

Thermally activated persulfate treatment and mineralization of a recalcitrant high TDS petrochemical wastewater

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Thermally activated persulfate efficiency for the treatment of a recalcitrant high TDS wastewater was investigated. The specific character of studied wastewater was high TDS content of around 23820 mg/L and BOD₅/COD ratio of 0.07. Effective operational parameters including initial pH values of 3–9, reaction temperature of 40–80°C and persulfate concentrations of 0.5–5 g/L for COD removal were investigated in batch mode experiments. Removal efficiency was pH and temperature dependent. The COD and TOC removal of 94.3% and 82.8% were obtained at persulfate concentration of 4 g/L, initial pH value of 5 and temperature of 70°C after 180 min for initial COD concentration of 1410 mg/L. The pseudo first-order kinetic model was best fitted with COD removal (R² = 0.94).

Keywords: Industrial wastewater treatment, Thermally activation, persulfate Petrochemical industry, High TDS wastewater.

INTRODUCTION

The rapid growth of petrochemical industries in last two decades and widespread use of petrochemical products has led to serious environmental contamination, especially water bodies receiving considerable amounts of wastewaters originated from these industries¹. Petrochemical effluents contain significant amounts of hazardous organic and inorganic chemical compounds such as halogenated hydrocarbons, aromatic compounds, phenolic substances, oil and grease, aliphatic, polycyclic aromatic hydrocarbons (PAHs) and heavy metals which all possess high toxicity to plants, animals and also human beings^{2–4}. In addition, a major portion of petrochemical wastewaters are characterized as high TDS that along with containing aromatic constituents make them resistant to biodegradation⁵. Many of halogenated hydrocarbons, aromatics and phenolic substances are categorized as priority pollutants causing carcinogenic and mutagenic effects which necessitate application of efficient treatment methods before being discharged to water bodies⁶. A range of physical, chemical and biological processes and their integration such as integration of advanced oxidation with coagulation, biodegradation using special microorganisms^{7,8} membrane filtration, chemical precipitation, photocatalytic degradation using nanoparticles⁹ advanced oxidation processes (AOPs) are investigated for treatment of petrochemical industries^{10–13}. Low BOD₅/COD ratio of less than 0.1 and high TDS content of produced wastewater limits direct application of biological processes. Additionally, conventional chemical oxidations and precipitations are not efficient enough especially in term of soluble organic matter and xenobiotics. AOPs are based on the generation of nonselective and strong oxidative radicals like hydroxyl and sulfate and recently are successfully employed for treatment of such recalcitrant wastewaters^{14–16}. Oxidation through activated persulfate is an attractive option due to its high stability, reactivity, solubility, oxidizing properties and rapid rate of organic matter destruction¹⁷. Persulfate

(S₂O₈²⁻) with the standard oxidation potential of E⁰ = 2.01 V is a quite new alternative used in chemical oxidation and recently received much attention in the treatment of biological resistant wastewaters. In addition, activation of S₂O₈²⁻ leads to initiate sulfate radical based-AOPs that are powerful oxidants¹⁸. Sulfate radical (SO₄^{-•}, E⁰ = 2.7 V), is a strong oxidant for the degradation of organic matter even at neutral pH and acts more selective for the treatment of wastewaters containing compounds with carbon–carbon double bonds and benzene rings¹⁹. Activation of persulfate can be accomplished by various methods including heat, transit metal, base (elevated pH > 11), UV-radiations, electron-beam and ultrasonication²⁰. For practical issues in term industrial wastewater treatment, UV irradiation cannot penetrate in wastewater efficiently and alkaline activation needs large amounts of alkaline chemical that produces considerable excess sludge. Furthermore, transit metal-catalyzed activation (for example Fe²⁺) exhibits best results in strict pH value range of 2–4 and may metal may act as a sulfate radical scavenger²¹. Compared to other activation technologies, thermally activated persulfate is considered as a green source of sulfate radicals and has already been studied for removal of organic contaminants^{22,23}. Thermally activation of persulfate has also advantages such as increasing the solubility of slightly soluble organic pollutants, enhancing the reaction rates and mineralization efficiency and least consumption of chemicals²⁴, ease of operation and simple simplicity²⁵, minimization of persulfate consumption caused by pre-mixture of the persulfate and the activator before injection²⁶. In the current study, thermally activated persulfate was investigated for the treatment of a high TDS petrochemical wastewater characterized by BOD₅/COD ratio of less than 0.1 which according to literature review has not been studied before. The influences of effective operational parameters as well as kinetics were investigated for treatment of a real petrochemical wastewater.

EXPERIMENTAL

Material

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%), Sodium hydroxide (NaOH , 96%) and hydrochloric acid (HCl , 99%) were all analytical grade and obtained from Merck, Germany. Real high TDS wastewater sample was taken from a petrochemical industry located in the south of Iran. The samples collected from the outlet line of raw effluent according to standard methods for the examination of water and wastewater²⁷. It was transported to the lab in cold box at 4°C daily and wastewater characteristics including COD, BOD_5 , TSS, TDS and pH were analyzed²⁷. The sampling was carried out during six months with weekly time intervals. Also the sampling was done in morning shift as the peak of the industrial manufacturing process and therefore wastewater production. For each sampling, 5 L of wastewater sample was prepared by mixing the separate samples originated from 1 h sampling intervals to prepare a composite sample in each day. The results of raw wastewater are the average of six months continuous monitoring.

Batch experimental procedure

Determination of optimum conditions of the operational parameters including initial pH (3–9), temperature (40–80°C) and persulfate concentration (0.5–5 g/L) according to one factor at the time experimental design were carried out in a 500 mL Erlenmeyer flask as completely mixed batch reactor using a magnetic stirrer equipped with an electronic contact thermometer (IKA, Model: C-MAG HS 7, Germany). In order to set the reactor temperature, rather than heater stirrer a water jacket was provided with adjustable temperature surrounding the reactor. The desired initial pH value was adjusted with NaOH (1 M) or HCl (1 M) solutions before starting the experiment. Sampling was implemented in 20 min time intervals during a contact time range of 0–120 min. Also, zero-order, pseudo-first-order and pseudo-second-order kinetic models were evaluated for experimental data.

Analytical methods

Characterization of raw wastewater in term of chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), Total dissolved solids (TDS), total suspended solids (TSS), electrical conductivity (EC) and pH were carried out according to standard methods for the examination of water and wastewater²⁷. Qualitative analysis of wastewater constituents were determined by gas chromatography–mass spectrometry (GC-MS) analysis (Model: Agilent 7890, USA) with HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm film thickness, 5% Phenyl – 95% Methyl Siloxane phase). A constant flow rate of 1 mL/min was employed to feed the carrier gas (Helium). The temperature rate of oven was firstly set to 40°C for 1 min then increased to 300°C at 5°C/min. This temperature was maintained for 3 min. Finally, the sample was injected into the instrument at a splitting ratio of 10:1. The removal efficiency (%) was calculated based on COD concentration via Eq (1):

$$\text{Removal (\%)} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

Where C_0 is the initial COD concentration (mg/L) and C_t is the COD concentration (mg/L) at specified reaction time t (min). Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, TOC-VCSH, Japan) to determine the mineralization. All the experimental data are expressed in terms of arithmetic averages obtained from at least three replicates.

RESULTS AND DISCUSSION

Petrochemical wastewater characterization

The average concentrations of total COD, BOD_5 , TDS and TSS of raw wastewater according to two week sampling with daily interval were 1320 mg/L, 95, 23820 mg/L and 63 mg/L, respectively (Table 1). The low BOD_5/COD ratio of 0.07 indicates the non-biodegradable nature of studied petrochemical wastewater and the necessity for investigation chemical transformation processes. According to a GC-MS analysis (Table 2), the principle identified organic compounds of raw wastewater included: benzene and benzene derivatives, naphthalene, o-terphenyl, p-Dicyclohexylbenzene, 1-phenyl-3-phenylthio-butane, n-benzhydrylimidazole and heptane.

Table 1. Characteristics of a real petrochemical wastewater sample

| Parameter | Value | |
|---------------------------|-------------|---------|
| | range | average |
| Total COD [mg/L] | 1080–1430 | 1320 |
| BOD_5 [mg/L] | 86–100 | 95 |
| BOD_5/COD | 0.05–0.09 | 0.07 |
| TOC | 780–925 | 842 |
| TSS | 56–70 | 63 |
| TDS | 19650–42780 | 23820 |
| pH | 7.8–9.4 | 8.7 |
| Turbidity | 18–30 | 20 |

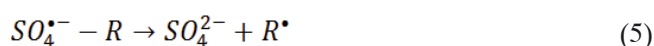
Table 2. GC-MS chromatogram of raw petrochemical wastewater

| Run time [min] | Substance | Structural formula |
|----------------|--------------------------|-------------------------------------|
| 14.485 | Benzene | C_6H_6 |
| 15.984 | 1-methyl-2-nitro-Benzene | $\text{C}_7\text{H}_7\text{NO}_2$ |
| 15.984 | 4-Nitrotoluene | $\text{C}_7\text{H}_7\text{NO}_2$ |
| 32.210 | Naphthalene | C_{10}H_8 |
| 31.450 | 2(5H)-Furanone | $\text{C}_4\text{H}_4\text{O}_2$ |
| 32.091 | o-Terphenyl | $\text{C}_{18}\text{H}_{14}$ |
| 34.002 | Hexane | C_6H_{14} |
| 34.254 | 3-phenyl thio-ethane | $\text{C}_8\text{H}_{10}\text{S}$ |
| 34.861 | 1,4-dicyclohexyl | $\text{C}_{18}\text{H}_{26}$ |
| 35.610 | 2-methyl benzaldehyde | $\text{C}_8\text{H}_8\text{O}$ |
| 36.354 | 9,10-Anthracenedione | $\text{C}_{14}\text{H}_8\text{O}_2$ |

Effect of temperature

To determine the effect of temperature on COD removal at different activation temperatures (40–80°C), a constant persulfate concentration of 1 g/L was added at initial pH value of 7. Increasing the activation temperature from 40 to 80°C enhanced the COD removal from 21.6% to 44.01% respectively (Fig. 1). However, the temperature of 70°C with removal efficiency of 42.3% was selected for investigation the effect of pH and persulphate dosage due to no significant difference between removal at 70°C and 80°C (p-value of 0.0146 < 0.05) according to non-parametric Kruskal Wallis statistical analysis. COD removal using $\text{SO}_4^{\cdot -}$ radicals is a temperature dependent process and removal could be enhanced through increase

in temperature. It could be attributed to the enhanced generation of sulfate based radicals at elevated²⁸. Results of current study in term of temperature effect are in accordance with literature^{29,30}. Mechanism of persulfate oxidation through heat catalysts which leads production of sulfate radicals for degradation of organic matter can be explained through Eqs. (2–6) as bellow³¹:



As indicated above (Eq. 2), persulfate can be catalyzed by heat which leads to formation of free radicals of $SO_4^{\bullet-}$ ³². Formation of sulfate radicals in aqueous phase would result in production of the hydroxyl radical (HO^{\bullet} , $E^{\circ} = +2.7V$) through radical inter-conversion reactions³³. In accordance with Eqs. 5 and 6, both $SO_4^{\bullet-}$ and HO^{\bullet}

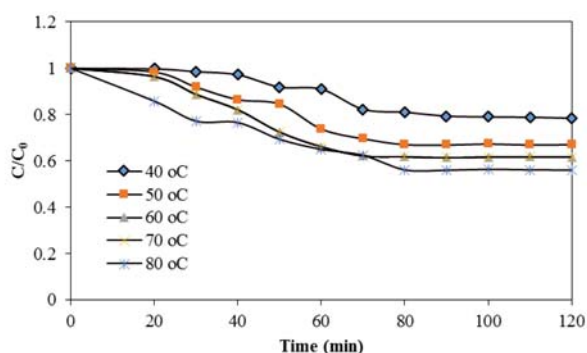
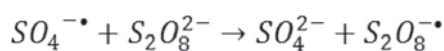


Figure 1. Effect of temperature on COD removal of petrochemical wastewater using thermally activated persulfate, pH: 7, reaction time: 0–120 min, persulfate concentration: 1 g/L

radicals are responsible for oxidation of recalcitrant organic matter in heat activated persulfate oxidation process.

Effect of the persulfate concentration

In order to determine the effect of persulfate concentration on COD removal, different persulfate concentrations (0.5–5 g/L) were added to solution at initial pH value of 7 and temperature of 70°C (Fig.2). Increasing persulfate concentration from 0.5 to 5 g/L, enhanced the COD removal from 17.76% to 72.96%. Near COD removal of about 87% for initial persulfate dosage of 4 and 5 g/L can be explained by this effect Persulfate concentration 4 g/L was considered as the selected level for remaining experiments because of acceptable removal efficiency, beside less chemical usage and non-significant difference of removal efficiency (p -value < 0.0065) according to non-parametric Kruskal Wallis statistical analysis. This is due to the fact that higher persulfate concentration will produce higher $SO_4^{\bullet-}$ radical in solution during heat activation³⁴. According to literature an increase in the initial persulfate dosage in acidic pH above a critical concentration would not continuously increase the removal efficiency, because persulfate acts as a scavenger of sulfate radicals as shown in Eq. (7)³⁵:



$$k = 5.5 \times 10^5 \text{ M}^{-1} \text{ S}^{-1} \quad (7)$$

Ji et al. (2015) observed that increasing the persulfate concentration from 0.1 mM to 2 mM enhanced the COD removal from 10% to 98% for groundwater remediation³⁶.

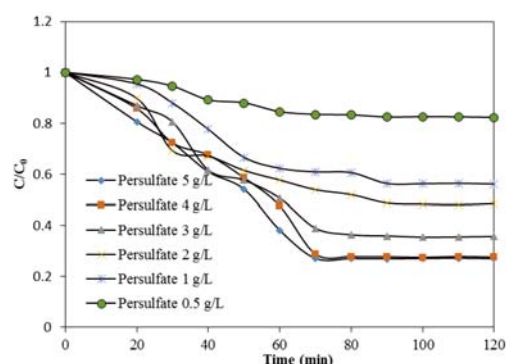
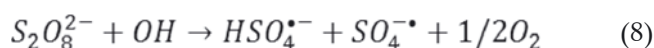


Figure 2. Effect of persulfate concentration on COD removal for petrochemical wastewater using thermally activated persulfate, pH: 7, temperature: 70°C, reaction time: 0–120 min

Effect of initial pH

Effect of pH on COD removal was evaluated at persulfate concentration of 4 g/L, temperature of 70°C and varying pH range of 3–9 (Fig. 3). Results indicated that acidic pH values favored COD removal and the most removal efficiencies of 87%, 86.67% and 86.02% were observed for initial pH values of 3, 4 and 5 respectively. This can be attributed to rapid conversion of $SO_4^{\bullet-}$ radicals to OH^{\bullet} radicals at basic conditions. In addition, more sulfate radicals could be generated through acid catalyzed persulfate activation in acidic condition, which might accelerate the COD removal^{22, 37, 38}. In accordance with current study finding, Kordkandi et al³⁹ (2014).reported that decreasing initial pH from 9.3 to 2.3 led to increase in dye removal from 65% to 96%. In another recent study by Zou (2014) on decolourization of methyl orange using persulfate, pH 5 was reported as optimized level⁴⁰. Also, Deng and Ezyske⁴¹ reported low pH value of 4 for as the optimum level. It should be noted that COD removal at initial pH value of 9 was still considerable (about 62%) which can be attributed to persulfate activation via alkaline condition. The effect of basic pH on persulfate activation has been discussed by Abu Amr (2013)¹⁸, as bellow (Eq. (8))⁴²:



Kinetic study

The kinetic parameters of zero, pseudo first and second-order kinetic models including rate of the persulfate oxidation reaction for petrochemical wastewater were determined by plotting C_t against time, $-\ln(C_0/C_t)$ against time and $1/C_t$ against time respectively (Fig. 4) in selected conditions including pH value of 5, persulfate concentration of 4 g/L and temperature of 70°C. The individual kinetic equations are as bellow (Eq. (9) zero order, Eq. (10) first – order and Eq. (11) second-order^{43, 44}:

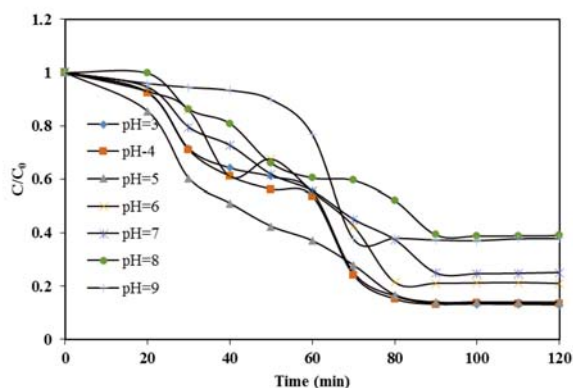


Figure 3. Effect of initial pH on COD removal of petrochemical wastewater using thermally activated persulfate, persulfate concentration: 4 g/L, temperature: 70°C, reaction time: 0–120 min

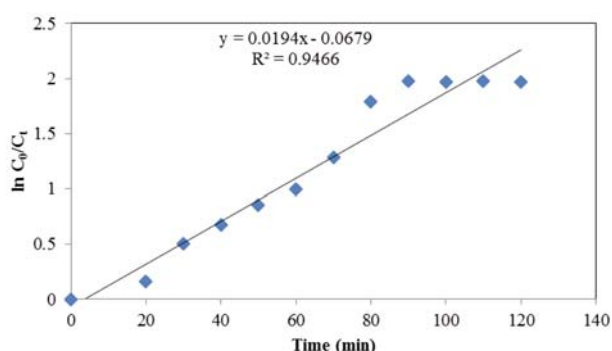


Figure 4. Pseudo first-order kinetic analysis of persulfate oxidation of petrochemical wastewater, pH: 5, persulfate concentration: 4 g/L, temperature: 70°C

$$C_t = C_0 - k_0 t \quad (9)$$

$$\ln C_0/C_t = k_1 t \quad (10)$$

$$1/C_t - 1/C_0 = k_2 t \quad (11)$$

where C_0 is the initial COD concentration in the solution (mg/L), C_t is the residual COD concentration in the solution (mg/L), t is the reaction time (min), and k_n is the corresponding rate constants ($n = 0, 1$ and 2). The reaction kinetics of COD removal through persulfate oxidation of petrochemical wastewater fitted well for pseudo first-order reaction with regression coefficient of 0.94 and rate constant of 0.019 min^{-1} . The details of the kinetic parameters are presented in Table 3.

Table 3. The kinetic parameters for zero order, pseudo first and pseudo second order models in thermally activated persulfate treatment of petrochemical saline wastewater

| Kinetic Model | Parameter | Amount |
|---------------|-----------|---------|
| Zero Order | K_0 | – |
| | R^2 | 0.892 |
| First Order | K_1 | 0.019 |
| | R^2 | 0.946 |
| Second Order | K_2 | 0.00005 |
| | R^2 | 0.895 |

Mineralization and intermediate metabolites

To determine the potential of thermally activated persulfate for mineralization of petrochemical wastewater, TOC removal compared to COD was evaluated at the reaction time of 180 min. Mineralization study was conducted at the initial COD concentration of 1410 mg/L,

persulfate concentration of 4 g/L, the initial pH of 5 and temperature of 70°C. Although a COD removal of 94.3% was observed within a reaction time of 180 min, the TOC removal reached 82.8% at the same operational conditions (Fig. 5). Production of intermediate byproducts such as Hexanoic acid, Cyclotrisiloxane, 5-Methyl-1-nitropyrazole, 1,1,1-trichloro-N-Acetylpyrrolidone, Benzaldehyde, Benzeneacetonitrile, Cyclotetrasiloxane, Benzene, O-Dichlorobenzene, Nitro-Benzene, Ethylbenzaldehyde, 1-ethenyl-4-methoxy, 2,5-Dihydroxyacetophenone, Bis(trimethylsilyl) ether, 2-Chloro-6-nitrotoluene, 6-Chitrotoluene, 1-Chloro-2-methyl-3-nitrobenzene, 4-Chloro-2-nitrotoluene, 2,5-Dichloronitrobenzen, 1-Nitro-3,4-dichlorobenzene, 2-methyl-1,3-dinitro-Benzene, Cyclohexyldimethylsilyloxyoctadecane, Pentachloro-Benzene, Thiocyanic acid carbazol-3,6-diyester, Octadecane, Sulfurous acid, Phthalic acid, 1,2-Benzenedicarboxylic acid, Isobutyl nonyl ester, Benzoic acid, 3,6-tricarbonitrile, Bis(2-ethylhexyl) phthalate, 1,2-Benzenedicarboxylic acid, Bis(2-ethylhexyl) phthalate is the main reason for lower TOC removal (Table 4). These organic byproducts are resistant to further degradation within studied time interval and proceeding the reaction or increasing persulfate concentration maybe effective for fully mineralization⁴⁵. In accordance with current study results Cai et al (2014), in their study on chemically activation of peroxydisulfate for degradation of Orange II dye reported that TOC removal was less than that of COD removal efficiency⁴⁶.

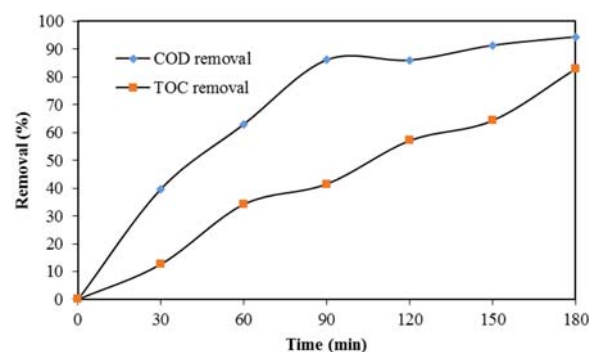


Figure 5. Mineralization of petrochemical wastewater by thermally activated persulfate within 180 min of reaction in comparison with COD removal efficiency [%]

Table 4. GC-MS chromatogram of treated petrochemical wastewater by thermally activated persulfate on produced intermediates, initial COD: 1410 mg/L, persulfate concentration: 4 g/L, pH: 5, temperature: 70°C, reaction time: 180 min

| Run time [min] | Constituent | Structural formula |
|----------------|-----------------------------------|-----------------------|
| 14.714 | Benzaldehyde | C_7H_6O |
| 16.711 | Cyclotetrasiloxane | $C_{48}H_{40}O_4Si_4$ |
| 17.289 | Acetic acid | CH_3COOH |
| 18.599 | Benzene | C_6H_6 |
| 18.777 | 1-chloro-2-methyl-3-nitro toluene | $C_7H_6ClNO_2$ |
| 22.771 | 1-Methyl-2,6-dinitrobenzene | $C_7H_6N_2O_4$ |
| 28.819 | Thiocyanic acid carbazol | $C_{14}H_7N_3S_2$ |
| 30.341 | Octadecane | $C_{18}H_{38}$ |
| 31.778 | Phthalic acid | $C_6H_4(COOH)_2$ |
| 32.233 | Benzoic acid | $C_7H_6O_2$ |
| 32.361 | Nonadecane | $C_{19}H_{40}$ |
| 36.143 | Heneicosane | $C_{21}H_{44}$ |
| 37.550 | Phenol | C_6H_6O |
| 43.593 | Bis(2-ethylhexyl) phthalate | $C_{24}H_{38}O_4$ |

Their results indicated that after 60 min, the removal efficiencies of (COD) and (TOC) were 52.1% and 31.9%, respectively and in contact time 24 h reached to 82.9% and 51.5%, respectively.

CONCLUSIONS

In the current study, COD removal from high TDS recalcitrant wastewater originated from petrochemical industry was subjected to thermally activated persulfate was investigated Operational parameters including temperature, persulfate concentration and initial pH were as evaluated. Increasing the persulfate concentration and the wastewater temperature up to a specified value, along with decreasing the initial pH to acidic range favored the COD removal. Organic matter removal of wastewater followed pseudo-first-order kinetic model. The experimental results showed that the degradation of COD was progressively influenced by reaction temperature and concentration of persulfate. In selected conditions, considerable mineralization of up to 82.8% was observed based on TOC removal after 180 min. remaining organic matter was comprised of intermediate metabolites such as Hexanoic acid, Benzaldehyde, 2, 5-Dichloronitrobenzen based on GC-MS analysis of final effluent. According to the findings of the current study, it can be concluded that thermally activated persulfate can be considered as an efficient and reliable alternative for treatment of high TDS wastewaters containing recalcitrant organic matter. Finally, more research for modification of obtained results is proposed specially in term of minimizing persulfate dosage. For high flow rates, a persulfate dosage of 5 mg/L is high and would be expensive.

ACKNOWLEDGEMENT

This research Project has been financially supported by Ahvaz Jundishapur University of Medical Sciences (Grant no ETRC 9504).

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