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Activation of persulfate by Fe^{2+} for saline recalcitrant petrochemical wastewater treatment: Intermediates identification and kinetic study

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ABSTRACT

Saline waste waters would be re-mediated via various physical, chemical and biological techniques. In recent years, the application of advanced oxidation processes, based on the production of radical per-sulfate instead of radical hydroxyl, has been favored, due to increasing potential for oxidation of per-sulfate (EO = 2.01 V), compared to hydroxyl (EO = 2.8 V). In this study, the efficiency of Fe^{2+}/per-sulfate process in COD removal from wastewater as well as improvement of wastewater biodegradability were studied. Result indicated that organic matter was rapidly degraded at pH = 3 which shows that lower pH values will be favorable for COD removal. The maximum removal efficiencies for COD were obtained 67 and 69% after 30 min and 120 min time intervals, respectively. With increasing per-sulfate/Fe^{2+} ratio from 0.5:1 to 6:1, the efficiencies of COD removal were increased from 35 to 67% and with a further increase of up to 10:1 ratio, the removal efficiency was declined. In this study, the AOS values before and after process optimization (pH = 3, PS: 10 mM and reaction time 30 min) were obtained +3.27 and +2.23, respectively. So, AOS indices showed an increasing trend of mineralization. The main products of the wastewater degradation were oxime-, 2-propanone, pentanamide, propanenitrile, benzenamine, 1, 4-dichloro-2-(methylthio) benzene, 4-cyclopentene-1,3-dione, 4-chloro-2e(chloromethyl)-1-butene, 4,5-bromm acetyl benzo cyclobutene, p-benzoquinone, niceke-6, hydroquinone.

Keywords: Saline petrochemical wastewater; Advanced oxidation process; Persulfate; Fe^{2+}

1. Introduction

The production of wastewater containing non-degradable and toxic compounds and treatment of high-saline wastewater is one of the serious challenges in chemical industries. The wastewater produced by the petrochemical industries has non-degradable and toxic compounds such as nitrobenzene, toluidine, chlorobenzene and also high salinity. Total dissolved solid (TDS) of saline wastewater is about 25,000–35,000 mg/l. Saline waste waters have been re-mediated using a wide range of physical, chemical and biological techniques [1–6]. Among various treatment techniques, advanced oxidation processes have been proposed, due to its high efficiency and also complete degradation of organic matter. This process is based on production of free radicals, especially hydroxyl radical. This radical has an oxidizing power of $E^0 = 2.8$ which can easily break organic bond and convert them to simpler compounds [7,8]. Commonly used techniques such as Fenton, Photo-Fenton, ZnO/UV, TiO_2/UV, all based on radical hydroxyl production, have been studied in various studies and mainly to purify the pollutants in synthetic conditions [8–10]. Recently, application of advanced oxidation processes, based on the production of radical per-sulfate (PS), instead of radical hydroxyl has been increased due to the increased potential for oxidation of per-sulfate (EO = 2.8 V), in comparison with hydroxyl (EO = 2.8 V). Per-sulfates, especially sodium per-sulfate have several advantages such as crystalline form, cost-ef-

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fectiveness, and easy maintenance and proper function in a wide pH range [11]. PS is activated with heat, UV light, and the transition metal elements (Me^{n+}), as shown in Eqs. (1) and (2) [11,12].

$$S_2O_8^{2-} + heat / Uv \rightarrow 2SO_4^{-\bullet} \tag{1}$$

$$S_2O_8^{2-} + \left(Me^{n+}\right) \rightarrow SO_4^{-\bullet} + \left(Men^{+1}\right) + SO_4^{2-} \tag{2}$$

Similar to transitional metal ions, $Fe^{\bullet}$ is applied as a source of Fe^{2+} and for activation of PS ions. However, the activated per-sulfate with Fe^{2+} can break down organic substances, but often incomplete degradation is occurred which leads to pause of reaction, because of additional Fe^{2+} as a scavenger of sulfate radicals [13]. On the other hand, organic chelating agents are applied for activation of per-sulfate and increasing the contaminant degradation organic matter [14]. Also, during process, Fe(II) was changed to Fe (III) during formation of sludge. While, a chelating agent i.e. EDTA is used to solve the sediments. The principal reactions with $Fe^{\bullet}$ are occurred, according to Eqs. (3) and (4) [13]:

$$S_2O_8^{2-} + Fe^{\bullet} \rightarrow SO_4^{-\bullet} + Fe^{2+} + 2SO_4^{2-} \tag{3}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet} + Fe^{3+} + SO_4^{2-} \tag{4}$$

Fe^{2+} as a transition metal starts the fallowing reactions to change per-sulfate into sulfate radical anions ($SO_4^{\bullet -}$) and sulfate radical ($SO_4^{\bullet}$), according to Eqs. (5) and (6). The generated sulfate radical can be combined with other radicals, in accordance with the following equations: [13,15,16].

$$-O_3S - O - SO_3^{-} + \left(Fe^{2+}\right) \rightarrow SO_4^{\bullet} + SO_4^{2-} \tag{5}$$

$$SO_4^{\bullet -} + H_2O \rightarrow OH + SO_4^{-\bullet} + H^{+} \tag{6}$$

Due to the presence of electron transfer reactions, radical sulfate has a longer half-life in the material. In addition, sulfate radical is more selective than hydroxyl radical to eliminate persistent organic pollutants [17]. In previous research, a large number of transition ions have been used to activate per-sulfate, but all the transition ions were not efficient. Copper is one of the high redox transition metals which can be usually found in the oxidation states of Cu(I) and Cu(II) [18]. In other studies, per-sulfate activation with copper oxide has been occurred, using a radical mechanism and main species hydroxyl radicals [19]. In this study, the efficiency of Fe^{2+}/per-sulfate (Fe^{+2}/PS) process in COD removal from wastewater as well as improvement of wastewater biodegradability were examined. The study of influence of effective parameters in the process, as well as determination of compounds in the wastewater and the final products derived from the process were one of the important aims of this study.

2. Materials and methods

2.1. Characteristics of raw wastewater

The raw wastewater was collected from a petrochemical industry, placed in Khuzestan province, Iran. The obtained samples were kept in a refrigerator at 4°C. The average concentrations of COD, BOD5, TDS, TSS, TOC and pH of raw saline wastewater are presented in Table 1.

2.2. Chemicals and instruments

All chemicals such as iron(II) sulfate, sodium hydroxide, sulfuric acid, sodium per-sulfate potassium dichromate, mercury sulfate and silver sulfate, were analytical grade and prepared from Merck, Germany Millipore. pH of solution was measured via a pH-meter (pH.Z.S.PTR79, Germany). A UV–vis spectrophotometer (DR6000, Hach USA) was used to determine COD concentration. Qualitative analysis of wastewater constituents was done by gas chromatography mass spectrometry (GC-MS) analysis (Model: Agilent 7890, USA) with HP-5MS capillary column (30 mm × 0.25 mm × 0.25 mm film thickness, 5% Phenyl–95% Methyl Siloxane phase). The carrier gas (helium) was fed with 1 ml/min constant flow rate. The temperature rate of oven was determined as 40°C at the 1 min which increased to 3000°C at 5°C/min for 3 min ultimately; the sample was injected into the instrument at a splitting ratio of 10:1.

2.3. Procedure

Effect of operational parameters including solution pH (3–11), sodium per-sulfate (NaPs) concentrations (5–20 mM), sodium per-sulfate (NaPS) to Iron (II) sulfate ratio (0.5–10) and contact time (15–120 min) were studied consecutively, according to one factor at the time methodology. In order to determine the effect of pH on Fe^{2+}/PS processes, in the per-sulfate : iron ratio of 4, and 30 min contact time, different pH values were measured in the range of 3, 6 and 9, and the performance of process was determined for removal of COD. The pH values were adjusted using sulfuric acid (1 N) and NaOH (1 N) solutions. In order to determine the effect of Fe^{2+}/PS process on improving wastewater biodegradability at optimal operational parameters, the process performance in COD and TOC removal were determined and the changes in degradability were studied. Per-sulfate was measured with spectrophotometric methods based on modification of the iodometric titration method. Intermediates of Fe^{2+}/PS process were identified by GC/MS analysis.

Table1
Characteristics of petrochemical wastewater

Parameter	Value
COD, mg L^{-1}	1650 ± 250
BOD5, mg L^{-1}	175 ± 10
pH	8.6 ± 0.8
Conductivity, µS/cm	49000 ± 580
TOC, mg L^{-1}	842 ± 110
TSS, mg L^{-1}	63 ± 7
TDS, mg L^{-1}	25500 ± 14700
Turbidity, NTU	24 ± 8
Appearance	Yellow

3. Result and discussion

3.1. Effect of initial pH

In all advanced oxidation processes, the most effective parameter in process which controls the process efficiency is initial pH of solution [20–22]. The influence of pH on Fe^{2+}/PS process was studied in the range of 3–9 (Fig. 1). Experiments were done at PS concentration of 10 mM, Fe concentration of 1.6 mM and Fe^{2+}/PS ratio of 6. As shown in Fig. 1, the acidic conditions caused higher organic matter decomposition since the COD removal efficiencies at pH 3.0, 6 and 9 were 69, 58.5 and 53%, respectively. The result indicated that organic matter was rapidly degraded at pH = 3 which showed the favorability of acid conditions for COD removal. In the advanced oxidation process with per-sulfate, which uses bivalent iron for the activation and production of sulfate radical, it influences both the type and state of iron present in the solution and the reactions of the per-sulfate anions with the pollutants. Thus, with a gradual increase in the acidic to alkaline range, the iron content of the oxidation system changes to iron trivalent species. Since only Fe^{2+} iron is capable of activating per-sulfate anion, with a decrease in the ratio of bivalent to trivalent iron, process efficiency was decreased. When pH is more than 4, solubility of the bivalent ions are decrease and becomes colloidal which in turn reduces process efficiency, according to Eq. (7) [22,23]:

$$Fe^{2+} + H_2O \rightarrow FeOH^- + H^+ \tag{7}$$

On the other hand, increasing the formation of species of ferric hydroxides, Fe $(OH)^{3+}$, Fe $(OH)^{4-}$, Fe $(OH)_3^{\bullet}$, Fe_2 $(OH)_3^{4+}$ has very little ability to activate per-sulfates anion [24]. The activation of per-sulfate anions with Fe^{2+}, which produces radical sulfate, can be changed by changing pH, and, radical hydroxyl will be produced instead of radical sulfate, under alkaline conditions. The pH values less than 7, especially 3 to 5 is superior to radical sulfate [Eq. (8)]. At pH 7 and 9, the presence of both radicals can be observed, but in alkaline conditions, especially at pH 9, hydroxyl radicals are superior [Eq. (9)]. Since in alkaline conditions, the potential for radical hydroxyl oxidation decreases sharply, the process efficiency even in the presence of the dominant radicals decreases [25]. Also, at high pH values, sulfate and hydroxyl radicals have a reactive effect, which in turn reduces the process efficiency, because of depletion of the oxidation system from radicals, according to Eqs. (10) and (11) [26,27].

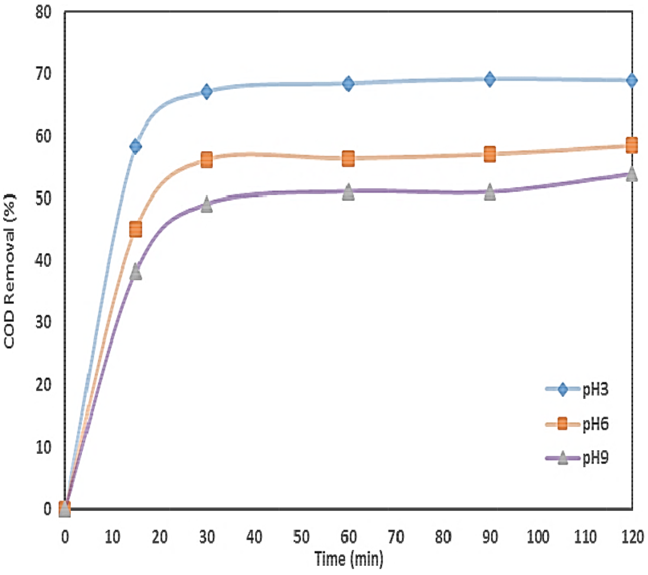


Fig. 1. The effect of initial pH on COD removal in Fe^{+2}/PS process (PS = 10 mM, PS/Fe^{+2}: 6).

$$SO_4^{\bullet} + H_2O \leftrightarrow OH^{\bullet} + H^+ + SO_4^{2+} \tag{8}$$

$$SO_4^{\bullet} + H^- \rightarrow OH^{\bullet} + SO_4^{2+} \tag{9}$$

$$SO_4^{\bullet} + OH^{\bullet} \rightarrow H^+ + SO_4^{2+} \tag{10}$$

The obtained optimum pH in this study has been reported in the literature [28,29].

3.2. The effect of contact time

Considering the importance of reaction time in the majority of chemical reactions, the optimum reaction time was determined according to the pre-selected conditions for other parameters based on previous studies [21,30,31]. In this step, experiments were carried out at the following operational conditions: pH = 3, PS concentration of 10 mM, Fe concentration of 1.6 mM and PS/Fe^{2+} ratio of 6. Effect of reaction time on Fe^{+2}/PS oxidation process was investigated in terms of COD removal. The reaction time varied between 15 to 120 min. The removal of organic matter showed an improving trend. Based on the results of this stage, the high efficiency of COD removal was determined at 30 min (Fig. 1). The maximum removal efficiencies for COD were obtained 67 and 69% after 30 and 120 min reaction times, respectively. Therefore, the optimum contact time for PS/ Fe^{2+} oxidation process was achieved in 30 min. Xu et al. (2010) reported that azo dye orange G - as a model azo dye in aqueous solution - was successfully degraded by the per-sulfate/Fe^{2+} and 99% of OG degradation was achieved in 30 min [32]. So, the results of this study are consistent with the results of present study.

3.3. The effect of PS/Fe^{2+} ratio

Per-sulfate as a source of sulfate radical generation in the per-sulfate/Fe^{2+} oxidation process - has a strong effect on the oxidation of organic materials [14]. To investigate the performance of Fe^{2+} in raising per-sulfate oxidation, the per-sulfate/Fe^{2+} ratios (g/g) were fixed at different values of 0.5, 1, 2, 4, 6, 8, 10 (Fig. 2). According to Fig. 2, with an increase in per-sulfate/Fe^{2+} ratio from 0.5:1 to 6:1, the efficiencies of COD removal were increased from 35 to 67%, respectively and with a further increase of up to 10:1 ratio, the removal efficiency was declined. Higher dosage of PS could improve the generation rate of sulfate radicals, partially, which accelerated the COD removal. With increas-

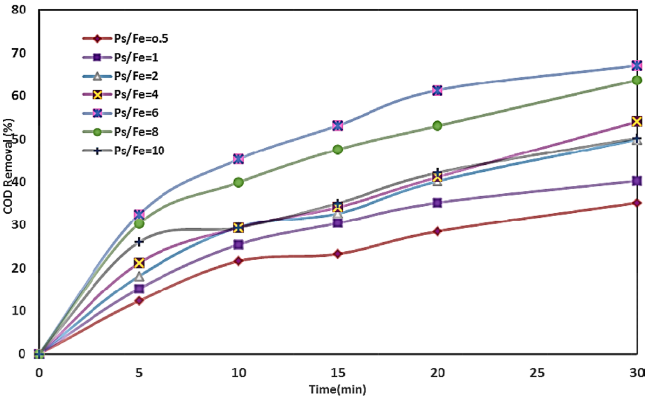


Fig. 2. The effect of per-sulfate/Fe^{2+} ratio on COD removal in Fe^{+2}/PS process (pH: 3, PS: 10 mM, Time: 30 min).

ing PS dosage, SO_4^{-} is produce too much can also act as an effective scavenger of sulfate radicals When Fe^{+2}/PS ratio is higher than 6:1, a balance between the generation and consumption of sulfate radicals was likely achieved, and the COD decay rate leveled off. In addition, sulfate radicals reacted with excessive PS to produce SO_4^{2-} that will act as a scavenger of sulfate radicals, base on Eq. (11) [33]:

$$SO_4^{-}+S_2O_8^{2-} \rightarrow SO_4^{2-}+S_2O_8^{-} \tag{11}$$

Similar findings have been reported in the literature on per-sulfate/Fe^{2+} oxidation process [14] who applied Fe^{2+} to activate per-sulfate.

3.4. Effects of per-sulfate dosages

Fe^{2+} reagent was used to improve per-sulfate oxidation efficiency during the oxidation of organic materials. The applied levels of per-sulfate and Fe^{2+} for enhancement of oxidation efficiency were determined. To survey the optimum amount of per-sulfate and Fe^{2+} in the oxidation of COD, different dosages of (PS/Fe^{2+}) were examined by setting the PS/Fe^{2+} ratio at 6:1 with varying levels of both per-sulfate and Fe^{2+} (Fig. 3). By increasing the per-sulfate dosages over 10 mM, the efficiency of oxidation process in removing organic materials was enhanced. The maximum removal of COD was obtained 67% at PS/Fe^{2+} dosage, 10 and 1.66 mM. The amount of residual per-sulfates remaining in the treated wastewater was negligible and per-sulfate was oxidized completely. The water content can be reduced to below 60% with sludge amount of 5 g, per-sulfate dosage of 10 mM.

3.5. Effect of iron dosage

In this study, the effect of different concentrations of iron on the process efficiency was investigated. Removal efficiency was investigated at specific COD concentration, 10 mM PS concentration, pH 3, 30 min reaction time and varied Fe^{2+} concentrations (1, 1.25, 1.6, 2.5, 5 and 10 mM). The aim of addition of iron ions was increasing the activation rate and decreasing reaction time and the results are presented in Fig. 4. As can be seen, changes in Fe^{2+} concentrations as one of the effective agents of per-sulfate radical will affect the removal efficiency. In 1.6 mM Fe^{2+} concentration, the removal efficiency was increased to 67.13%. By changing Fe^{2+} concentration, the removal efficiency was also declined. In the process of advanced oxidation with per-sulfate anion which uses Fe^{2+} for activation and generation of sulfate radicals, pH of solution affected both the species and the iron content of the solution, as well as the reaction of the per-sulfate anions with the pollutants. With a gradual increase in solution pH from acidic to alkaline, the iron content of the Fe^{2+}/ PS oxidation system was changed to Fe^{3+}, since only Fe^{2+} is capable of activating per-sulfate anions, by reducing the ratio of Fe^{2+} to Fe^{3+}, the process efficiency was greatly reduced [22–24]. The amount of residual iron remaining in the treated wastewater was 0.5 mg/l base on spectrophotometric methods.

3.6. TDS variation of effluent

In chemical and electrochemical processes, adding a chemical agent affects the total dissolved solids [34]. Addition of PS increased TDS significantly as TDS were increased from 25500 to 44350 mg/L for sole application of PS. All processes that had used PS enhanced TDS of effluent considerably resulting from hydrolyzing the inor-

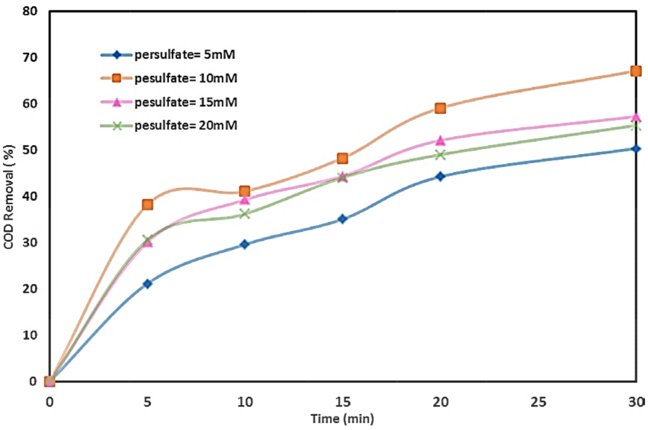


Fig. 3. The effect of per-sulfate dosage on COD removal in Fe^{+2}/PS process (pH: 3, PS/Fe^{2+}: 6, Time: 30 min).

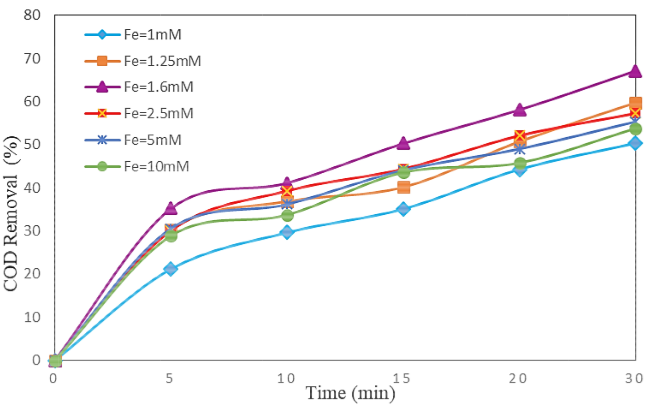


Fig. 4. The effect of Fe^{2+} dosage on COD removal in PS/Fe^{2+} process (pH: 3, PS/Fe^{2+}: 6, Time: 30 min).

ganic salt. Besides, adding chemical form of Fe(II) also increased TDS significantly. The processes of chemical and electrochemical coagulation showed different behavior in amount of TDS of effluent which was due to the presence of sulfate ion in chemical form of Fe(II). As a conclusion, although the presence of Fe(II) and PS is necessary for production of oxidative and coagulation agents, these agents remain in effluent and increase TDS of treated wastewater consequently.

3.7. Biodegradability

Due to the presence of toxic compounds, biological processes cannot efficiently treat petrochemical wastewater. On the other hand, AOPs are very expensive when they are used only for the treatment of organic material. Due to their capability of improving effluent quality, AOPs are uses before biological processes. In order to evaluate the biodegradability of treated effluent, the BOD/COD index was selected as the most common index [35]. The BOD/COD ratio of raw wastewater was 0.1, indicating that the biodegradability of this wastewater was low since BOD/COD values of <0.30 indicating that biodegradation done with difficulty. During the treatment of petrochemical wastewater, non-biodegradable compounds are changed to biodegradable compounds, since the BOD/COD ratio is raised. This trend was also observed in the Fe^{2+}/Ps process as BOD/COD increased to 0.35, indicating as non-biodegradable compounds are oxidized to simple compound that their biodegradabilities were easier than those of maternal compounds.

3.8. Mineralization

Per-sulfate and Fe^{2+} together act better as oxidants. The highest removal efficiency was obtained 67% in the Ps/Fe^{2+} oxidation process under optimum experimental conditions. In terms of finding the performance of per-sulfate/Fe^{2+} oxidation process on the mineralization of organic materials, TOC of wastewater was measured before and after oxidation process. The removal efficiency of TOC under optimum experimental conditions of oxidation process was 45% which indicates the mineralization of pollutants. Fig. 5 shows the removal efficiency of organic material at reaction time of 30 min. The COD and TOC removal efficiencies were 67 and 45%, respectively.

Any amount of contaminated mineralization is likely to reduce the environmental risk associated with discharging effluents. The rate of TOC removal was related to the per-sulfate concentrations from 1 to 10 mM. Increasing the dosage of per-sulfates does not result in further increase in the removal of TOC, due to the effects of sulfate on the performance of reactive species (XU et al., 2012, Anipsitakis 2004). The average oxidation state (AOS) was considered as a useful parameter to determine the oxidation degree of mixed solutions as well as providing indirect information about the possibility of degradation [36–39]. AOS index is a combination of COD and TOC to reveal the mineralization of organic matters, according to Eq. (12) [40]:

$$AOS = \frac{4(TOC - COD)}{TOC} \tag{12}$$

AOS index was measured before and after per-sulfate/Fe^{2+} oxidation process and the results are presented in Fig. 6. The range of AOS can be varied between +4 and -4. AOS 4 means the most oxidized form of carbon which belongs to carbon dioxide. AOS -4 is ascribed to methane which is the most reduced form of carbon [41]. In this study, AOS before the process and under process optimization (pH =3, PS: 10mM, PS/Fe^{2+}:6 and reaction time 30 min) were obtained +1.06 and +2.23, respectively. So, AOS indices showed an increasing mineralization trend.

3.9. Reaction intermediates

In oxidation systems, intermediate substances would be produced during wastewater treatment, which may be dangerous to the environment [11,42]. Generally, the organic pollutants are not degraded to CO_2, but organic intermediates are produced in many cases, the final product of wastewater depends on organic compounds for an

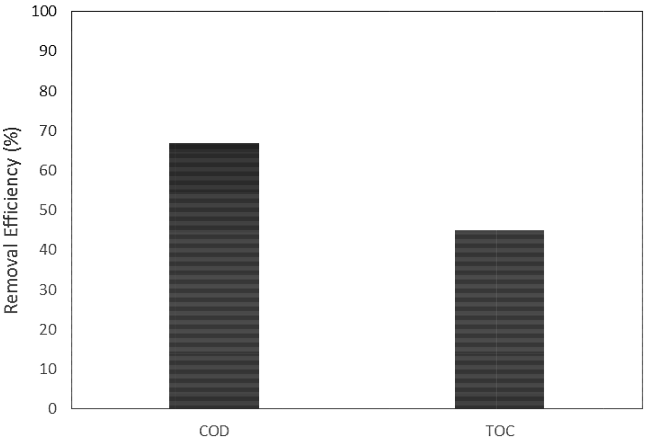


Fig. 5. COD and TOC removal efficiency in optimal conditions (pH: 3, PS/Fe^{2+}: 6, Time: 30 min).

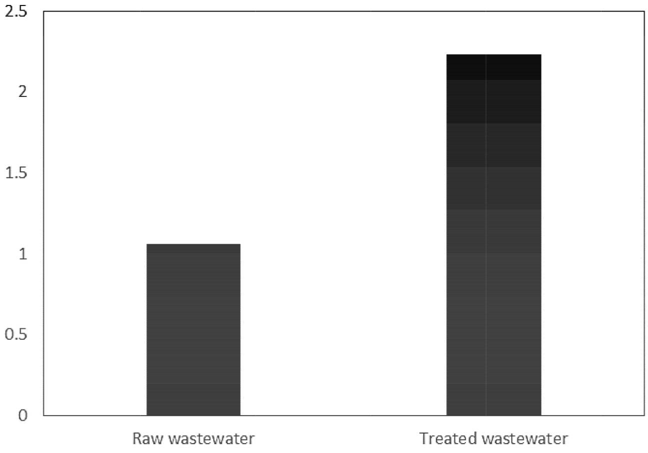


Fig. 6. AOS index measured before the PS/Fe^{2+} process and after the PS/Fe^{2+} process (pH: 3, PS/Fe^{2+}: 6, Time: 30 min).

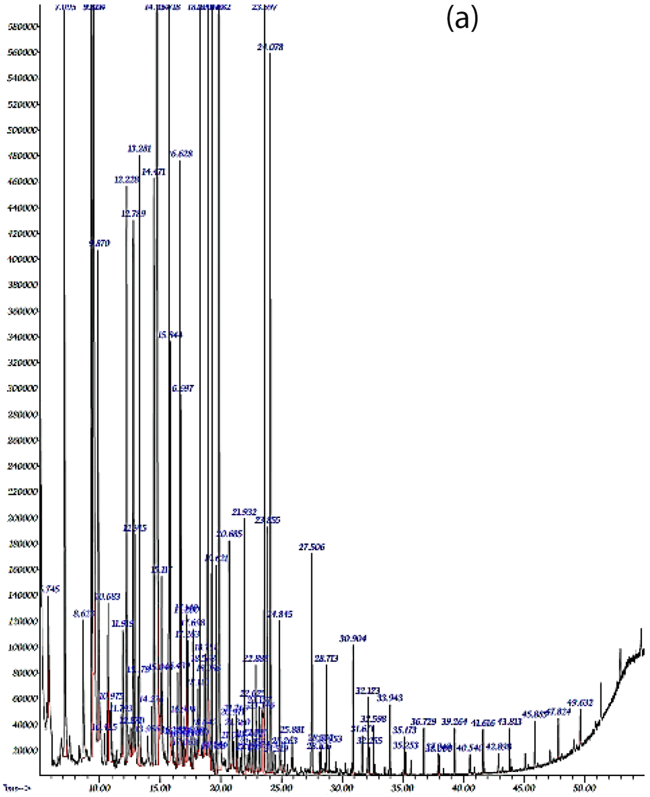


Fig. 7. (a) GC-MS chromatogram of raw petrochemical wastewater.

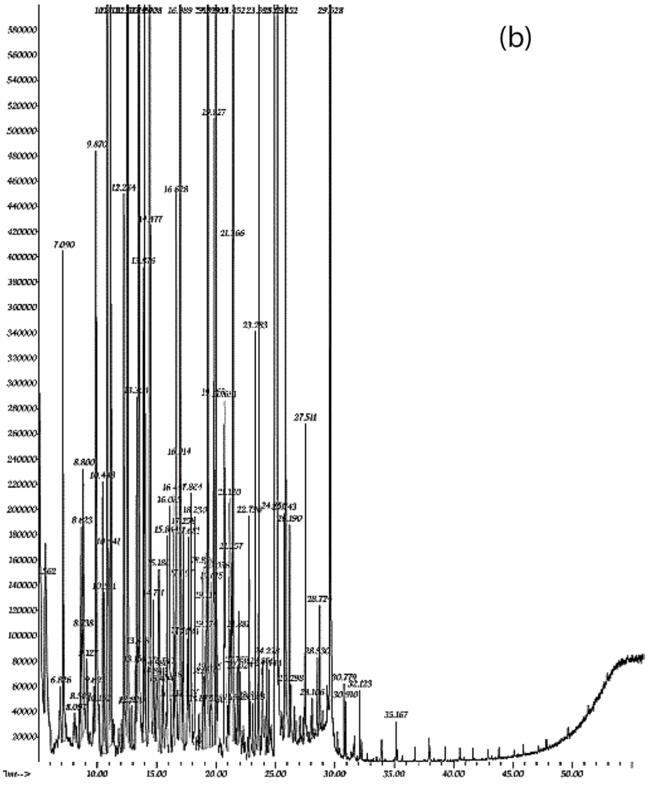


Fig. 7. (b) GC-MS chromatogram of intermediates after oxidation process (pH: 3, PS/Fe^{2+}: 6, Time: 30 min).

initial pH: 3, Fe^{2+}: 1.6 Mm and PS: 10 mM. To illustrate the effect of per-sulfate on COD decomposition, determination of intermediate compounds and investigation of intermediate product during Fe^{2+}/PS oxidation process was conducted. Phenol is the most important pollutant before the reaction, which is lost after the oxidation process. In the present research, the intermediate were identified using GC-MS device (Figs. 7a and b). Result showed that the principal products of wastewater degradation were oxime-, 2-propanone, pentanamide, propanenitrile, benzenamine, 1, 4-dichloro-2-(methylthio) benzene, 4-cyclopentene-1,3-dione, 4-chloro-2e(chloromethyl)-1-butene, 4,5-brommacetyl benzo cyclobutene, p-benzoquinone, niceke-6, hydroquinone (Table 2). The degradation of per-sulfate in aqueous solution generated hydroxyl and sulfate radicals which formed lots of organic contaminants into carbon dioxide [43].

3.10. Kinetic studies

Fig. 8 presents the kinetic studies of wastewater degradation in PS/Fe^{2+} process. Chemical kinetics were applied to study the chemical reaction rate. Results represented that the reaction kinetics under the optimal conditions (Ps: 10 Mm, pH = 3 and reaction time: 30 min), follows first-order kinetics model. For the first-order kinetics model, the half-life is independent of the initial concentrations of reactants, while in the second and zero-orders reaction, half-life are different from initial concentrations [33]. The PS/Fe^{2+} process data were proportionate to a first-order kinetic model, according to Eq. (13):

$$\frac{-dc}{dt} = kc \cdot C \qquad (13)$$

In these reaction orders, increasing concentration of oxidizing agent led to the enhancement of reaction rate [44]. In addition, the kinetic energy of materials was increased with increasing PS and which can increase the reaction rate as well.

4. Conclusion

This work was studied efficiency of Fe^{2+}/PS process in COD removal from wastewater as well as improvement of wastewater biodegradability. The result indicated that organic matter was rapidly degraded at pH = 3, which showed the favorability of lower pH values for COD removal. With an increase in PS/Fe^{2+} ratio from 0.5:1 to 6:1, the efficiency of COD removal showed an increasing trend from 35 to 67%, but further increase up to 10:1, caused decreasing the removal efficiency. By increasing per-sulfate dosages up to 10 mM led to declining the efficiency of oxidation process for organic matter removal. Findings illustrated that the principal products of wastewater degradation were oxime-, 2-propanone, pentanamide, propanenitrile, benzenamine, 1, 4-dichloro-2-(methylthio) benzene, 4-cyclopentene-1,3-dione, 4-chloro-2e(chloromethyl)-1-butene, 4,5-bromm acetyl benzo cyclobutene, p-benzoquinone, niceke-6, hydroquinone.

Table 2
The main intermediate of petrochemical wast water after PS/Fe^{2+} process

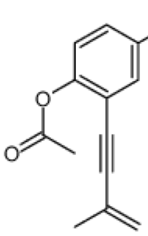
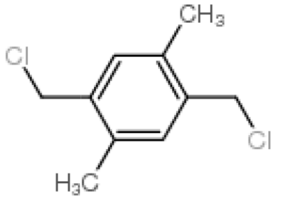
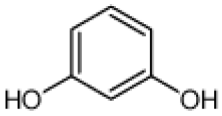
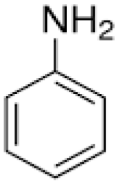
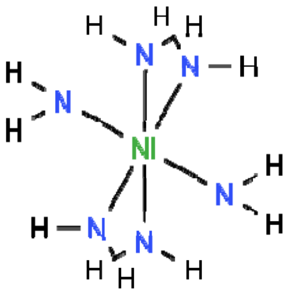
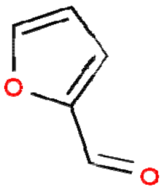
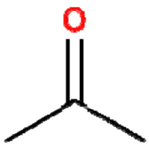
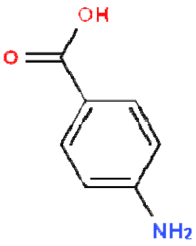
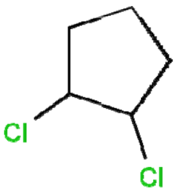
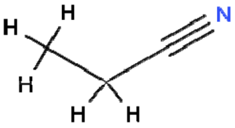
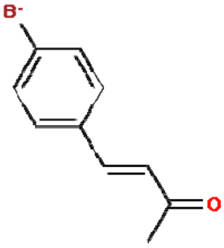
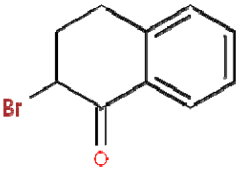
Intermediate	Chemical formula	Chemical structure	Area (%)
p-Benzoquinone	$C_{14}H_{12}O_3$		14.41
1,4-dichloro-2-(methylthio) benzene	$C_{10}H_{12}C_{12}$		11.09
Hydroquinone	$C_6H_6O_2$		9.09
Benzenamine	$C_6H_5NH_2$		6.55
Nickel-6	$H_{12}N_6Ni_{-6}$		6.05
4-Cyclopentene-1,3-dione	$C_5H_4O_2$		3.09
2-Propanone	C_3H_6O		3
Pentanamide	$C_7H_7NO_2$		2.95

Table 2
The main intermediate of petrochemical wast water after PS/Fe^{2+} process *(Continued)*

Intermediate	Chemical formula	Chemical structure	Area (%)
4-Chloro-2-(chloromethyl)-1-butene	$C_5H_8C_{12}$		2.77
Propanenitrile	C_3H_5N		2.29
4,5-Bromoacetylbenzocyclobutene	$C_{10}H_9BrO$		2.26
Oxime-	RR'C=NOH		1.49

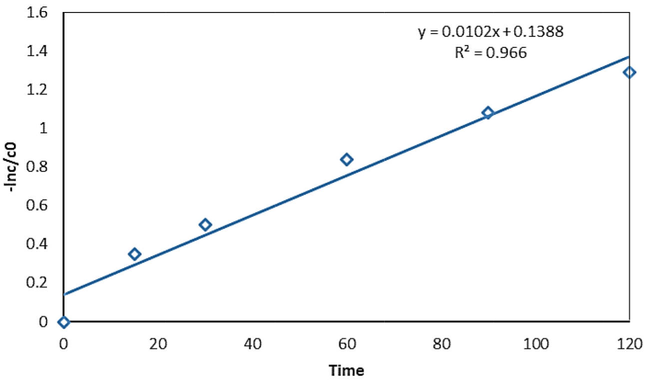


Fig. 8. Kinetic studies of wastewater degradation in PS/Fe^{2+} process (pH: 3, PS/Fe^{2+}: 6, Time: 30 min).

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