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Treatment of a saline petrochemical wastewater containing recalcitrant organics using Electro-Fenton process: persulfate and ultrasonic intensification

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ABSTRACT

Integration of persulfate and ultrasonic (US) irradiation with electro-Fenton (EF) process was studied for treatment of a saline petrochemical wastewater, and the effect of operational parameters was investigated. First, effects of pH, applied voltages, electrode distance (ED), US irradiation and reaction time on COD removal were evaluated for combination of US and EF (US/EF). Afterwards, the enhancement of COD removal efficiency was studied through persulfate addition (PUEF). A COD removal of 94.1% was observed for US/EF process with initial COD concentration of 850 mg/L and the reaction time of 210 min. Persulfate addition decreased the reaction time significantly and yielded a COD removal of 91.7% in 120 min. Efficiency of PUEF process over US/EF was also confirmed with higher pseudo-first order reaction rate constant of 0.0169 1/min, compared with 0.0126 for US/EF. GC-MS analysis revealed the significant destruction of recalcitrant and aromatic compounds of raw wastewater to the simpler and aliphatic forms. This finding was confirmed with biodegradability enhancement of effluent with BOD_5/COD ratio of 0.41. Current work indicated that PUEF is a reliable and efficient technology for treatment of saline industrial wastewaters containing recalcitrant aromatic organics.

Keywords: Saline petrochemical wastewater; Electro-Fenton; Ultrasonic irradiation; Persulfate; Advanced oxidation technology

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1. Introduction

Petrochemical wastewater contains significant amounts of organic and hazardous substances such as halogenated hydrocarbons, aromatic compounds, phenolic materials, oil and grease, aliphatic and polycyclic aromatic hydrocarbons and heavy metals, which have high toxicity for plants, animals and humans [1]. A large portion of petrochemical wastewaters are characterized as saline effluents, along with some aromatic compounds, which make them resistant to biodegradation [2]. Aromatic and aliphatic hydrocarbons possess detrimental environmental effects as well as carcinogenic and mutagenic effects, which must be treated by efficient techniques prior to discharging in water resources [3]. Different processes including biodegradation, membrane processes, adsorption and chemical processes have been evaluated for treatment of petrochemical wastewaters [4,5]. The low BOD_5/COD ratio

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less than 0.1 and high TDS contents of such wastewaters cause high toxicity to the activity of microorganisms and consequently, the application of biological processes would be restricted. Advanced oxidation processes, which is a work based on the creation of hydroxyl radical, have recently been considered for destruction of recalcitrant substances in saline media [6]. Fenton process is a simple, efficient and inexpensive process to treat recalcitrant industrial wastewaters, whose oxidation mechanism is based on creation of hydroxyl radicals from ferro ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) reaction in acidic media (Eq. (1)) [7]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \tag{1}$$

$HO^{\bullet}$ radicals are strong oxidizing agents ($E^0 = 2.8$ V) that oxidize organic molecules efficiently. Classic Fenton process intrinsically has several drawbacks including (i) low regeneration rate of ferric to ferrous iron which is necessary for decomposition of H_2O_2, (ii) production of large amounts of iron sludge and subsequent difficulties related to its treatment and disposal, (iii) operation in acidic media that restrict its efficiency in wastewater treatment practices [8].

Electrochemically production of H_2O_2 and Fe^{2+} ions, called electro-Fenton (EF) process provides the significant improvements in all aspects over classic Fenton. The basis mechanism of the EF system includes the regeneration of Fe^{2+} and H_2O_2, which will generate $HO^{\bullet}$ radicals without additional H_2O_2 through the Fenton reaction as Eq. (1). In EF called green approach, the anode is the source of Fe^{2+} and H_2O_2 would be produced in cathode [9]. In green EF process, oxygen molecules are reduced in carbon-based cathode and H_2O_2 is generated electrochemically, based on Eq. (2):

$$O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O_2 \tag{2}$$

In addition, ferrous ions are produced at iron anode, according to Eq. (3):

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{3}$$

As can be seen from Eq. (4), Fe(III) generated in Eq. (1), can be continuously reduced at the cathode to Fe(II), considering Eq. (4) [10]:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{4}$$

Another enhancement in EF process is combination with ultrasonic irradiation, called "Sono-EF" process (US/EF) as a new hybrid oxidation method. Ultrasonic is a sound wave with frequency higher than approximately 20 kHz. Various studies have demonstrated the high efficiency of US/EF [11]. The mechanism of destruction of contaminants by US irradiation relies on the chemical construction, volatility and solubility of the target pollutants. The two main dominant mechanisms in US-assisted destruction of pollutants are (i) pyrolysis of volatile substances in bubbles in a direct stae and (ii) oxidation of non-volatile substances by oxidizing factors produced in solution. In US oxidation, various species (e.g., H_2O_2 and $HO^{\bullet}$) can be formed in aqueous media, due to sonolysis of water, which is known as cavitation phenomenon. The cavitation caused further chemical reactions in different phases: internal cavity, interface boundary layer and liquid bulk. The reactions with $HO^{\bullet}$ can be taken place in the interfacial boundary layer regions or in the surrounding aqueous media at normal temperature and pressure. The overall scheme of reaction is as expressed in Eqs. (5)–(7) [12,13]:

$$H_2O +))) \rightarrow OH^{\bullet} + H^{\bullet} \text{ (Pyrolysis)} \tag{5}$$

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

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{7}$$

In US/EF process, formation of nuclei species as well as the creation of cavitation bubble increases creation of free radicals, based on Eqs. (8) and (9):

$$Fe^{2+} + H_2O_2 \xrightarrow{\text{US waves}} Fe^{3+} + HO_2^{\bullet} + H^{+} \tag{8}$$

$$Fe^{2+} + H_2O \xrightarrow{\text{US waves}} Fe^{2+} + HO^{\bullet} + H^{+} \tag{9}$$

This promotion enhances the degradation of recalcitrant substances in aqueous solutions. As can be seen from Eq. (7), the production of H_2O_2 through US irradiation is another enhancing effect of US/EF process. Another modification to enhance the removal efficiency is persulfate ($S_2O_8^{2-}$) addition to US/EF process (PUEF). Persulfate provides advantages such as high stability, reactivity, solubility and rapid destruction of recalcitrant organics [14]. Activation of persulfate through iron ions leads to the generation of sulfate radical ($SO_4^{-\bullet}$, $E_0 = 2.7$ V), which is a strong oxidant agent and acts with higher selectivity for the treatment of wastewater constituents as shown in Eq. (10) [15].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \tag{10}$$

In this research, the efficiency of US/EF and PUEF processes in removal of COD from a saline petrochemical wastewater was investigated using graphite cathode for in-situ production of H_2O_2 as the first report and effect of operational parameters and kinetics was also studied.

2. Materials and methods

2.1. Material

Sulfuric acid (H_2SO_4, 99%), silver sulfate (Ag_2SO_4, 99.99%), mercuric sulfate (99% $HgSO_4$, 99.99%), potassium dichromate ($K_2Cr_2O_7$, 99.5%) and sodium hydroxide (NaOH, 99.8%) were of analytical grade and purchased from Merck Co., Germany. Iron and graphite electrodes as sacrificial anode and the cathode with dimensions of 5 × 30 × 140 mm, respectively, were purchased from Seraj Company (Iran). A high TDS petrochemical wastewater was prepared from Mahshahr city in southwestern Iran and transferred to experimental laboratory using a cold box at 4°C on a weekly basis and its characteristics including COD, BOD_5, TOC, TDS, TSS and pH were analyzed.

2.2. Experimental setup

A cylindrical glass lab-scale setup (60 mm × 150 mm) with effective volume of 0.45 L was used to evaluate the treatment of petrochemical wastewater at room temperature (25°C ± 1°C). Electrodes (5 × 30 × 140 mm) were placed in a desired distance from each other inside the reactor and connected to a laboratory DC power supply with wire (model: PS 303D, 30 V, 5 A). The voltage could be set using the tuning screw (supplementary information). The solution was sonicated using a 50-kHz ultrasound generator (Hielscher: UP 400S, Germany), contained a 7-mm titanium probe. The probe tip was placed 20 mm below the surface of the solution and was sonicated in an on/off (5 s/5 s) pulse state in a desired power. The process of monitoring of solution pH was performed which was followed by adjusting to the specific value using HCl 1 N or NaOH 1 N via a digital pH meter model: Metrohm-827, Switzerland). In order to control temperature increase during the oxidation process, the whole reactor chamber was placed in a water bath containing ice cubes. All experiments were performed in batch mode.

2.3. US/EF and PUEF oxidation

A portion of 300 mL wastewater sample was poured into the reactor. Reactions were initiated following the turning on the DC power supply and sonication apparatus. Effects of operational variables including the initial pH (3–8), voltage (0.3–1.4 V), electrode distance (ED) (2–5 cm), reaction time (60–240 min) and the US power (200–400 W) on COD removal were investigated based on one factor at the time experimental design. Finally, addition of persulfate (0.25–1 mM) as an enhancer was studied. All of the experiments were carried out in room temperature (21°C–25°C). The reactor was aerated by means of an aerator pump with an injection rate of 6 Lair mim^{-1} to provide oxygen and mixing the reactor contents.

2.4. Experimental analysis

The specifications of saline petrochemical wastewater for chemical oxygen demand (COD), biochemical oxygen demand (BOD$_5$), total dissolved solids (TDS), total suspended solids (TSS) and pH were determined based on standard methods for examination of water and wastewater [16]. The process efficiency was calculated based on the COD analysis and the removal was calculated according to Eq. (11):

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \tag{11}$$

where C_0 and C_t represent the concentrations of COD (mg/L) at the beginning and end of reaction, respectively. A TOC analyzer (Shimadzu, TOC-VCSH, Japan) was applied for measurement of total organic carbon (TOC). Qualitative analysis of wastewater composition was carried out using GC-MS (model: Agilent 7890, USA) using capillary column HP-5MS (30 mm × 0.25 mm × 0.25 mm film thickness, 5%, 95% Fynyl-methyl siloxane phase). The carrier gas (helium) was fed using a steady-state 1 mL/min flow rate. The temperature of the stove was first adjusted to 40°C for 1 min and then increased to 300°C at 5°C/min. This temperature was maintained for 3 min. Finally, the sample was injected into a device by a 10: 1 ratio. The final data were reported in terms of the calculated average of at least three replicates, respectively.

3. Results and discussion

3.1. Characterization of raw wastewater

Table 1 shows some selected features of raw wastewater. The average concentrations of COD, BOD$_5$, TDS, TSS and turbidity of raw petrochemical wastewater were 800 mg/L, 114 mg/L, 25,000 mg/L, 215 mg/L and 25 NTU, respectively, based on two weekly intervals. Considering the low BOD$_5$/COD ratio (0.13), it can be noted that the studied petrochemical wastewater can be considered as a recalcitrant and biodegradation resistant sample. In addition, the high TDS content makes the selection of treatment process difficult. Since this wastewater contained a variety of aliphatic and aromatic compounds as well as halo-aromatic compounds at different concentrations and a BOD$_5$/COD ratio of 0.13 is classified as highly resistant against biodegradation and requires application of advanced oxidation processes for treatment.

3.2. US/EF oxidation

According to literature, the initial pH of solution is an important and key controlling parameter for oxidation of recalcitrant organics using EF-based reaction, because the solution pH determines Fe^{2+}/Fe^{3+} speciation and affects the creation of free radicals in aqueous media [17,18]. Since the low pH values reported in literature [19] limit the practical aspects of Fenton-based reactions, in current work, the influence of initial pH on the treatment of a high TDS petrochemical wastewater using US/EF process was investigated at the pH range of 3–8. The remaining variables including US power, voltage, ED and reaction time were set at 200 W, 1 V, 2 cm and 120 min, respectively. Results indicated that COD removal through US/EF process was highly pH dependent and according to Fig. 1a, the COD removal was decreased along with increasing the initial pH. Results indicated that the highest COD removal efficiencies of 55.5%, 55.4% and

Table 1
Characteristics of raw wastewater

Parameter	Value	
	Range	Average
COD (mg/L)	710–890	800 ± 122
BOD$_5$ (mg/L)	90–138	114 ± 23
BOD$_5$/COD	0.12–0.15	0.13
TOC	480–690	590 ± 48
TSS (mg/L)	160–270	215 ± 16
TDS (mg/L)	18,500–31,600	25,000 ± 3,470
Cl (mg/L)	13,890–19,600	15,070 ± 3,120
pH	7.4–8.8	8.1 ± 0.7
Turbidity (NTU)	20–30	25 ± 4

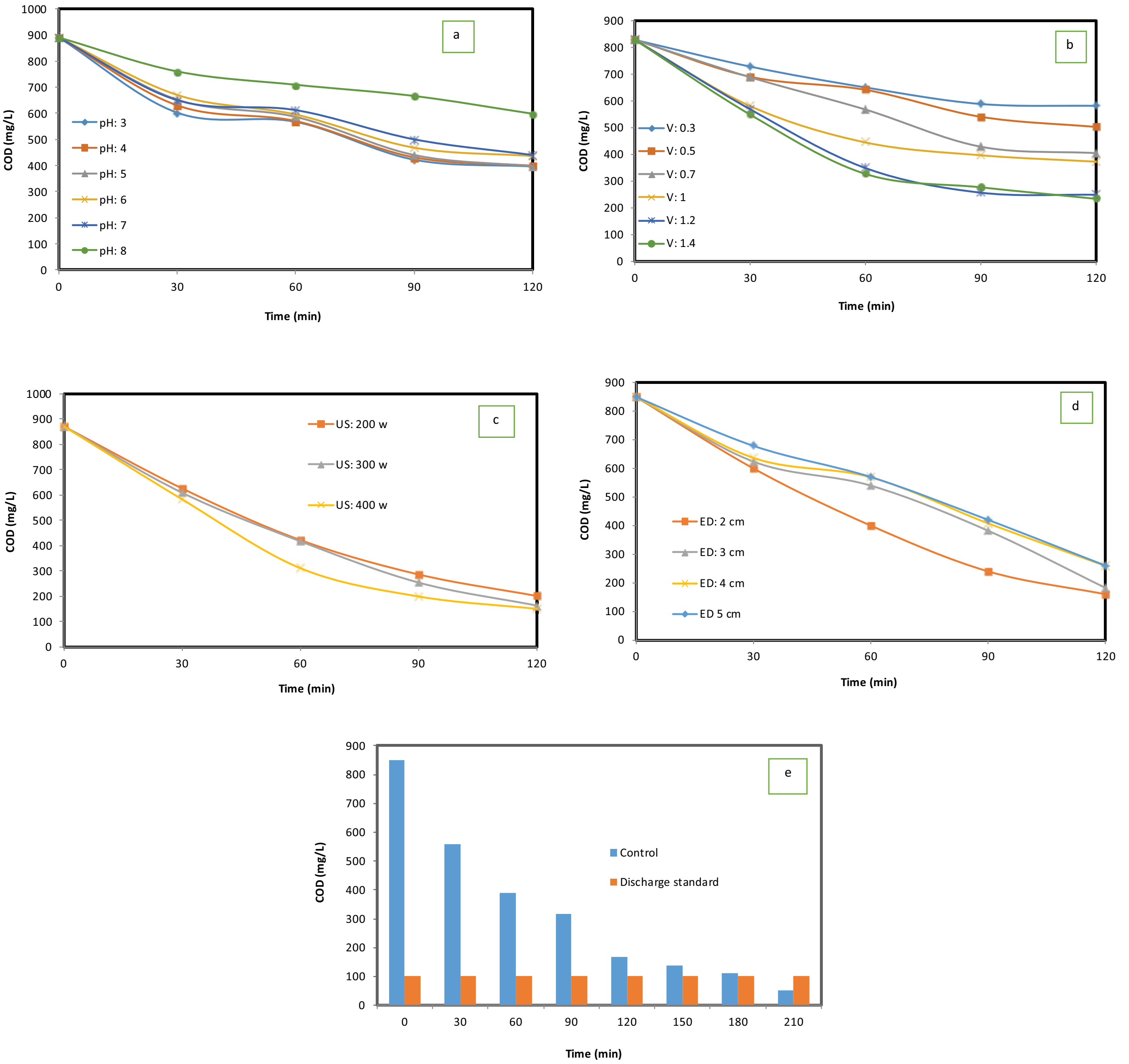

Fig. 1. Effect of operational parameters on COD removal using US/EF process, (a) effect of initial pH: voltage 1 V, US 200 W and ED 2 cm, (b) effect of voltage: pH 5, US 200 W and ED 2 cm, (c) effect of US power: pH 5, voltage: 1.2 V and ED 2 cm, (d) effect of ED: pH 5, voltage: 1.2 V and US 300 W and (e) effect of reaction time: pH 5, voltage: 1.2 V, US 300 W and ED 2 cm.

55.1% were observed for initial pH values of 3, 4 and 5, respectively. Higher H^+ concentrations would be present in acidic pH values, which in turn results in higher amounts of H_2O_2 (Eq. (12)) and consequently more $HO^{\bullet}$ radicals due to reaction of H_2O_2 with iron ions [20].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (12)$$

It should also be noted that at very low pH values (<3), H^+ acts as a radical scavenger [21]. The reduced COD removal at pH > 5 would be ascribed to instability of in-situ produced H_2O_2 and its self-decomposition into oxygen and water, according to Eqs. (13)–(15) [22,23]. In addition, the reaction rate of HO_2^- with $HO^{\bullet}$ radical is extensive ($k = 7.5 \times 10^9\ M^{-1}\,s^{-1}$), which leads to the creation of superoxide anions ($^{\bullet}O_2^-$) with lower redox potential, in comparison with $HO^{\bullet}$ (Eq. (16)). As the main purpose was investigation of the US/EF performance for remediation of a real petrochemical wastewater and practical issues are important, pH 5 was chosen for remaining experiments.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (13)$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{14}$$

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \tag{15}$$

$$HO^\bullet + HO_2^- \rightarrow H_2O + {}^\bullet O_2^- \tag{16}$$

Variation of pH in electrokinetics-based reaction is an important issue. The solution pH near the anode was 3.72, while the pH near the cathode was about 5.61. Production of H^+ ions in graphite electrode and their movement toward opposite charged electrode is the main reason of acidic conditions in the reactor.

Changes in applied voltage significantly influenced on the COD removal in a way that, by increasing voltage, the removal was enhanced. In order to determine the best technical and cost-effective level, a voltage range of 0.3–1.4 V was investigated under the operational conditions mentioned before and the initial pH 5. The most COD removal efficiencies of 69.78% and 71.68% were observed for voltages of 1.2 and 1.4 V, respectively (Fig. 1b). The enhancing effect of voltage can be attributed to increasing rate of H_2O_2 production as well as iron ions from victim anode, which results in the rapid production of $HO^\bullet$ radical according to Eq. (17) [24].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{17}$$

An extra increase in voltage level, due to increased hydrogen gas production in the cathode as well as increasing energy consumption can adversely affect the process efficiency. When the voltage is increased, the side reactions presented in Eqs. (18)–(21) occur at the cathode, which leads to higher generation of hydrogen gas that impedes EF reaction [25,26].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{18}$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \tag{19}$$

$$2HO^\bullet \rightarrow H_2O_2 \tag{20}$$

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{21}$$

Because of the lower power consumption and an insignificant difference (p-value > 0.05) in COD removal between voltages 1.2 and 1.4 V, the voltage level of 1 V was selected for remaining experiments.

US irradiation is known as one of the most effective factors in enhancement of EF reactions [27]. According to Fig. 1c, by increasing US power between 200 and 400 W, the COD removal showed an enhancing trend from 76.83% to 82.68%, respectively, in which COD removal for US levels of 300 and 400 W was almost same. Enhancement of the US power provides more energy for pulsation and collapse of bubbles. Accordingly, higher cavitation bubbles and reactive radicals would be produced in solution [28,29]. Along with US irradiation, a variety of oxidizing species (H_2O_2 and $HO^\bullet$) can be created in aqueous media because of cavitation phenomenon or water sonolysis which causes further chemical reactions in different phases: internal cavity, interface boundary layer and liquid bulk [30]. The reactions with $HO^\bullet$ would occur in the interfacial boundary layer regions at normal temperature and pressure as previously expressed in Eqs. (5)–(7) [31].

The US power of 300 w was selected as the desired level, due to an insignificant difference between COD removal in 300 W (81.1%) and 400 W (82.68%) and less energy consumption.

Effect of ED on COD removal was also studied at four levels (2, 3, 4 and 5 cm) under operational conditions including initial pH value of 5, the voltage 1.2 V, US power 300 W during 120 min time period. Based on Fig. 1d, the COD removal efficiencies at EDs of 2, 3, 4, and 5 cm were 81.1%, 78.58%, 69.52% and 69.41%, respectively. Results indicated that increasing ED adversely affected the performance of US/EF system. Increasing ED led to an increase in resistance and subsequently energy consumption. In addition, oxidation of H_2O_2 due to changing ED is possible, which can vary the concentration of H_2O_2 in solution [32,33].

Since obtaining the discharge standards to receiving waters was defined as a critical goal of current work, improving the COD removal was attempted with increasing the reaction time and using pre-determined operational conditions. Results showed the significant effect of contact time on COD removal with a sharp gradient up to 120 min, but by passing further reaction time up to 210 min, the COD removal rate increased at a slower rate. The COD removal of 80.2% in 120 min, reached to 94.1% by increasing the reaction time to 210 min (Fig. 1e). Degradation of readily degradable and simple structured compounds occurred at first 120 min, but mineralization and destruction of more resistant substances and intermediates required more reaction times of up to 210 min [34,35].

3.3. Persulfate enhancement

Effect of persulfate addition to US/EF oxidation was evaluated, due to the fact that persulfate could be activated using iron ions present in the solution. Fig. 2 indicates that increasing the persulfate concentration from 0.25 to 1 mM enhanced

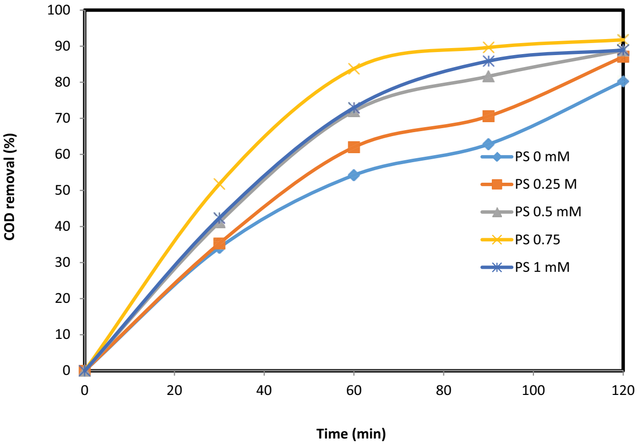

Fig. 2. Effect of persulfate addition on COD removal of high-TDS petrochemical wastewater in PUEF process (pH 5, voltage 1.2 V, US 300 W, ED 2 cm, COD 850 mg/L).

COD removal from 80% to 91.7%, while further increase in the concentration of persulfate up to 1 mM did not promote the system performance significantly, and a slight decrease was even observed. Persulfate ions as the main precursors for generating $SO_4^{\bullet-}$, directly related to any increase in persulfate concentration solution [36]. Continuous production of iron ions in scarified anode is the main activation source of persulfate through Fe^{2+} (Eq. (10)), to produce $SO_4^{\bullet-}$ radicals.

However, higher persulfate concentrations (beyond 1 mM) caused side reactions between as-generated $SO_4^{\bullet-}$ and persulfate ions in liquid phase as presented in Eq. (22), which led to a slight decrease in system efficiency [37].

$$S_2O_8^{2-} + SO_4^{-\bullet} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \tag{22}$$

As can be seen from Fig. 3, the enhancement of US/EF process using persulfate (PUEF) provided higher COD removal efficiency of 91.7% in significantly less reaction time of 120 min, compared with plain US/EF.

3.4. Kinetic study

In order to determine the reaction rates of US/EF and PUEF processes, pseudo-first-order kinetic was evaluated under selected conditions using Eq. (23) [38]:

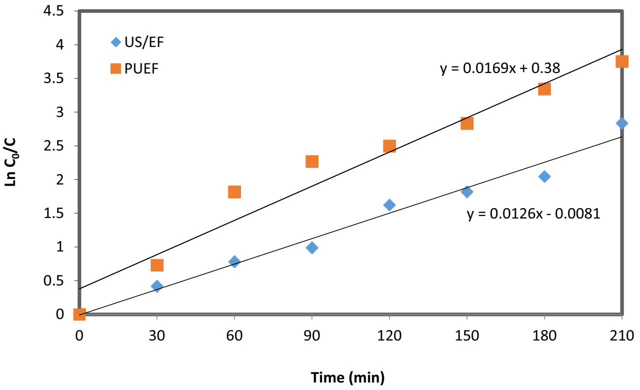

Fig. 3. Pseudo-first-order kinetic modeling of US/EF and PUEF processes for treatment of high-TDS petrochemical wastewater (pH 5, voltage 1.2 V, ED 2 cm, US 300 W and PS 0.75 mM).

$$\mathrm{Ln}\,\frac{C_0}{C_t} = k_1 t \tag{23}$$

where C_0 and C_t represent the concentrations of COD at beginning and end of reaction in saline petrochemical wastewater (mg/L), respectively, t is the reaction time (min), and k_1 is the corresponding rate constant (1/min).

The reaction rate constant and correlation coefficient of pseudo-first-order model for COD removal of petrochemical wastewater using US/EF and PUEF processes were obtained thereby plotting ln (C_0/C_t) against time. According to Fig. 3, the kinetic parameters of pseudo-first-order model were well fitted with experimental data of COD removal with R^2 values of 0.979 and 0.952 for US/EF and PUEF processes, respectively. The observation of higher COD removal in a significantly less reaction time for PUEF over US/EF is consistent with higher k value of 0.0169 (1/min) for PUEF, compared with that of 0.0126 (1/min) for US/EF.

3.5. Consumption of energy

The consumed electrical energy (P, kWh/m^3) during the electrokinetics-based oxidations is an important issue and was calculated using Eq. (24) [39]:

$$P = \frac{UIt}{V} \times 1{,}000 \tag{24}$$

where U is the cell voltage (V), I is the average cell current (A), t is the reaction time (h) and V is the treated volume (m^3). The sonication power was equal in both alternatives and which therefore neglected. Energy consumption was measured in different input variables for each process and initial COD concentration of 850 mg/L. As can be seen from Table 2, the energy consumption of 11 kWh/m^3 was obtained for US/EF and the value of 4.2 kWh/m^3 for PUEF in terms of treatment of saline petrochemical wastewater. The lower reaction time of 120 min for PUEF compared with 210 min for US/EF as well as lower current intensity is the main reasons for less energy consumption of PUEF rather than high COD removal as another advantage.

Table 2
Comparison of energy consumption for treatment of industrial wastewaters using electrokinetics-based processes

Process	Wastewater type or target pollutant	COD or TOC removal (%)	Energy consumption (kWh/m^3)	Study
US/EF[a]	Petrochemical	94.1	11	Current work
PUEF[b]	Petrochemical	91.7	4.2	Current work
UV/EF	Benzotriazole	76.3	14.95	[39]
Electrolysis	Petrochemical	94	32	[15]
Photo peroxi-coagulation	Petrochemical	89.44	1.1	[20]
Electrocoagulation	Resin manufacturing	78.7[c]	13	[40]

[a] Operational conditions: pH 5, voltage 1.2 V, ED 2 cm, US 300 W, reaction time 210 min.
[b] Operational conditions: pH 5, voltage 1.2 V, ED 2 cm, US 300 W, PS 0.75 mM and reaction time 120 min.
[c] TOC removal.

3.6. Catalytic potential and synergetic effect

The reliability of PUEF process on treatment of saline petrochemical wastewater with some control tests was investigated in similar selected input variables and an initial COD concentration of 850 mg/L. According to Fig. 5, 91.7% COD removal was observed for PUEF followed by 80.2% for US/EF and 72% for PS/EF process. The high efficiency of PUEF can be attributed to the simultaneous application of EF, US and oxidation, due to sulfate radicals in treatment of saline petrochemical wastewater. As can be seen from Fig. 4, the least COD removal rates of 11% and 5% belonged to persulfate alone and US irradiation alone, respectively, indicating the significant influence of these methods. For PS/EF and EF processes, 72% and 59% COD degradation was seen as other oxidative degradation controls respectively, which shows that oxidation potential of these systems are less than PUEF. Using the COD removals of control alternatives, the catalytic potential of PUEF as the superior process was calculated by comparing between COD removal rates obtained by alternative systems, according to Eq. (25) [41]:

$$\text{Catalytic potential (\%)} = R_{(\text{PUEF})} - \left[R_{(\text{US})} + R_{(\text{EF})} + R_{(\text{PS})}\right] \tag{25}$$

where R is the COD removal for each considered process. The calculated catalytic potential range of 16.5%–44.9% (Fig. 5) in different time intervals for PUEF implies that the integration of PS, US irradiation and EF is an efficient and reliable technology for treatment of saline petrochemical wastewater. The significant role of US irradiation on conversion of water molecules to $HO^{\bullet}$ through cavitation phenomenon as well as persulfate activation by continuous production of iron ions in anode is the main reason for this high catalytic potential.

3.7. Biodegradability assay of effluent

Characterization of final effluent in terms of biodegradability is an important issue which indicates the toxicity status as well as possibility for integration of biological process to complete the treatment process and lowering the contribution of chemical-based technologies [42]. Under selected operational conditions, the effect of PUEF process on improvement of biodegradability of effluent was evaluated using biodegradability assessment indices including carbon oxidation state (COS), average oxidation state (AOS) and BOD_5/COD ratio. AOS and COS values lie between –4 and 4 for methane and carbon dioxide as the most reduced and oxidized states of C, respectively. AOS and COS were calculated via Eqs. (26) and (27) [8,43]:

$$\text{AOS} = \frac{4 - 1.5\ \text{COD}}{\text{TOC}} \tag{26}$$

$$\text{COS} = \frac{4 - 1.5\ \text{COD}}{\text{TOC}_0} \tag{27}$$

where COD is chemical oxygen demand (mg/L), TOC is total organic carbon (mg/L) of the effluent after oxidation and TOC_0 is initial TOC (mg/L) of wastewater sample. The final COD and TOC of final effluent were determined to be 88 mg/L (89.6%) and 60 mg/L (90.3%), respectively. Fig. 6 demonstrates that AOS and COD values varied from 1.94 (mg/L) to 1/8 and 3/78 (mg/L), respectively. Furthermore, BOD_5/COD ratio increased to 0.41, which all mean that the effluent was changed to a more easily biodegradable medium, in comparison with raw wastewater, indicating the removal of the majority of recalcitrant constituents or destruction to simpler structured forms [44].

Based on the GC-MS analysis, the majority of the known organic compounds in raw wastewater were 1,3-cyclopentadiene, indene, azulene, decanoic acid and other hydrocarbons with lower concentrations. A qualitative GC-MS analysis was also carried out to observe the intermediate metabolites. Comparison between the GC-MS chromatograms of raw wastewater and effluent (Fig. 7) shows that initial heavy and aromatic compounds are broken down into simpler, aliphatic and cleavage ringed structures such as acetamide, benzoic acid, oxime, 1-hexanol, benzenamine, trichloroacetic acid, nonanal, decanoic acid and pentadecane. These findings confirmed the remarkable degree of mineralization and also cleavage of heavy ringed molecules to more biodegradable intermediates. Detailed variations of

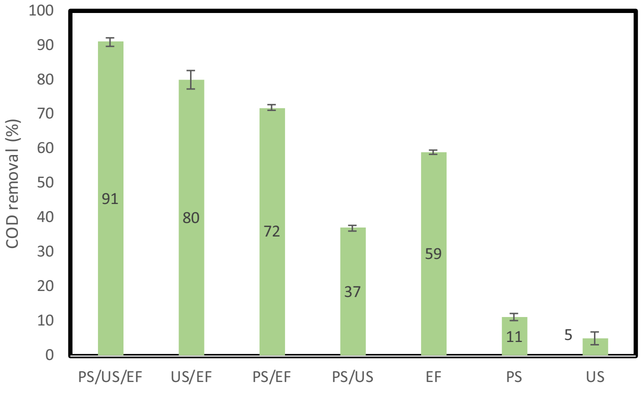

Fig. 4. Comparison of COD removal in different alternative process (pH 5, voltage 1.2 V, ED 2 cm, US 300 W, PS 0.75 mM, reaction time 120 min).

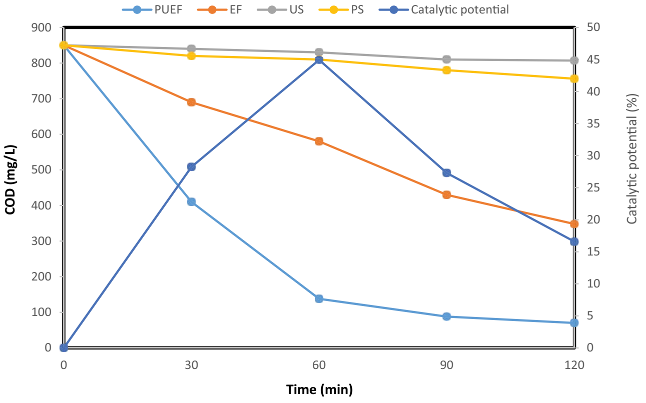

Fig. 5. Catalytic potential of PUEF process on COD removal of high-TDS petrochemical wastewater in selected conditions (pH 5, voltage 1.2 V, ED 2 cm, US 300 W and PS 0.75 mM).

main organic compound in raw petrochemical wastewater are presented in Table 3. As can be seen, a high removal efficiency (16%–100%) can be observed for the majority of organics. Of course production of new metabolites should be considered using GC-MS analysis of final effluent. Because of the non-selectiveness of obtained oxidized materials in these systems, creation of lots of intermediates is logical and extra oxidation of intermediates requires higher time periods.

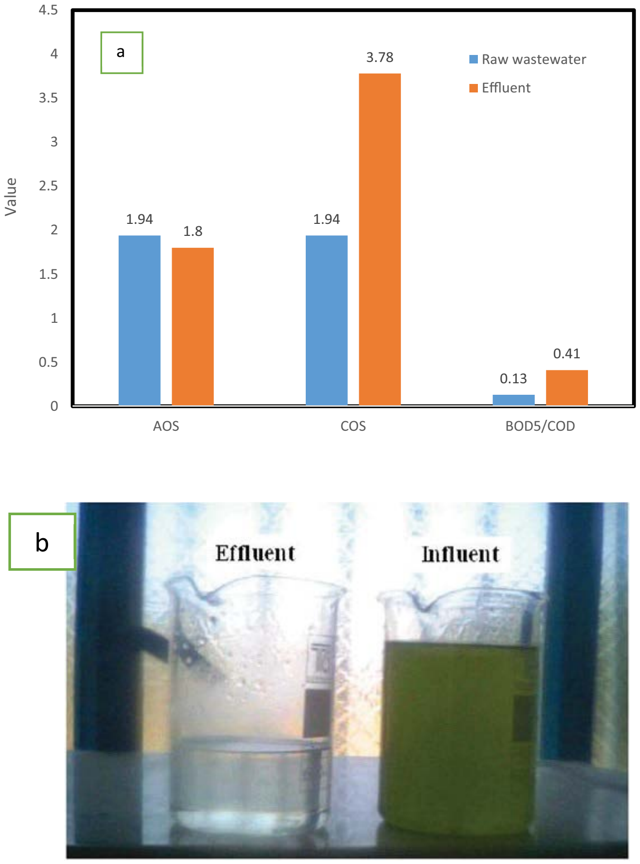

Fig. 6. (a) AOS, COS and BOD_5/COD values before and after oxidation of high-TDS petrochemical wastewater and (b) pictorial view of raw and treated sample (initial COD 850 mg/L, initial TOC 620 mg/L, pH 5, voltage 1.2 V, ED 2 cm, US 300 W and PS 0.75 mM).

4. Conclusion

Two electrokinetics-based processes including US/EF and PUEF were investigated for treatment of a real saline petrochemical wastewater containing different hydrocarbons with low biodegradability. Effect of operational variables including initial pH, voltage, US power, electrode distance, reaction time and persulfate addition was studied to determine the most efficient conditions for COD removal. Results indicated that both processes were pH dependent and the best results were observed in acidic pH conditions. Also, increasing voltage, US and reaction time improved the COD removal significantly through enhancement of the production rate of $HO^•$ radicals and H_2O_2. Evaluation of removal results with conventional kinetic models demonstrated that COD removal by two studied processes

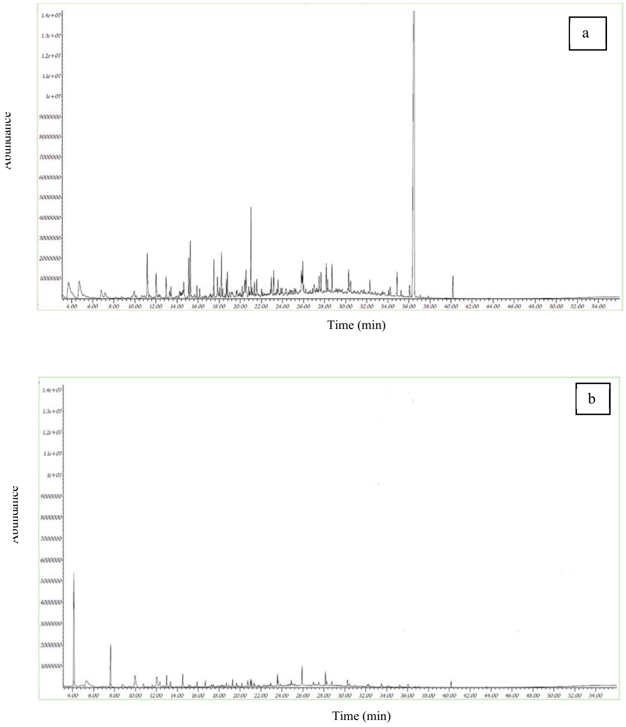

Fig. 7. GC-MS analysis of raw saline petrochemical wastewater compared with final effluent.

Table 3
Variations of the main organic constituents of raw wastewater compared with final effluent as well as most important metabolites

Organic compound	Area in raw wastewater (%)	Area in final wastewater	Removal (%)
Cyclopentane	1.79	0.58	67.5
1,3-Cyclopentadiene	3.08	0	100
Indene	1.62	0.16	90.1
Benzenamine	0.85	0.67	20.1
o-Tolic acid	0.93	0	100
Azulene	1.35	0.17	87.4
Decanoic acid	1.85	0.61	67
4-Methylvaleric acid	0.96	0	100

followed pseudo-first-order kinetics. Increasing the BOD_5/COD ratio and AOS and COS indices of final effluent proved the enhancement of biodegradability characteristics of such saline wastewater. The COD removal of around 91.7% in reaction time of 120 min as well as low-energy consumption of 4.2 kWh/m^3 for PUEF process indicate that this technology is a reliable, efficient, promising and cost-effective alternative for treatment of saline industrial wastewaters containing recalcitrant hydrocarbons, and supplemental pilot and full-scale studies are proposed to develop the technology and identifying all aspects as a trade technology.

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Supplementary information: