

Advanced Chemical Oxidation with Pre-coagulation for Treatment of Paint Manufacturing Wastewater

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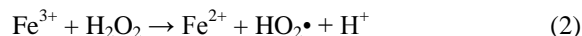
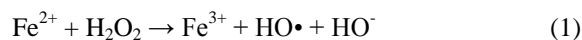
Abstract— A water-based paint wastewater, generated mainly during a periodic equipment-cleaning, was subjected to the combined pre-coagulation and advanced chemical treatment ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$, $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$, $\text{S}_2\text{O}_8^{2-}/\text{OH}^-$, or $\text{S}_2\text{O}_8^{2-}/\text{H}_2\text{O}_2$ system). The results of ferric pre-coagulation trials indicated a high efficacy in wastewater treatment, resulted in 4 and 15 % residual COD and DOC, respectively, and in more than a 10-fold increase in a BOD_7/COD ratio. The Fenton treatment of the pre-coagulated wastewater at the optimal $\text{COD}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ weight ratio of 1:2:0.4 resulted in respective 14 and 31 % residual COD and DOC. The BOD_7/COD ratio increase was the highest at the optimal ratio and resulted in more than 6-fold and 81-fold increase compared to the pre-coagulated and initial wastewater, respectively. The COD and DOC removal remained nearly identical in all trials with the ferrous-ions activated persulfate treatment of the pre-coagulated wastewater and did not exceed 35 and 7 %, respectively. The BOD_7/COD remained unchanged after treatment of the pre-coagulated wastewater with $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ process. Both alkaline and peroxide activated persulfate oxidation demonstrated insignificant efficacy in the pre-coagulated wastewater treatment. The combination of pre-coagulation and Fenton treatment proved a feasible solution to treat effectively water-based paint wastewater and resulted in 99.5 and 96.5 % COD and DOC removal, respectively.

Keywords—activated persulfate, coagulation, Fenton process, oxidation, water-based paint wastewater

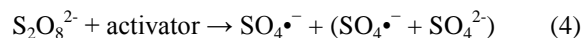
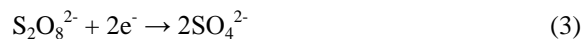
I. Introduction

Water-based paints consist of a mixture of binder (synthetic polymers), organic and inorganic pigments, solvent, fillers and additives (biocides, antioxidants, coalescing agents, emulsifiers, surfactants, light stabilizers, UVA absorbers, among others). The components of paint determine not only the main characteristics of the product but also of wastes generated in its manufacture and use. The major source of wastewater from the manufacture of paint is the periodical equipment-cleaning, which is responsible for nearly 80 % of the total liquid waste generated during the manufacturing process [1]. These effluents of paint manufacturing industry are highly loaded, contain highly toxic and bio-refractory compounds, cannot be directly subjected to the conventional secondary biological wastewater treatment, and consequently require physical or physicochemical pre-treatment before they could be discharged into sewer.

The application of advanced oxidation technologies (AOTs), chemical treatment methods involving the generation of hydroxyl radicals ($\text{HO}\cdot$), has shown a great potential to degrade recalcitrant and bio-refractory organic compounds presented in various industrial wastewaters. The hydroxyl radical can be generated by the combination of hydrogen peroxide and/or ozone with activators (transition metals, semiconductors), UV/visible and ultrasonic irradiation. The advantages of AOTs, as water/wastewater treatment techniques, include high reaction rates and non-selective oxidation due to hydroxyl radicals, which allow the simultaneous degradation of multiple contaminants and potentially reduce a toxicity of water/wastewater [2-5]. Among AOTs, the Fenton treatment is a widely studied and used technique for wastewater purification [3,6-9] based on the generation of hydroxyl radicals from hydrogen peroxide with ferrous-iron ions acting as homogeneous activator at acidic pH. The generally accepted mechanism of the Fenton reaction consists of the sequence of reactions, where hydroxyl radicals are produced in accordance with Eq. (1) and the activator is regenerated through Eq. (2), or from reaction of ferric-iron ions with organic radicals [6]:



Recently, the innovative treatment technology based on the persulfate oxidation has been studied as an alternative to conventional AOTs both for water/wastewater treatment and in situ chemical oxidation application [10-14]. The persulfate anion ($\text{S}_2\text{O}_8^{2-}$) is a strong oxidant ($E^\circ=2.1$ V, Eq. (3)) that through the activation can form even stronger sulfate radical ($\text{SO}_4\cdot^-$, $E^\circ=2.6$ V, Eq. (4)) [10]. The main techniques used for sulfate radicals generation are heat, UV light or ultrasound activation, transition metal (M^{n+}) activation, alkaline activation ($\text{pH} > 10$), or peroxide activation [10,11].



The sulfate radical oxidation has several advantages over AOTs. Accordingly, different from hydroxyl radicals, sulfate radicals are more stable and more selective for oxidizing unsaturated bond and aromatic constituents [15]. Persulfate (mainly its sodium salt) could be characterized by high water solubility at the ambient temperature, while the sulfate ions which are the main products of persulfate decomposition are harmless for the environment. In general, the application of persulfate is a feasible option for the advanced chemical oxidation of a wide range of contaminants.

The application of electrocoagulation for a highly loaded water-based paint wastewater resulted in an effective COD removal but non-biodegradable treat

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other hand, the Fenton treatment proved an effective technique for the diluted water-based paint wastewater purification [17]. Thus, a combination of pre-coagulation and subsequent advanced chemical treatment is a potentially feasible method to reduce overall organic load as well as improve biodegradability of the paint wastewater. The main objective of this study was to assess and compare the efficacy of the Fenton and activated persulfate oxidation as a polishing treatment of the pre-coagulated paint manufacturing wastewater. The effect of the operating conditions such as operating time, oxidant dose, activator type and dose were investigated both for the activated hydrogen peroxide and sodium persulfate treatment.

II. Experimental

A. Chemicals and Materials

Hydrogen peroxide (PERDROGEN™, ≥30 %), sodium persulfate (Na₂S₂O₈, ≥99 %), and ferrous sulfate heptahydrate (FeSO₄·7H₂O, ≥99 %) were purchased from Sigma-Aldrich. All other chemicals of reagent grade were used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System). NaOH and H₂SO₄ aqueous solutions were used to adjust the pH.

The paint manufacturing wastewater was obtained from a plant manufacturing multicolor water-based paints used for painting both interior and exterior surfaces. The wastewater represented mainly equipment-cleaning liquids as well as contained residue of the product. The main properties of the investigated wastewater are listed in Table 1. The wastewater samples were stored at 2-4 °C.

TABLE I. THE MAIN WASTEWATER PARAMETERS

Parameter	Value	Unit
COD	42221±576	mg/L
DOC	2640±22	mg/L
BOD ₇	247±45	mg/L
Biodegradability, BOD ₇ /COD	0.006	-
pH	7.72±0.05	-
Conductivity	612±11	µS/cm
TSS (105 °C)	1600±0.09	mg/L
TS (105 °C)	66650±28	mg/L
TFS (600 °C)	7960±11	mg/L

B. Experimental procedure

The coagulation with ferric sulfate (KEMIRA PIX-322, Fe_{total} 12.5±0.3 %) was performed in a jar test apparatus (Kemira, Finland). The wastewater volume in each jar was 0.6 L. The coagulant doses (Fe_{total}) varied in the range of 100 to 1000 mg L⁻¹. The operating conditions were as follows: 1 min of fast mixing at 400 rpm, 30 min of slow mixing at 40 rpm, and 24 h of sedimentation. Afterwards, the supernatant was collected for further analysis.

All the Fenton and persulfate process trials were performed in batch mode and in non-buffered solutions. Wastewater samples (0.5 L) were treated in 1 L cylindrical glass reactor with a permanent agitation speed (400 rpm) for a period of 1-24 h. The activator (FeSO₄·7H₂O) was added, and after complete dissolution of the activator, the Fenton reaction or activated persulfate oxidation was initiated by adding an oxidant (H₂O₂ or Na₂S₂O₈) all at once, if not specified otherwise. The pH of the wastewater samples was adjusted to 3 in the subsequent treatment. The oxidation was halted by neutralizing the treated samples with NaOH (10 M) to a pH approximately 9 under mechanical stirring. This process was followed by a ferric-hydroxy complexes settling period of 24 h. Finally, the supernatant was collected for further analysis.

The experiments on wastewater 24-h oxidation with non-activated hydrogen peroxide/persulfate, alkaline (pH 11) and peroxide activated persulfate were conducted in identical reactors and treatment conditions for the respective Fenton or activated persulfate treatment trials. In the case of peroxide activated persulfate, both oxidants were added simultaneously.

All experiments were duplicated; the results of the analysis are presented as the mean with a standard deviation below 5 % in all cases. The experiments were performed at ambient room temperature (22±1 °C).

C. Analytical methods

The chemical oxygen demand (COD) was determined with a closed reflux colorimetric method [18]. The correction for the hydrogen peroxide interference on COD test was performed by the correlation equation reported by Kang et al. [19]. The total suspended solids (TSS), total solids (TS), total fixed solids (TFS), and a 7-day biochemical oxygen demand (BOD₇) were determined according to APHA [18]. The pH was measured using a digital pH meter (Schott CG-840, Germany) and the electrical conductivity was measured using a digital EC meter (HANNA Instruments HI9032, USA). The total and ferrous-iron concentration in the solution was measured by the phenanthroline method [18]. The initial hydrogen peroxide concentration in the stock solutions was measured spectrophotometrically at 254 nm; the residual hydrogen peroxide concentration in the treated samples was measured by a spectrophotometric method with Ti⁴⁺ [20] by a Helios-β UV/VIS spectrophotometer (Thermo Electron Corporation, USA). The residual persulfate concentration in the treated samples was measured spectrophotometrically at 446 nm with o-dianisidine [21]. The dissolved organic carbon (DOC) was measured in filtered (Puradisc Aqua, 0.45 µm, CA membrane) wastewater samples by a TOC analyzer multi N/C® 3100 (Analytik Jena, Germany).

III. Results and Discussion

A. Coagulation

The coagulation process was utilized to remove suspended organic and inorganic compounds from the highly loaded wastewater (Table 1) and provide a pre-treatment step before subsequent advanced chemical o

reduction in the amount of oxidant required. A commercial formulation containing ferric sulfate was used as a common coagulant in the treatment of water-based paint wastewater. The results of COD and DOC removal after treatment with different coagulant doses (Fe_{total} , mg/L) at initial pH are presented in Fig. 1.

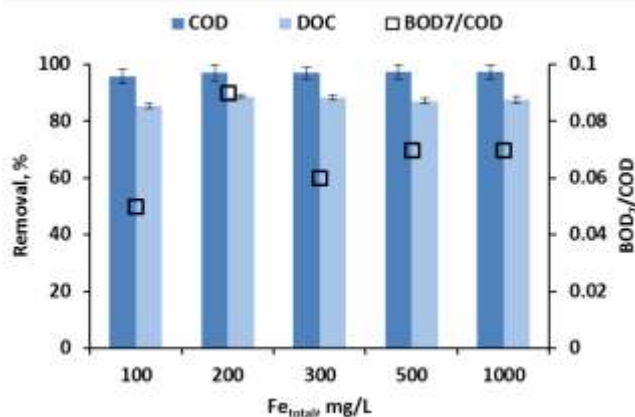


Figure 1. COD and DOC removal and the BOD₇/COD ratio versus the coagulant dose during the coagulation of wastewater.

Up to 96 and 85 % removal of COD and DOC, respectively, was achieved in the pre-coagulated wastewater at all the studied coagulant doses, mainly because of a considerable decrease in the TS (≥ 95 %) and TSS (≥ 50 %) content. To assess the options available for subsequent biological treatment of the treated wastewater, along with the overall quality improvement, the biodegradability of pre-coagulated samples, estimated by the BOD₇/COD ratio, was evaluated. Consequently, more than a 10-fold increase in a BOD₇/COD ratio was observed for all the pre-coagulated wastewater samples, indicating effective toxic and bio-refractory compounds removal during the coagulation step but still insufficient to ensure no inhibitory effect on the microbial activity of biomass.

From the results, coagulation proved an effective pre-treatment technique for the water-based paint manufacturing plant effluent. The optimal coagulant dose was estimated at Fe_{total} of 200 mg/L with a residual COD of 1166 ± 32 mg/L, residual DOC of 298 ± 2 mg/L, and residual Fe_{total} concentration of 8.2 ± 0.4 mg/L. Therefore, the subsequent advanced chemical oxidation trials were done only with the pre-coagulated with Fe_{total} at a dose of 200 mg/L wastewater.

B. The Fenton treatment

The results of pre-coagulated wastewater Fenton treatment, presented in this part, indicate a purification efficacy of the subsequent Fenton process only. The weight ratio of H_2O_2/Fe^{2+} was maintained at 5:1 in all the Fenton process trials, which is optimal for highly loaded wastewater treatment [22]. The effect of the oxidation time as well as hydrogen peroxide concentration was studied for the Fenton treatment of pre-coagulated water-based paint wastewater.

In order to assess the optimal oxidation time the trials with different duration of the Fenton oxidation ($COD/H_2O_2/Fe^{2+}$ w/w/w of 1:2:0.4) and 24-h neutralization/sedimentation step were performed. In general, the results indicated that prolonged oxidation of up to 24 h was needed to ensure complete hydrogen peroxide utilization and achieve considerable removal of COD and DOC (Fig. 2).

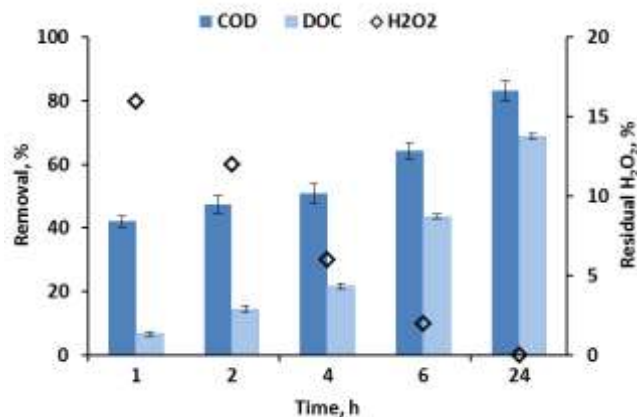


Figure 2. COD and DOC removal and residual H_2O_2 concentration versus the oxidation time during the Fenton treatment of pre-coagulated wastewater at a $COD/H_2O_2/Fe^{2+}$ weight ratio of 1:2:0.4.

The continuous increase in treatment efficacy up to 64 and 44 % of COD and DOC removal, respectively, was observed during the first 6 h of the Fenton oxidation. The residual hydrogen peroxide concentration decreased within 6-h oxidation step till 2 %. Notably, the measurements of the residual hydrogen peroxide were performed after neutralization and 24-h sedimentation steps (usually referred to as the coagulation step in the Fenton process), during which the hydrogen peroxide could auto-decompose as well. Further increases in oxidation time, up to 24 h, resulted in 19 and 25 % additional COD and DOC removal, respectively, and in complete hydrogen peroxide utilization. The residual COD and DOC after 24-h oxidation step was 166 ± 5.3 and 93 ± 0.8 mg/L, respectively. The pre-coagulated wastewater proved recalcitrant due to the prolonged oxidation time required; in general, the Fenton oxidation step proceeded rapidly and the duration of the Fenton oxidation step could be limited to 2 hours for majority of the wastewater types [3,7].

Determining the optimal oxidant to contaminant ratio is essential to optimize the Fenton-based oxidation. Fig. 3 presents the results of the treatment of the wastewater with different hydrogen peroxide to COD weight ratios after 24-h oxidation step and 24-h neutralization/sedimentation phase.

A relation between COD and DOC removal and the hydrogen peroxide dose was different for various $COD/H_2O_2/Fe^{2+}$ weight ratios. An increase in the COD/H_2O_2 ratio led to an improvement in wastewater treatment efficacy. Irrespective of hydrogen peroxide dose, the mineralization (DOC removal) was lower than COD reduction. Notably, at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1:1:0.2 the reduction in DOC was twice less effective than COD removal. For higher H_2O_2 doses (COD/H_2O_2 w/w ratios of 1:2 and 1:3) the mineralization

extent was more comparable with reduction in COD. In the treated wastewater samples, irrespective of hydrogen peroxide dose applied, no traces of residual hydrogen peroxide were detected after 24 h of the Fenton oxidation

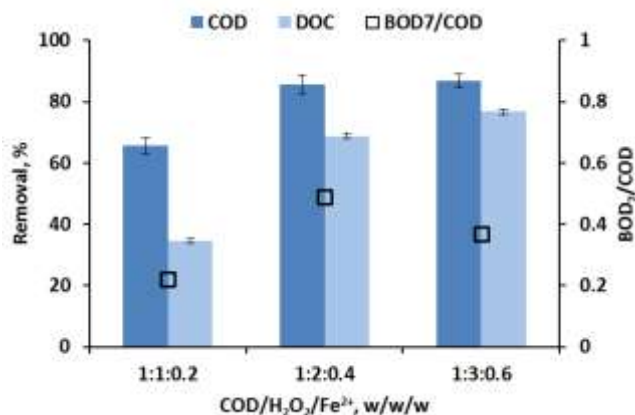


Figure 3. COD and DOC removal and the BOD₇/COD ratio versus the oxidant dose during the Fenton treatment of pre-coagulated wastewater.

The optimal COD/H₂O₂/Fe²⁺ weight ratio for pre-coagulated wastewater was 1:2:0.4 with respective 14 and 31 % residual COD and DOC. The overall treatment, the pre-coagulation and Fenton process at the optimal treatment conditions, efficacy comprised 99.5 and 96.5 % COD and DOC removal, respectively. Additionally, the BOD₇/COD ratio increase was the highest at the optimal ratio and resulted in a final value of 0.49, which means more than a 6-fold and 81-fold increase compared to the pre-coagulated and initial wastewater, respectively.

The oxidative potential of non-activated hydrogen peroxide was studied as well. The results of the oxidation at a COD/H₂O₂ w/w 1:2 indicated a negligible COD removal and more than 50 % of unused H₂O₂ in the wastewater sample after 24 h of treatment.

C. The activated persulfate treatment

Similarly to the activated hydrogen peroxide system, the results of pre-coagulated wastewater treatment by activated persulfate specify a purification efficacy of the subsequent advanced chemical treatment only. The effect of the activator type and dose as well as persulfate concentration was studied for the of pre-coagulated water-based paint wastewater.

The structure of persulfate is a symmetrically substituted derivative of hydrogen peroxide [23]. In general, the action of Fe²⁺-activated persulfate has substantial degree of similarity to Fe²⁺-activated hydrogen peroxide, and the efficacy of both could be easily compared. The degradation of organic contaminants by activated persulfate is known to be slower than by the Fenton process [10], thus trials with ferrous-ions activated persulfate were performed with a 24-h oxidation and 24-h neutralization/sedimentation step to ensure the complete utilization of persulfate and to overcome problems associated with the possible prolonged treatment needed.

To optimize the Fe²⁺-activated persulfate oxidation the effect of different oxidant doses was studied. The COD removal remained nearly identical in trials with COD/S₂O₈²⁻/Fe²⁺ weight ratios of 1:1:0.2, 1:2:0.4 and 1:3:0.6 and did not exceed 35 % as presented in Fig. 4. The DOC removal was similar as well throughout the trials. In general, the mineralization was less effective than COD reduction and comprised no more than 7 %. The residual S₂O₈²⁻ was detected in all trials, but comprised less than 10 %. Similar to the other studied parameters, the BOD₇/COD ratio was steady after the Fe²⁺-activated persulfate treatment and nearly identical for the pre-coagulated wastewater sample. The reason for this observation may be the interference of the residual persulfate in the BOD₇ measurements of the treated samples resulted in lower BOD₇ values.

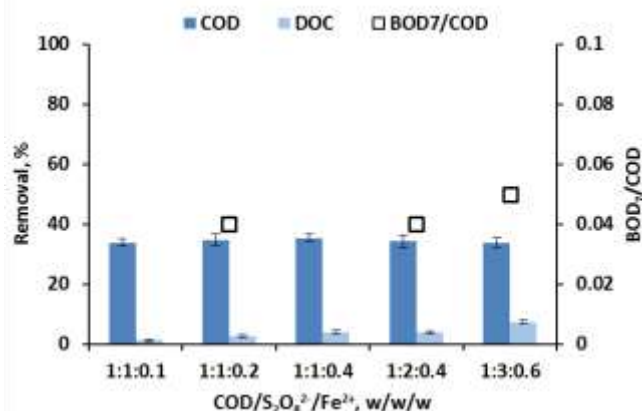
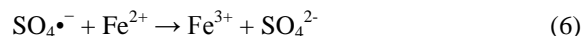
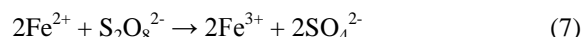


Figure 4. COD and DOC removal and the BOD₇/COD ratio versus the COD/S₂O₈²⁻/Fe²⁺ weight ratio during the Fe²⁺-activated persulfate treatment of pre-coagulated wastewater.

In the treatment of wastewater by the Fe²⁺-activated persulfate, the observed lower efficacy, compared to the Fenton treatment, can be explained by the absence of simultaneous ferrous-ions oxidation and ferric-ions reduction in the activated persulfate system as presented in Eq. (2) for the Fenton process. The possible mechanism of persulfate reaction activated with Fe²⁺ may be described as follows [23]:



The overall reaction between persulfate and ferrous-ion could be presented as follows:



The reaction between persulfate and ferrous-ion (Eq. (5)) results in fast formation of sulfate radicals. However, the sulfate radical also reacts with Fe²⁺ and rapidly converts it to Fe³⁺ through Eq. (6). Thus, the oxidation of ferrous-ion to ferric-ion occurs not only in the generation of sulfate radical, but also in the conversion of SO₄^{•-} to SO₄²⁻. The newly generated SO₄^{•-} reacts immediately though the competitive reaction (Eqs. (5) and (6)) with the target compound and excess Fe²⁺, which results in lower degradation efficiency of the target contaminant. In order to control the reaction presented in Eq. (6), the optimizat

activated persulfate oxidation could be done by adjustment of iron dose or by stepwise iron addition.

In the ferrous-ions activated persulfate trials the used ferrous-ion/persulfate weight ratio was less than the theoretical stoichiometric ratio of 0.6 (according to Eq. (7)). Three different COD/S₂O₈²⁻/Fe²⁺ weight ratios of 1:1:0.1, 1:1:0.2, and 1:1:0.4 were used to treat the pre-coagulated wastewater as presented in Fig. 4. The increase in COD and DOC removal was negligible with increase in the ferrous-ions content. The stepwise ferrous-ions addition (at 0, 30, and 60 min of oxidation) at a COD/S₂O₈²⁻/Fe²⁺ weight ratio of 1:1:0.2 resulted in only 2-3 % supplementary COD and DOC removal. On the other hand, the utilization of persulfate was dependent of ferrous-ions content. Thus, the residual persulfate concentration comprised 10, 7, and 0.9 % at COD/S₂O₈²⁻/Fe²⁺ w/w/w ratios of 1:1:0.1, 1:1:0.2, and 1:1:0.4, respectively. The results of stepwise addition also indicated higher persulfate decomposition and comprised 6 %.

The oxidative potential of non-activated persulfate was studied as well. The results of the oxidation at a COD/S₂O₈²⁻ weight ratio of 1:2 indicated no changes in COD and DOC values and more than 93 % of unused persulfate in the wastewater sample after 24 h of treatment.

During the iron-activated hydrogen peroxide or persulfate treatment of wastewater, the oxidation and coagulation of ferric-hydroxy complexes both contribute to the removal of the organic compounds. On the other hand, practical application of these processes could be limited because of the large amount of ferric sludge produced during neutralization step which follows oxidation. The solid waste sludge, which is potentially hazardous, requires proper treatment and disposal to specific sites. In order to assess option of post-treatment without the subsequent sludge formation the alkaline and peroxide persulfate activation techniques were also studied.

It is suggested that alkaline activation is one of the least efficient approaches due to the very fast decomposition of persulfate under alkaline conditions [10]. The activation mechanisms behind this method are still unclear [10]. The alkaline activation (S₂O₈²⁻/OH⁻) at COD/S₂O₈²⁻ weight ratios of 1:0.25 and 1:0.5 resulted in 8 and 5 % of COD removal, respectively, with more than 65 % of unused persulfate after 24-h oxidation.

The mechanism of peroxide activation of persulfate is still uncertain as well; the suggested activation mechanisms include the hydroxyl radicals generated from peroxide or the heat from the exothermic hydrogen peroxide reactions [10]. In the experiment with peroxide activation (S₂O₈²⁻/H₂O₂) no temperature increase was detected. The 24-h oxidation at a COD/S₂O₈²⁻/H₂O₂ weight ratio of 1:0.5:0.5 showed a negligible COD and DOC removal and resulted in more than 90 % of unused H₂O₂.

As a result, the application of the ferrous-iron activated persulfate process to treat the water-based paint wastewater was lower in efficacy than the Fenton process, but demonstrated the highest oxidative potential among the studied activated persulfate systems. The overall COD and DOC removal by the combined pre-coagulation and ferrous-

ions activated persulfate treatment of wastewater was 98 and 89 %, respectively.

IV. Conclusions

The ferric coagulation proved an effective technique to pre-treat the water-based paint wastewater and considerably reduce the amount of oxidant required in the subsequent advanced chemical oxidation step.

The optimized Fenton treatment was the most feasible post-treatment technique and resulted in substantial COD and DOC removal as well as considerable the BOD₇/COD ratio increase in the pre-coagulated wastewater samples. The residual COD and DOC after the application of combined pre-coagulation and Fenton treatment was 0.5 and 3.5 %, respectively. The overall BOD₇/COD ratio improvement comprised more than an 81-fold increase compared to the untreated wastewater.

Irrespective of S₂O₈²⁻ and Fe²⁺ dose, the S₂O₈²⁻/Fe²⁺ system was less effective in the wastewater treatment than the Fenton process. The residual COD and DOC comprised more than 65 and 93 %, respectively. The alkaline and peroxide activation proved ineffective to treat the pre-coagulated wastewater and resulted in considerable amount of unused oxidants in the treated samples. In general, the application of the ferrous-iron activated persulfate system to treat the water-based paint wastewater was lower in efficacy than the Fenton process, but demonstrated the highest oxidative potential among the studied activated persulfate systems. The residual COD and DOC after the combined pre-coagulation and ferrous-ions activated persulfate treatment of wastewater was 2 and 11 %, respectively.

The results of this study could provide important information for practical purposes both in a water/wastewater treatment and in-situ chemical oxidation applications.

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