD and DOC removal remained nearly identical after treatment at the fixed COD/PS weight ratio of 1/0.4 applying different PS/Fe^{2+} weight ratios. Conversely, a 2-fold increase in the PS concentration up to a COD/PS/Fe^{2+} weight ratio of 1/0.8/0.16 at the fixed PS/Fe^{2+} weight ratio of 5/1 resulted in an additional COD and DOC removal of 10 and 15%, respectively.

The results of the non-activated persulfate treatment at a COD/PS weight ratio of 1/0.4 resulted in considerable organic load elimination (COD and DOC removal comprised 47 and 11%, respectively). The BOD7 reduction was similar in all of the trials, resulting in a lower BOD7/COD ratio after treatment at a COD/PS/Fe^{2+} weight ratio of 1/0.8/0.16. Only traces of oxidant and more than 25% of undissociated PS were observed in the treated S2 samples after application of the ferrous ion-activated and non-activated persulfate, respectively. Similar to the HP/Fe^{2+} experiments, a fast decrease in the pH of the reaction mixture was observed at the beginning of the persulfate oxidation without pH_0 adjustment resulting in the pH_f values lower than 2.4 in all of the systems. The regulation of the pH_0 to ~3 applied to ensure presence of the Fe^{2+} at the beginning of the oxidation and thus to improve the treatment efficacy showed negligible improvement in the COD, DOC and BOD_7 removal.

Additionally, the efficacy of the studied AOTs in phenolic compounds degradation was evaluated. The results indicated that ≥90% decrease in TPC was attained both after the Fenton treatment and ferrous ion-activated PS process application.

C. Municipal Landfill Leachate Treatment

In the case of S3 trials, the oxidant dose was determined as the COD/PS or COD/HP molar ratio. The HP/Fe^{2+} molar ratio of 10/1 was considered optimal [8]; for comparison, the PS/Fe^{2+} molar ratio was also fixed at 10/1. In both ferrous ion-activated systems the pH_0 was adjusted to 3 in order to provide activator in its reduced state and also to facilitate the comparison of considered AOTs.

As presented in Fig. 5, the removal of organic load proved dependent on the applied Fenton reagent dose. The COD and DOC removal was improved along with the oxidant concentration increase in COD/HP/Fe^{2+} molar ratio from 1/0.1/0.01 to 1/1/0.1 resulting in 65.5 and 60%, respectively. Notably, the dissociation of HP was complete in all the studied Fenton systems. Regarding the efficacy of phenolic compounds removal, the application of Fenton process at a COD/HP/Fe^{2+} molar ratio of 1/0.1/0.01 resulted in 60% decrease in TPC concentration; further increase of oxidant dose up to a COD/HP/Fe^{2+} molar ratio of 1/0.25/0.025 resulted in degradation of 90% of phenolic substances. The results of the non-activated oxidation of S3 at a COD/HP molar ratio of 1/1 resulted in negligible organic load removal after 24 h of treatment

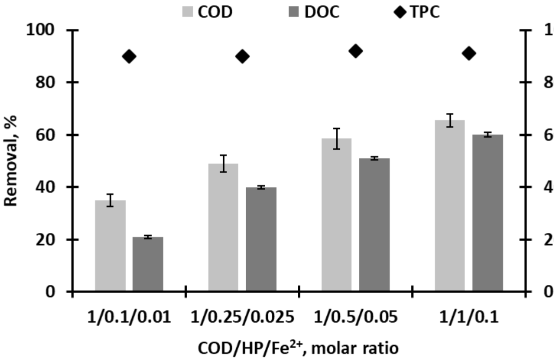

Fig. 5. COD, DOC and TPC removal as a function of the COD/HP/Fe^{2+} molar ratio in the HP/Fe^{2+} treatment of S3 wastewater.

The effect of different oxidant doses on the efficacy of the PS/Fe^{2+} treatment at the fixed PS/Fe^{2+} molar ratio of 10/1 is shown in Fig. 6. The results indicated steady improvement in COD, DOC, and TPC removal with the PS concentration increasing in COD/PS/Fe^{2+} molar ratio from 1/0.1/0.01 to 1/1/0.1. Accordingly, a 10-fold oxidant dose increase in COD/PS/Fe^{2+} molar ratio from 1/0.1/0.01 to 1/1/0.1 resulted in enhancement of COD removal form 19% to 36.5%, respectively. Similarly, the mineralization extent was the highest at a COD/PS/Fe^{2+} molar ratio of 1/1/0.1 reaching 36%.

The non-activated PS oxidation at a COD/PS molar ratio of 1/0.25 and 1/0.5 resulted in 6-11% of COD and 3-10% of DOC removal after 24-h treatment of S3 samples. Therefore, the activation of PS proved essential to facilitate the removal of total organic load and degradation of specific phenolic compounds during municipal landfill leachate treatment.

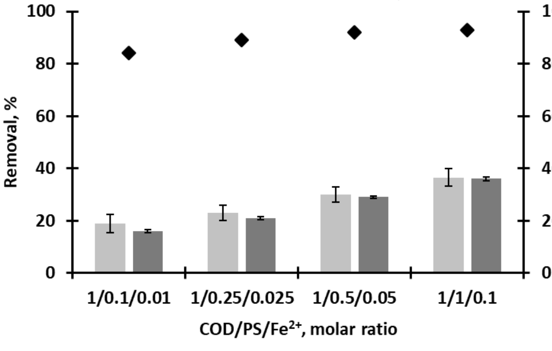

Fig. 6. COD, DOC and TPC removal as a function of the COD/PS/Fe^{2+} molar ratio in the PS/Fe^{2+} treatment of S3 wastewater.

The changes in temperature and foam formation were also measured during S3 treatment by the PS/Fe^{2+} and HP/Fe^{2+}. The results of the Fenton treatment at a COD/HP/Fe^{2+} molar ratio of 1/1/0.1 indicated a moderate T↑ of 12 ℃. In contrast, the application of ferrous ion-activated PS process at the same oxidant concentration proved to have negligible exothermic effect. Furthermore, the production of excessive foam caused by the CO_2 and O_2 evolution as a result of HP decomposition was observed in the HP/Fe^{2+} systems.

Comparison of the obtained results suggests that the HP/Fe^{2+} process is more efficient for organic load removal from landfill leachate. On the other hand, the PS/Fe^{2+} process proved to have no restrictions by temperature rise or excessive foam formation.

IV. CONCLUSIONS

The results of this study demonstrate that both the HP/Fe^{2+} and PS/Fe^{2+} systems are promising treatment techniques to reduce the organic load, degrade persistent organic pollutants and improve the biodegradability in different highly contaminated industrial effluents. Generally, the application of the Fenton process demonstrated a higher treatment efficacy than the PS/Fe^{2+} system for all the studied wastewater samples. On the contrary, the HP/Fe^{2+} oxidation was characterized by a temperature increase and excessive foam formation. Thus, the ferrous ion-activated PS process could be suggested as a practical alternative technique due to the reasonable working conditions and sustainable treatment of the effluents. The application of the studied AOTs proved to be an effective option that improved the overall wastewater quality and increased the possibility of subsequent biological treatment of the effluents. The results of this study are unique and may provide important insight for further implementation in treatment of heavily contaminated water matrices.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

ND and EK planned experiments. EK conducted laboratory experiments and samples analysis. ND interpreted the results and wrote the paper. MT provided critical feedback on the research and paper writing. All authors approved the final version.

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