COD Removal from High Salinity Petrochemical Wastewater Using Photo-assisted Peroxi-coagulation

S. Jorfi,[a,b] S. Alavi,[b] N. Jaafarzadeh,[a,b] F. Ghanbari,[c] and M. Ahmadi[a,b]

[a]Environmental Technologies Research Center,
Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

[b]Department of Environmental Health Engineering,
Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

[c]Department of Environmental Health Engineering,
Abadan School of Medical Sciences, Abadan, Iran

Photo-assisted peroxi-coagulation (PPC) was investigated for treatment of high TDS (total dissolved solids) wastewater. The most important characteristics of the studied wastewater were high TDS of around 16428 mg L^{-1} and BOD$_5$/COD ratio of 0.07. Effective operating parameters, including initial pH values of 3–8, reaction time of 60–240 min, electrode distance values of 2–6 cm, and voltage values of 0.5–3 V were investigated in batch mode experiments. Optimum conditions were obtained at pH = 3, voltage = 1.5 V, electrode distance = 2 cm, and reaction time = 420 min, corresponding to 89.44 % COD removal, which meets the Iran environmental discharge legislation (COD = 100 mg L^{-1}). Kinetic analysis showed that pseudo first-order kinetic model was best fitted (R^2 = 0.97). GC mass chromatograms before and after treatment showed degradation of complex compounds to more simple constituents.

Keywords:
photo-assisted peroxi-coagulation, Fenton oxidation, high salinity wastewater, petrochemical industries, degradation

Introduction

Some industries produce high salinity wastewaters with high non-biodegradable organic compounds. Discharge of their non-treated streams into the environment causes serious damage to soil, groundwater, and surface water. Petrochemical effluents contain significant amounts of hazardous organic and inorganic chemical substances, such as halogenated hydrocarbons, aromatic compounds, phenolic substances, oil and grease, aliphatic and polycyclic aromatic hydrocarbons (PAHs), and heavy metals, which all possess high toxicity to plants, animals, and humans. In addition, a major portion of petrochemical wastewater is characterized as high TDS (total dissolved solids) that, together with their aromatic constituents, make them resistant to biodegradation. Most halogenated hydrocarbons, aromatics and phenolic substances have been categorized as priority pollutants, causing carcinogenic and mutagenic effects, which have to be removed from aqueous solution using efficient treatment techniques before being discharged into water bodies[1,2]. A range of physical, chemical, and biological processes and their integration, such as integration of advanced oxidation with coagulation, biodegradation using special microorganisms, membrane filtration, chemical precipitation, catalytic ozonation, photocatalytic degradation using nanoparticles as advanced oxidation processes (AOPs), have been investigated for treatment of petrochemical effluents[3–6].

Low efficiency and incomplete removal of non-biodegradable organic compounds due to plasmolysis and reduced cell activity are the most significant challenges in biological treatment of high salinity wastewater. Low BOD$_5$/COD ratio of less than 0.1 and high TDS content of produced wastewater have limited direct application of biological processes[2,7]. Additionally, conventional chemical oxidation and precipitation are not efficient enough, especially in terms of soluble organic matter and xenobiotics. AOPs, which work as a function of generation of non-selective and strong oxidative hydroxyl radicals, have recently been successfully employed for treatment of such recalcitrant wastewaters. AOP processes can generate hydroxyl radicals as a powerful agent for degradation of xenobiotic compounds[8].

Fenton oxidation is the most common technique for hydroxyl radical generation, (Eq. 1[9,10]):

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow OH^\bullet + Fe^{3+} + H_2O \quad (1)$$

*Corresponding author: Email: Ahmadi241@gmail.com

The application of Fenton oxidation has been limited due to storage, delivery, and economic constraints[8]. In the green chemistry approach, oxygen molecule was reduced carbon base cathode and H_2O_2 is generated electrochemically at acidic electrolyte, according to Eq. (2)[11,12]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$
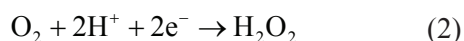
On the other hand, ferrous ion is generated at iron anode, according to Eq. 3.[13,14]

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (3)$$
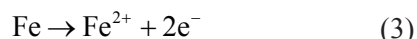
Moreover, ferric ion produced in Eq. (1), is reduced at the cathode and ferrous ion is regenerated consequently (Eq. 4). This phenomenon propagates chain reactions of Fenton oxidation.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$
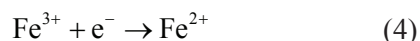
Iron hydroxide produced by the aforementioned mechanisms can remove organic pollutants through the coagulation process, as in Eq. (5). Coagulation and oxidation mechanisms are simultaneously fulfilled in the electrochemical cell, which is called peroxi-coagulation[13,14].

$$Fe^{3+} \text{ or } Fe^{2+} + nOH^- \rightarrow Fe(OH)n(s) \qquad (5)$$
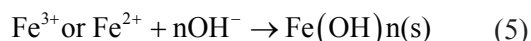
Application of UV irradiation can accelerate degradation performance of Fenton-base process through direct decomposition of hydrogen peroxide to hydroxyl radical (Eq. 6), and ferrous ion regeneration by photo-reduction of ferric ion to produce more hydroxyl radicals, as shown in Eq. (7)[15,16]:

$$H_2O_2 + UV \rightarrow HO + OH^\bullet \qquad (6)$$

$$Fe(OH)^{2+} + UV \rightarrow Fe^{2+} + OH^\bullet \qquad (7)$$
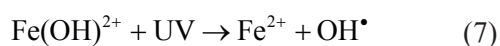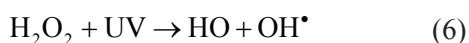
PPC is a hybrid process consisting of UV irradiation and electro-Fenton, which has not been applied for high salinity petrochemical wastewater.

Even though many AOPs, like photocatalysis, UV/H_2O_2, ozonation, electro-photocatalysis have been applied for COD removal from high salinity wastewater[17–25], no research has yet been performed to degrade COD in high salinity wastewater by PPC. In the present research, the efficiency of PPC to degrade COD in aqueous solution with graphite electrode cathode was studied.

Materials and methods

Material

All principal reagents applied for COD analysis were of analytical grade and purchased from Merck Company, which included sulfuric acid (H_2SO_4-99 %), silver sulfate (Ag_2SO_4-99.99 %), mercury sulfate ($HgSO_4$-99 %), potassium dichromate ($K_2Cr_2O_7$-99.5 %), sodium hydroxide (NaOH–99 %), ammonium chloride (NH_4Cl-99.5 %), and potassium de-hydrogen phosphate (kH_2PO_4–98 %). Graphite electrode was provided from Seraj Company (Iran). Real high TDS wastewater sample was obtained from a petrochemical industry located in the south of Iran and brought to the laboratory in cold box at 4 °C weekly, and its features such as COD, BOD_5, TOC, TDS, TSS, organic constituents, and pH were analyzed.

Experimental setup

The experiments were carried out in a 0.8-L quartz cylindrical batch reactor 6 cm in diameter and 16 cm in height. Graphite (3×15 cm, thickness of 3 mm) and iron (3×15 cm, thickness of 3 mm) were used as cathode and anode electrodes, respectively. The electric power was supplied by a laboratory DC power supply (Model: PS 303D). Air was injected to cathode at flow rate of 2 L min⁻¹. Low-pressure UVC lamps (6 W-Philips Company) were placed around the electrochemical cell at a distance of 3 cm to provide ultraviolet irradiation. The influence of UV light power was tested by application of zero, one, two, and three lamps corresponding to 0, 6, 12, and 18 W, respectively. The quartz vessel and the light sources were placed inside a black box to prevent UV emission. For each run, 0.6 L of wastewater was introduced into the reactor. The solution was magnetically stirred during the experiment. The reaction temperature was kept at 26–28 °C. The pH value of solution was continuously monitored and adjusted to desired value with 0.5 N H_2SO_4 every 5 min, where the volume of the acid was less than 3 mL. All of the experiments were conducted in batch mode. The effect of operating parameters, including initial pH (3–8), voltage (0.5–3 V), distance between electrodes (2–6 cm), reaction time (60 – 240 min), and UVC intensity (1, 2, 3 UV lamp) on COD removal were investigated consecutively according to one factor at a time experimental design.

Analytical methods

Raw high salinity petrochemical wastewater was obtained from a local petrochemical corporation, Mahshahr city, Iran, and transferred to laboratory within 2 h. Characterization of raw wastewater, in terms of chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total dissolved solids (TDS), total suspended solids (TSS), and pH was performed based on standard methods for the examination of water and wastewater[26]. The removal

efficiency (%) was calculated based on COD concentration via Eq. (8):

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \cdot 100 \qquad (8)$$

where, C_0 and C_t are the initial and residual COD concentrations (mg L^{-1}) at specified reaction time t (min). The pH of solution was continuously monitored using a pH-meter (Eutech, Cyberscan 1500).

Qualitative analysis of wastewater constituents was carried out 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). The carrier gas (helium) was fed using a stable 1 mL min^{-1} flow rate. The temperature rate of oven was firstly set to 40 °C for 1 min, and then increased to 300 °C at 5 °C min^{-1}. This temperature was maintained for 3 min. Finally, the sample was injected into the instrument at a splitting ratio of 10:1. All experimental data are expressed in terms of arithmetic averages obtained from at least three repetitions.

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 intervals were 1271 mg L^{-1}, 89 mg L^{-1}, 16428 mg L^{-1} and 168 mg L^{-1}, respectively (Table 1). From the low amount of BOD$_5$/COD ratio (0.07), it can be implied that the studied petrochemical wastewater has non-biodegradable features, and the study of chemical transformation processes is critical. Based on the GC-MS analysis (Table 2), the major organic substances recognized in raw wastewater were as follows: chlorobenzene, phenol, 3-(1,1-dimethylethyl), phe-

nol, 2-chloro-4-(1,1-dimethylethyl), ethyl ester, phenol-2,4-bis-(1,1-dimethylethyl), and hexadecanoic acid (palmitic acid). Since raw wastewater contains a variety of linear and cyclic compounds, as well as halo-aromatics at various concentrations, the BOD$_5$/COD ratio of 0.07 and high salinity content indicate the wastewater to be highly resistant to biodegradation, which justifies the necessity to apply advanced oxidation processes for its purification.

Photo-assisted peroxi-coagulation process

Effect of pH

In an electrochemical oxidation process, pH of aqueous media is an important variable for the electrogeneration of H$_2$O$_2$. In H$_2$O$_2$ production, the acidic condition is theoretically suitable for the production of H$_2$O$_2$ generation, due to the proton consumption, which occurs when dissolved oxygen converts to H$_2$O$_2$. Furthermore, the acidic conditions improve production of hydrogen, thereby declining the quantity of reactive sites for H$_2$O$_2$ production.

The influence of pH on the removal of COD was evaluated in the range of 3–8 at a constant voltage of 1 V, position of two UVC lamps around the reactor, the electrode distance of 2 cm, and reaction time of 240 min. The results shown in Fig. 1 indicate that acidic pH values favored COD removal, and the highest removal efficiencies of 66.15 and 64.92 % were observed for initial pH values of 3 and 4, respectively. Therefore, in this study, pH 4 was chosen as the best level and used for further experiments.

COD removal decreases with increasing pH from 3 to 8, attributed to decreasing OH$^{\bullet}$ oxidation potential with enhancing pH (2.65 to 2.80 V at pH 3, while it reached 1.90 V at pH 7) Hence, OH$^{\bullet}$ is a weaker oxidant at near neutral pH than at acidic pH. In addition, the reduction of Fe^{3+} to Fe^{2+} together

Table 1 – *Characteristics of high saline petrochemical wastewater*

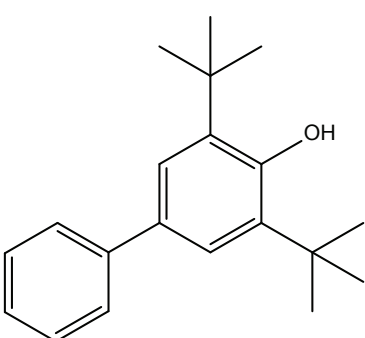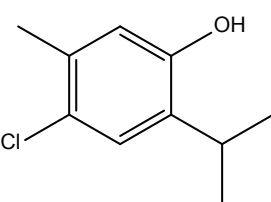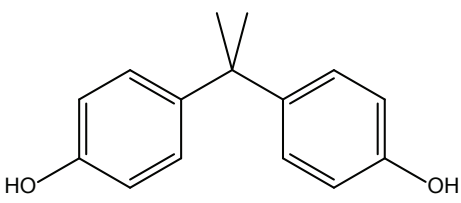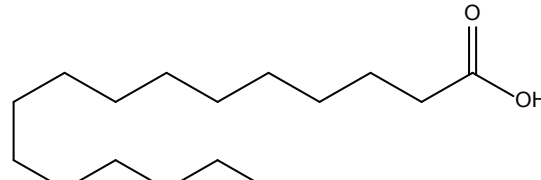| Parameter	Value	
	Range	Average
COD (mg L^{-1})	370–2900	1271
BOD$_5$ (mg L^{-1})	50–128	89
BOD$_5$/COD	0.05–0.09	0.07
TOC (mg L^{-1})	780–1925	842
TSS (mg L^{-1})	130–240	168
TDS (mg L^{-1})	15000–45400	16428
pH	7.8–8.9	8.1
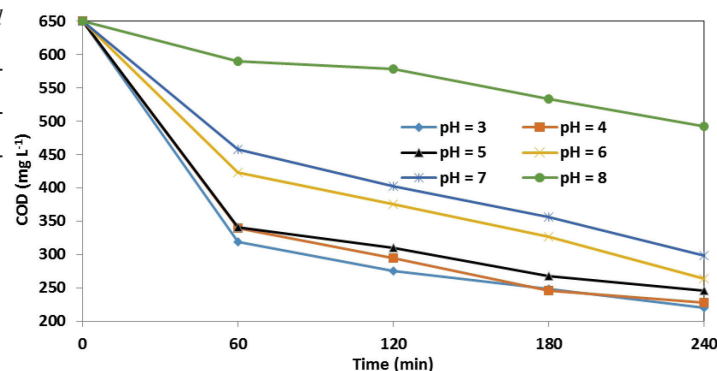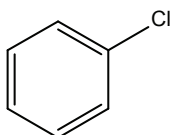
Fig. 1 – *Effect of pH on COD removal of high salinity petrochemical wastewater using PPC (Electrode distance: 2 cm, voltage: 1 V, reaction time: 240 min, UV lamps: 2)*

Table 2 – *GC-MS chromatogram of raw petrochemical wastewater*

RT (min)	Substance	Area	Molecular Formula	Structural formula
5.071	Chlorobenzene	3.59	C_6H_5Cl	
18.321	2,6-Di-tert-butyl-4-phenylphenol	1.02	$C_{20}H_{26}O$	
18.907	6-Chlorothymol	1.30	$C_{10}H_{13}ClO$	
23.908	bisphenol	1.80	$C_{22}H_{22}O$	
33.510	Hexadecanoic acid	1.59	$C_{16}H_{32}O_2$	

with production of hydroxyl radicals can be possible, due to the application of UV light radiation, as illustrated in Eqs. (4) and (6)[27].

Effect of voltage

In order to determine the most appropriate amount of voltage to reach optimal COD removal, the experiments were carried out at three various voltage levels (0.5–3 V) at pH 4, the electrode distance of 2 cm, position of two UVC lamps around the reactor, and reaction time of 240 min. The findings are illustrated in Fig. 2. The COD removal efficiency was 40.6, 67.5, 76.8, 77.5, 78.4, and 79.6 % at voltages of 0.5, 1, 1.5, 2, 2.5, and 3 V, respectively. Results indicated that the COD removal rate
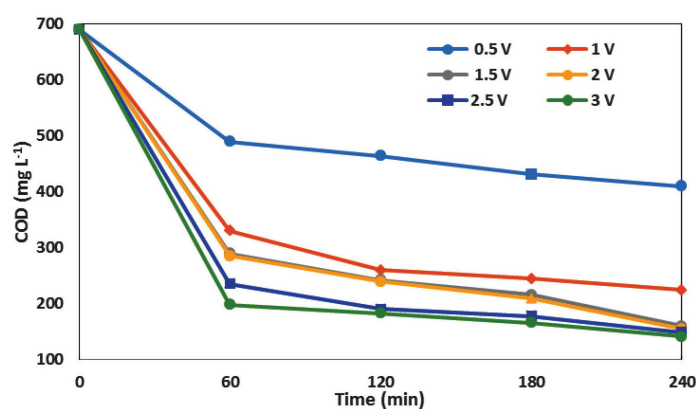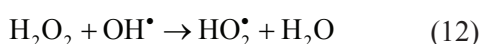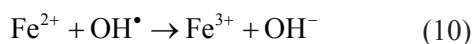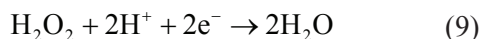
Fig. 2 – *Effect of voltage on COD removal of high salinity petrochemical wastewater using PPC (Electrode distance: 2 cm, pH = 4, reaction time: 240 min, UV lamps: 2)*

increased with increasing voltage, meaning that enhancement in the applied voltage will improve the generation of hydrogen peroxide, which will lead to improving the generation of hydroxyl free radicals[28]. An extra enhancement in the voltage level did not lead to improved performance of the process[28]. The side reactions in Eqs. (9), (10), (11), and (12) presumably occur at the cathode at higher voltages[29–31]. Moreover, this leads to higher generation of hydrogen gas at the cathode that impedes the principal Fenton reaction.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (9)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (10)$$

$$2OH^\bullet \rightarrow H_2O_2 \qquad (11)$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \qquad (12)$$

However, due to the insignificant difference in obtained removal efficiency and ease of implementation, voltage = 1.5 V corresponding to 76.81 % COD removal efficiency was selected for the subsequent experiments.

Effect of electrode distance

The influence of electrode distance on COD removal was evaluated at a constant pH of 4, voltage of 1.5 V, position of two UVC lamps around the reactor, and electrolysis time of 240 min. The distance between electrodes at three levels of 2, 4, and 6 cm were studied. Results indicated that maximum removal efficiency (73.33 %) was obtained at electrode distance of 2 cm (Fig. 3). By increasing the electrode distance to 6 cm, COD removal efficiency decreased to 73.17, without a significant decrease. On the other hand, greater distance between electrodes attributed to higher current intensity, and consequently more electrical power required for the same COD removal. In this regard, from the economical point of view, the electrode distance of 2 cm was selected as the optimum distance.
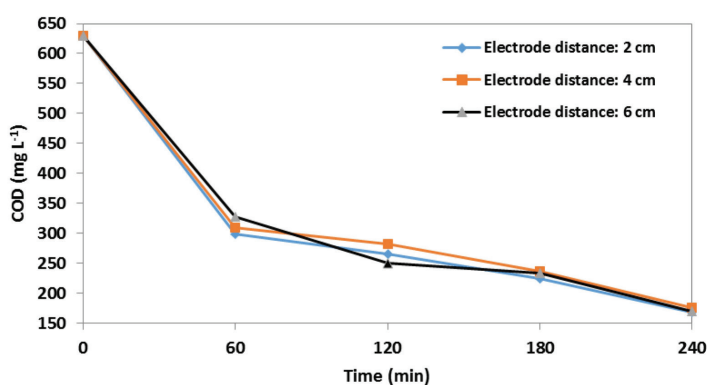

Fig. 3 – *Effect of electrode distance on COD removal of high salinity petrochemical wastewater using PPC (Voltage: 1.5 V, pH = 4, reaction time: 240 min, UV lamps: 2)*

In the electro-Fenton process, the reduction of ferric ion at the cathode leads to the regeneration of ferric ion that stimulates the Fenton chain reaction. However, since the distance between the electrodes is so short, the oxidation of electro-regenerated ferrous ion to ferric ion at the anode will occur, which will have a negative effect on the performance of Fenton chain reactions. Conversely, at greater distances between electrodes, there is a limitation against transferring ferrous ions towards the cathode surfaces, governing the regeneration of ferrous ion[27,32]. Similar findings have been reported by Ting *et al.*[33] for degradation of benzene sulfonic acid through electro-Fenton approach, where Ti and SS were anode and cathode, respectively. Any variation in the distance between electrodes has significant influence on the amount of H_2O_2 in the aqueous media, which is derived from the oxidation of hydrogen peroxide.

According to the obtained findings, 2 cm was obtained as an optimum distance between electrodes, and applied for the subsequent experiments.

Effect of UV intensity

UV light intensity determines the concentration of generated hydroxyl radicals. To evaluate the impact of UV light intensity on COD removal efficiency, some experiments were done at a constant pH of 4, voltage of 1.5 V, electrode distance of 2 cm, and reaction time of 240 min. Results indicated that with increasing UV lamps from one to three, COD removal efficiency increased from 55.58 to 77.64 %, respectively, 77.2 % for two UV lamps. This result can be explained by the fact that higher UV light intensity can enhance the generation of hydroxyl radicals to remove COD from wastewater[20,34–36]. On the other hand, at low UV light intensity, the rate of photolysis of H_2O_2 was limited, resulting in decreasing COD removal efficiency. With regard to the insignificant difference in removal efficiency for two and three UV lamps, two UV lamps were considered as optimum. Moreover, 40.29 % COD degradation in the case of no UV lamp is attributed to the effect of electro-Fenton process. Fig. 4 shows the effect of UV light intensity on COD removal efficiency. It appears that increasing UV light intensity increased COD removal efficiency.

Effect of reaction time

The influence of contact time on removal of COD was evaluated at a constant pH of 4, voltage of 1.5 V, and electrode distance of 2 cm. Results showed a high COD removal rate by increasing the reaction time up to 180 min, but from 120 to 240 min, removal rate increased at a slower rate. In the first 180 min, residual COD concentration reached
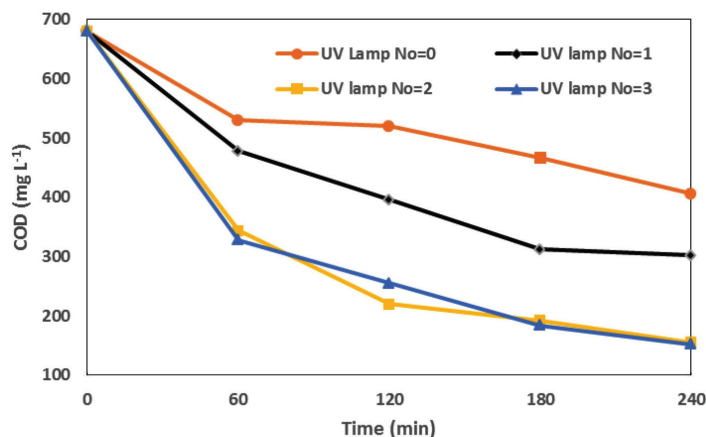
F i g . 4 – *Effect of UV intensity on COD removal of high salinity petrochemical wastewater using PPC (Voltage: 1.5 V, pH = 4, reaction time: 240 min, and electrode distance: 2 cm)*
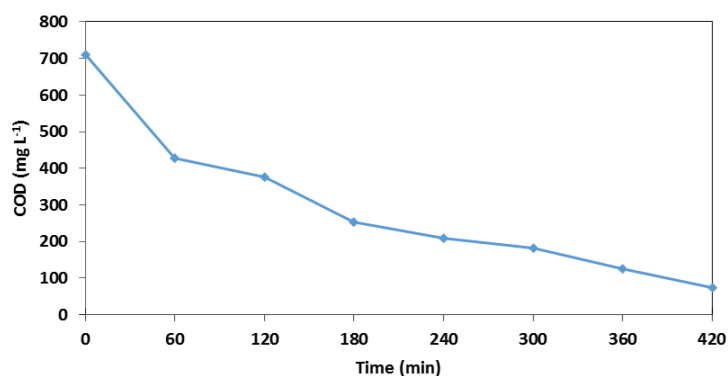

F i g . 5 – *Effect of reaction time on COD removal of petrochemical wastewater using PPC (Voltage: 1.5 V, pH = 4, electrode distance: 2 cm)*
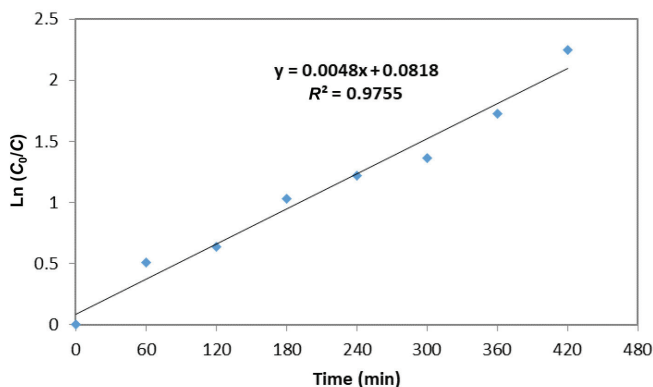

F i g . 6 – *Pseudo first-order kinetic analysis of PPC process for high salinity petrochemical wastewater (pH = 4, voltage: 1.5 V, electrode distance: 2 cm, reaction time: 240 min)*

254 mg L^{-1}, and thereafter decreased to 75 mg L^{-1} in 420 min. Complete degradation and mineralization to more simple compounds occurred in the first 180 min, and degradation of resistant compounds and intermediates continued in the remaining reaction time[37,38].

Kinetic study

The kinetic parameters of first-order kinetic models, including rate of PPC oxidation reaction for high TDS petrochemical wastewater, were determined by plotting ln (C_0/C_t) against time. The individual kinetic equations are as follows Eq. (13).

$$\ln C_0 / C_t = kt \qquad (13)$$

Where, C_0 is the initial COD concentration in the solution (mg L^{-1}), C_t is the residual COD concentration in the solution (mg L^{-1}), t is the reaction time (min), and k is the corresponding rate constant.

As shown in Fig. 6, in selected experimental conditions, such as pH 4, voltage 1.5 V, electrode distance of 2 cm, and the reaction time of 240 min, the reaction kinetics of COD removal through PPC of high salinity petrochemical wastewater fitted well to pseudo first-order reaction with regression coefficient of 0.97 and rate constant of 0.0048 min^{-1}.

Energy consumption

The electrical energy consumed (P, Wh m^{-3}) during the process was calculated using Eq. (14):

$$P = UIt / V \qquad (14)$$

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}).

Energy consumption was calculated in selected experimental conditions, such as initial pH 4, electrode distance of 2 cm, current intensity of 0.11 A, voltage of 1.5 V, reaction time of 240 min, initial COD concentration of 710 mg L^{-1} and TDS concentration of raw high salinity petrochemical wastewater with corresponding value of 25000 mg L^{-1}, which resulted in COD removal of 89.4 %. According to the obtained results, the energy consumption of 1.1 kWh m^{-3} was obtained for treatment of investigated wastewater. In addition, the specific energy consumption was equal to 1.73 kWh kg^{-1} COD removed.

Intermediate metabolites

Metabolic intermediates after oxidation were evaluated in the final steps of our study. Tables 3 and 4 show intermediate compounds after 4 and 24 hours oxidation, respectively. Results show dodecanoic acid, pentatonic acid, 1-hexanol, di-isobutyl phthalate and dibutyl phthalate were formed in 24 hours of oxidation.

Comparison between raw and treated sample in 4 and 24 hours shows formation of more stable and simple compounds through ring cleavage and hy-

Table 3 – *GC-MS chromatogram of treated saline petrochemical wastewater by PCC process on produced intermediates (Initial COD: 710 mg L^{-1}, voltage: 1.5 V, pH: 4, electrode distance: 2 cm, reaction time: 4 h)*
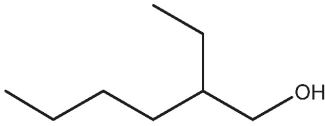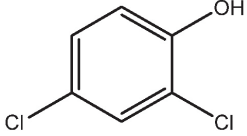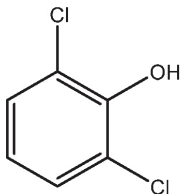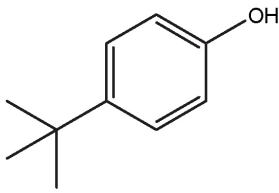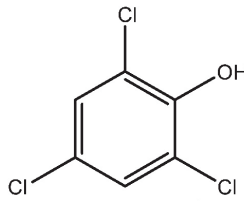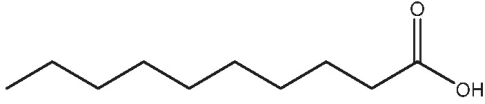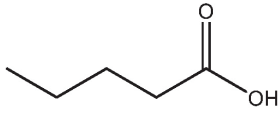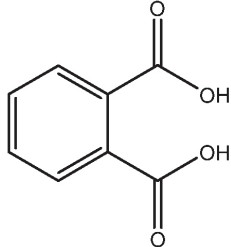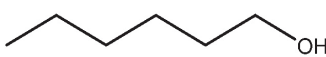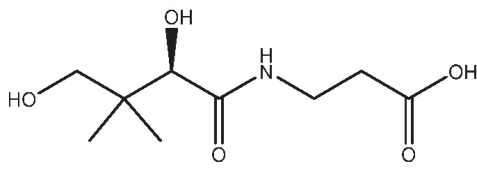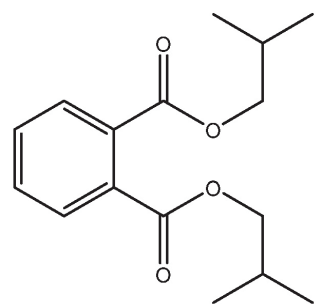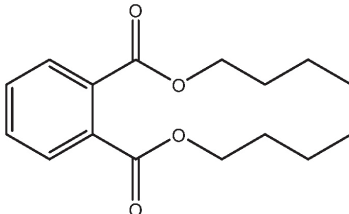
RT (min)	Substance	Area	Molecular Formula	Structural formula
10.738	2-Ethylhexanol	5.12	$C_8H_{18}O$	
14.787	2,4-Dichlorophenol	5.65	$C_6H_4Cl_2O$	
15.770	2,6-dichlorophenol	1.99	$C_6H_4Cl_2O$	
18.332	4-tert-butyl-Phenol	1.46	$C_{10}H_{14}O$	
19.885	2,4,6-Trichlorophenol	2.23	$C_6H_3Cl_3O$	
21.008	Decanoic acid	2.46	$C_{17}H_{34}O_2$	
25.935	Pentanoic acid	4.39	$C_{16}H_{30}O_4$	
31.721	1,2-Benzenedicarboxylic acid	1.54	$C_{24}H_{38}O_4$	

Table 4 – *GC-MS chromatogram of treated saline petrochemical wastewater by PPC process on produced intermediates (Initial COD: 710 mg L^{-1}, voltage: 1.5 V, pH: 4, electrode distance: 2 cm, reaction time: 24 h)*

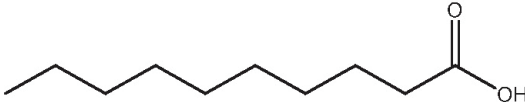| RT (min)	Substance	Area	Molecular Formula	Structural formula
10.740	1-Hexanol	3.34	$C_6H_{14}O$	
21.002	Decanoic acid	2.17	$C_{10}H_{20}O_2$	
25.929	Pantothenic acid	1.10	$C_5H_{10}O_2$	
31.742	Di isobutyl Phthalate	13.30	$C_{16}H_{22}O_4$	
33.564	Di butyl phthalate	2.46	$C_{16}H_{22}O_4$	

droxylation of aromatic ring structures. Since the produced oxidizing agents in such processes are non-selective, production of a wide range of intermediates is reasonable and further oxidation of intermediates needs a relatively longer reaction time. The salinity of studied wastewater was mainly comprised of NaCl. Therefore, chlorophenols may form during oxidation.

Conclusions

PCC method was applied in this research for treatment of a saline wastewater. Different factors, such as reaction time, pH, and voltage, electrode distance, and UVC intensity were studied to find their influence on the treatment efficiency. Results indicated that acidic pH values favored COD removal. In addition, the results indicated that with increasing voltage and UV intensity, COD removal increased due to enhancement of the production rate of hydrogen peroxide, which subsequently led to the production of more hydroxyl radicals. Oxidation reactions in the PPC process followed pseudo-first-order kinetics. Considering the severe conditions of studied wastewater, including recalcitrance of organics and high salinity content, it is very difficult to handle alternative treatment processes, such as biological methods, and application of advanced oxidation processes for such wastewater is necessary. According to observations of the current work, especially the COD removal of around 90 % in a reaction time of 7 h, as well as reasonable energy consumption, it can be concluded that PPC process is a reliable, efficient, promising, and cost-effective alternative for treatment of such saline petrochemical wastewaters, and supplemental studies in pilot and full scale are required to make the process applicable as a competitive technology.

References

1. *Ahmadi, M., Jorfi, S., Kujlu, R., Ghafari, S., Soltani, R. D. C., Haghighifard, N. J.*, A novel salt-tolerant bacterial consortium for biodegradation of saline and recalcitrant petrochemical wastewater, J. Environ. Manage. **191** (2017) 198.
doi: https://doi.org/10.1016/j.jenvman.2017.01.010

2. *Ahmadi, M., Kakavandi, B., Jaafarzadeh, N., Babaei A. A.*, Catalytic ozonation of high saline petrochemical wastewater using PAC@Fe^{II}Fe$_2^{III}$O$_4$: Optimization, mechanisms and biodegradability studies, Sep. Purif. Technol. **177** (2017) 293.
doi: https://doi.org/10.1016/j.seppur.2017.01.008

3. *Ahmadi, M., Amiri, H., Martinez, S. S.*, Treatment of phenol-formaldehyde resin manufacturing wastewater by the electrocoagulation process, Desalin. Water Treat. **39** (2012) 176.
doi: https://doi.org/10.1080/19443994.2012.669172

4. *Ahmadimoghaddam, M., Mesdaghinia, A., Naddafi, K., Nasseri, S., Mahvi, A. H., Vaezi, F., Nabizadeh R.*, Degradation of 2,4-dinitrophenol by photo Fenton process, Asian J. Chem. **22** (2010) 1009.

5. *Esmaeli R., Hassani, A. H., Eslami, A., Ahmadi Moghadam, M., Safari, A. A.*, Di-(2-ethylhexyl) phthalate oxidative degradation by fenton process in synthetic and real petrochemical wastewater, Iran J. Environ. Healt. **8** (2011) 201.

6. *Ahmadi, M., Ghanbari F.*, Optimizing COD removal from greywater by photoelectro-persulfate process using Box-Behnken design: Assessment of effluent quality and electrical energy consumption, Environ. Sci. Pollut. Res. **23** (2016) 19350.
doi: https://doi.org/10.1007/s11356-016-7139-6

7. *Ramavandi, B., Jafarzadeh, M., Sahebi, S.*, Removal of phenol from hyper-saline wastewater using Cu/Mg/Al–chitosan–H$_2$O$_2$ in a fluidized catalytic bed reactor, React. Kinet. Mech. Cat. **111** (2014) 605.
doi: https://doi.org/10.1007/s11144-013-0664-0

8. *Ahmadi, M., Kakavandi, B., Jorfi, S., Azizi, M.*, Oxidative degradation of aniline and benzotriazole over PAC@FeII Fe$_2$IIIO$_4$: A recyclable catalyst in a heterogeneous photo-Fenton-like system, J. Photochem. Photobiol. A Chem. **336** (2017) 42.
doi: https://doi.org/10.1016/j.jphotochem.2016.12.014

9. *Babuponnusami, A., Muthukumar, K.*, A review on Fenton and improvements to the Fenton process for wastewater treatment, J. Environ. Chem. Eng. **2** (2014) 557.
doi: https://doi.org/10.1016/j.jece.2013.10.011

10. *Nidheesh, P. V., Gandhimathi, R.*, Trends in electro-Fenton process for water and wastewater treatment: An overview, Desalination. **299** (2012) 1.
doi: https://doi.org/10.1016/j.desal.2012.05.011

11. *Brillas, E., Martínez-Huitle, C. A.*, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Appl. Catal. B Environ. **166** (2015) 603.
doi: https://doi.org/10.1016/j.apcatb.2014.11.016

12. *Ghanbari, F., Moradi, M., Mohseni-Bandpei, A., Gohari, F., Abkenar, T. M., Aghayani, E.*, Simultaneous application

of iron and aluminum anodes for nitrate removal: A comprehensive parametric study, Int. J. Environ. Sci. Technol. **11** (2014) 1653.
doi: https://doi.org/10.1007/s13762-014-0587-y

13. *Ghanbari, F., Moradi, M., Mohseni-Bandpei, A., Gohari, F., Abkenar, T. M., Aghayani, E.*, A comparative study of electrocoagulation, electrochemical Fenton, electro-Fenton and peroxi-coagulation for decolorization of real textile wastewater: Electrical energy consumption and biodegradability improvement, J. Environ. Chem. Eng. **3** (2015) 499.
doi: https://doi.org/10.1016/j.jece.2014.12.018

14. *Zarei, M., Niaei, A., Salari, D., Khataee, A. R.*, Removal of four dyes from aqueous medium by the peroxi-coagulation method using carbon nanotube–PTFE cathode and neural network modeling, J. Electroanal. Chem. **639** (2010) 167.
doi: https://doi.org/10.1016/j.jelechem.2009.12.005

15. *Moradi, M., Ghanbari, F., Minaee Tabrizi, E.*, Removal of acid yellow 36 using Box–Behnken designed photoelectro-Fenton: A study on removal mechanisms, Toxicol. Environ. Chem. **97** (2015) 700.
doi: https://doi.org/10.1080/02772248.2015.1060975

16. *Boye, B., Brillas, E., Dieng, M. M.*, Electrochemical degradation of the herbicide 4-chloro-2-methylphenoxyacetic acid in aqueous medium by peroxi-coagulation and photoperoxi-coagulation, J. Electroanal. Chem. **540** (2003) 25.
doi: https://doi.org/10.1016/S0022-0728(02)01271-8

17. *Azbar, N., Yonar, T., Kestioglu, K.*, Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere **55** (2004) 35.
doi: https://doi.org/10.1016/j.chemosphere.2003.10.046

18. *Bila, D. M., Montalvao, A. F., Silva, A. C., Dezotti, M.*, Ozonation of a landfill leachate: Evaluation of toxicity removal and biodegradability improvement, J. Hazard. Mater. **117** (2005) 235.
doi: https://doi.org/10.1016/j.jhazmat.2004.09.022

19. *Grebel, J. E., Pignatello, J. J., Mitch, W. A.*, Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters, Environ. Sci. Technol. **44** (2010) 6822.
doi: https://doi.org/10.1021/es1010225

20. *Huang, Y., Li, S., Wang, C., Min, J.*, Simultaneous removal of COD and NH$_3$-N in secondary effluent of high salinity industrial wastewater by electrochemical oxidation, J. Chem. Technol. Biotechnol. **87** (2012) 130.
doi: https://doi.org/10.1002/jctb.2692

21. *Amour, L, R. J. A., Azevedo, E. B., Leite, S. G. F., Dezotti, M.*, Removal of phenol in high salinity media by a hybrid process (activated sludge+ photocatalysis), Sep. Purif. Technol. **60** (2008) 142.
doi: https://doi.org/10.1016/j.seppur.2007.08.008

22. *Li, G., An, T., Chen, J., Sheng, G., Fu, J., Chen, F., Zhang, S., Zhao, H.*, Photoelectrocatalytic decontamination of oilfield produced wastewater containing refractory organic pollutants in the presence of high concentration of chloride ions, J. Hazard. Mater. **138** (2006) 392.
doi: https://doi.org/10.1016/j.jhazmat.2006.05.083

23. *Liu, W., Zhang, H., Cao, B., Lin, K., Gan, J.*, Oxidative removal of bisphenol A using zero valent aluminum–acid system, Water Res. **45** (2011) 1872.
doi: https://doi.org/10.1016/j.watres.2010.12.004

24. *Martini, E., Tomassetti, M., Campanella, L., Fortuna, A.*, Reducing the pollutant load of olive mill wastewater by photocatalytic membranes and monitoring the process using both tyrosinase biosensor and COD test, Front. Chem. (2013) 36.
doi: https://doi.org/10.3389/fchem.2013.00036

25. *Rice, R. G.*, Applications of ozone for industrial wastewater treatment—a review, Ozone Sci. Eng. **18** (1996) 477.
doi: https://doi.org/10.1080/01919512.1997.10382859

26. A.P.H.A, WEF., Standard methods for the examination of water and wastewater. American. Public Health. Association. Washington, DC, USA. 2005.

27. *Babuponnusami, A., Muthukumar, K.*, Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, Chem. Eng. J. **183** (2012) 1.
doi: https://doi.org/10.1016/j.cej.2011.12.010

28. *Wang, C. T., Chou, W. L., Chung, M. H., Kuo, Y. M.*, COD removal from real dyeing wastewater by electro-Fenton technology using an activated carbon fiber cathode, Desalination. **253** (2010) 129.
doi: https://doi.org/10.1016/j.desal.2009.11.020

29. *Diagne, M., Oturan, N., Oturan, M. A.*, Removal of methyl parathion from water by electrochemically generated Fenton's reagent, Chemosphere **66** (2007) 841.
doi: https://doi.org/10.1016/j.chemosphere.2006.06.033

30. *George, S. J., Gandhimathi, R., Nidheesh, P. V., Ramesh, S. T.*, Electro fenton oxidation of salicylic acid from aqueous solution: Batch studies and degradation pathway, Clean-soil Air Water **42** (2014) 1701.
doi: https://doi.org/10.1002/clen.201300453

31. *Marselli, B., Garcia-Gomez, J., Michaud, P. A., Rodrigo, M. A., Comninellis, C.,* Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes, J. Electrochem. Soc. **150** (2003) 150.
doi: https://doi.org/10.1149/1.1553790

32. *Zhang, H., Zhang, D., Zhou, J.*, Removal of COD from landfill leachate by electro-Fenton method, J. Hazard. Mater. **135** (2006) 106.
doi: https://doi.org/10.1016/j.jhazmat.2005.11.025

33. *Ting, W. P., Lu, M. C., Huang, Y. H.*, The reactor design and comparison of Fenton, electro-Fenton and photoelectro-Fenton processes for mineralization of benzene sulfonic acid (BSA), J. Hazard. Mater. **156** (2008) 421.

34. *Modirshahla, N., Behnajady, M. A.*, Photooxidative degradation of Malachite Green (MG) by UV/H_2O_2: Influence of operational parameters and kinetic modeling, Dye. Pigment. **70** (2006) 54.

35. *Huang, K. Y., Wang, C. T., Chou, W. L., Shu, C. M.*, Removal of polyvinyl alcohol using photoelectrochemical oxidation processes based on hydrogen peroxide electrogeneration, Int. J. Photoenergy **2013** (2013) 1.
doi: https://doi.org/10.1155/2013/841762

36. *Muruganandham, M., Swaminathan, M.*, Photochemical oxidation of reactive azo dye with $UV–H_2O_2$ process, Dye. Pigment. **62** (2004) 269.
doi: https://doi.org/10.1016/j.dyepig.2003.12.006

37. *Kurt, U., Apaydin, O., Gonullu, M. T.,* Reduction of COD in wastewater from an organized tannery industrial region by Electro-Fenton process, J. Hazard. Mater. **143** (2007) 33.
doi: https://doi.org/10.1016/j.jhazmat.2006.08.065

38. *Umar, M., Aziz, H. A., Yusoff, M. S.*, Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate, Waste Manag. **30** (2010) 2113.
doi: https://doi.org/10.1016/j.wasman.2010.07.003