

ORIGINAL RESEARCH PAPER

Treatment of Petrochemical wastewater by Modified electro-Fenton Method with Nano Porous Aluminum Electrode

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ABSTRACT

This research reported a study on COD removal from petrochemical wastewater (ml/l) by the electro-Fenton process via the effects of different parameters such as reaction time, current density, pH, H₂O₂/Fe²⁺ molar ratio, and volume fraction of H₂O₂. For this purpose, first, the Nanopores on the aluminum electrode surface were prepared as the AAO films were fabricated using the two-step anodization of 6063 aluminum alloy sheets at ambient temperature in sulfuric acid and phosphoric acid electrolyte solutions respectively. The nanostructures created on electrode confirmed by Scanning Electron Microscopy (SEM). Then, Efficiency of electrochemical oxidation process was tested by COD determination via electrolyte cell contain waste water, Fe²⁺, H₂O₂ and AAO electrode based on experimental design. The optimum COD removal (65.03%) was obtained at pH of 2.96, the reaction time of 89.51 min, the current density of 69.57 mA, the H₂O₂/Fe²⁺ molar ratio of 3.42 and volume fraction of H₂O₂ to petrochemical wastewater of 1.93 (ml/l).

Keywords: COD, Electro-Fenton, Nanoporous Aluminum Electrode.

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INTRODUCTION

Petrochemical plants, including polluting industries environment through emissions of carbon monoxide, hydrogen and synthesis gas etc. The petrochemical industry, including oil refining, petrochemical processing, and natural gas production, generates large amounts of wastewater [1]. Such wastewater is usually characterized by significant concentrations of suspended solids, chemical oxygen demand (COD), oil and grease, sulfide, ammonia, phenols, hydrocarbons, benzene, toluene, ethylbenzene, xylene and polycyclic aromatic hydrocarbons (PAHs) [2,3]. Large quantities of wastewater are generated from petrochemical industries. The discharge of petrochemical wastewater (PCW) could cause

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serious environmental pollution and human health concerns [4]. The treatment method used for petrochemical wastewater is generally contained pretreatment for improving the biodegradation and reduction of toxicity, via different methods of biological treatment such as activated sludge process, anoxic-oxic (A/O) process, fluidized bed reactor, membrane bioreactor and biofilm process [5,6,7]. Ultrasonic, flocculation, Fenton and ozone oxidation, as well as anaerobic hydrolysis-acidification, are methods that used for pretreatment processes [8].

Several methods are used for removal of COD from petrochemical wastewater, low sludge generation, the high removal efficiency of pollutants and on-site generation of hydrogen peroxide (H₂O₂)

are advantages that advanced oxidation processes (AOPs) among them are considered as promising technologies with [9,10]. These methods are based on the strong oxidant formation, mostly the hydroxyl radical ($\text{OH}\cdot$) a powerful oxidizing agent of organic contaminant materials via processes of photochemical, chemical, and electrochemical [11]. In the AOP methods, the electro-Fenton (EF) way is able to catalysis total mineralization of organic compounds for short time; this way for produce the hydroxyl radical in solution requirement Fe^{2+} ions and oxygen. The raw materials are suitable to treat wastewater. Since they generally include specified amount of Fe^{2+} ions, therefore, the oxygen required for the preparation of air bubbles from compressed air [12, 13]. The E-Fenton method has intricate in the reaction mechanism. However, the main reactions of production of hydroxyl radical can be explained in the following equations [14]:



Hydroxyl radicals, with a standard potential of 2.8 V and a half lifetime of about 9-10 seconds, enable fast and non-selective oxidation of a wide range of molecules of environmental concern. Usually cathode material for electro-Fenton processes evaluated base on reducing ability oxygen to hydrogen peroxide and ferric ions reducing to ferrous ions and in next step, promoting the reaction leading to $\text{OH}\cdot$ radical production. Electro-generation of hydrogen peroxide has different applications such as for electro-Fenton application, direct oxidation, disinfection, and nanomaterial based cathodes [15, 16, 17, 18]. Torrades and coworkers reported using of Fenton and photo-Fenton for the treatment of textile wastewater [19]. Cruz-González and coworkers used the electro-Fenton method for Acid Yellow 36 decolorization [20] and Li reported electro-Fenton used for COD reduction of tannery industrials waste water [21]. removal of synthetic dyes waste water by electro-Fenton and photo-electro-Fenton method [22].also in 2014 reported using of Al and Fe electrode in petrochemical wastewater treatment by electro-Fenton processes [23]. Flores and coworkers reported wastewater removal of olive oil industrials by electro-Fenton and pho electro-Fenton via diamond electrode [24].

Anodic Aluminum Oxide (AAO) was produced

via an electrochemical process by anodization of aluminum (Al). Ordered AAO has resistant because of chemical and mechanical properties [25]. Nanopore structures demonstrate a dramatic increase in a surface-to-volume ratio that enhances the signals corresponding to an interaction between analytic and surfaces [25]. All these properties make AAO an excellent candidate with exciting opportunities for development of advanced, smart, simple, cost-effective electrodes for Electrochemical wastewater treating applications.

In this work, the removal of chemical oxygen demand (COD) from petrochemical wastewater (PCWW) was experimentally done by using electro-Fenton (EF). It seems using of nanoporosity in the electrode surface can help to improve the act of purification. Due to the very small size of proposition AAO electrode as well as their high active surface it was suggested that also these electrodes use as an auxiliary agent in order to accelerate the production of hydroxyl ions in the reaction medium.

EXPERIMENTAL

Chemicals and materials

All chemicals used here were of reagent grade and used without further purification. Sodium sulfate anhydrous, ferric chloride, sodium borohydride, sulfuric acid, reduced iron powder and other chemical reagents were all of the analytical grades and purchased from Shanghai Chemical Reagents Company. All the solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity > 18 MX cm at 25 °C. Their initial pH was adjusted with analytical grade sulfuric acid supplied by Merck. Heptahydrate ferrous sulfate used as a catalyst was of analytical grade purchased from Merck.

Preparation of the Nanoporous anodic aluminum oxide (AAO)

The AAO films were fabricated using the two-step anodization of 6063 aluminum alloy sheets (1mm thickness). The aluminum sheet was initially cut into 1cm×5cm pieces and degreased in acetone, without further thermal treatment or chemical polishing. The first anodization step was then carried out on the aluminum specimen, suspended in the electrolyte as an anode, under the constant current density of 5mA/cm² for 10 h. Another aluminum specimen was used as the cathode. Sulfuric acid solution (0.4M concentration)

was used as the electrolyte, and the electrolyte temperature was ambient. The formed AAO film was chemically removed by immersing the specimen in 0.4M phosphoric acid solution for 1 h. The second anodization step was subsequently conducted under the same condition mentioned before for the first step, to produce the final AAO film with a regular Nanopore array. Some final samples were immersed in 0.2M phosphoric acid to widen the pores. Finally, the specimens were rinsed several times with deionized water and then dried in the air [26].

SEM of Nanoporous Anodic Aluminum Oxide

Fig. 1 shows that nanopores are formed on aluminum oxide. From the end of anodic alumina pores with hexagonal condensed arrays of nanopores, after unfolding of pores, nanostructures were arrayed under anodizing and produced in the acidic electrolyte at ambient temperature. The size of nanopores between 223.81 nm to 448.76 nm.

Electro-Fenton experiments

The electrolysis was performed in a small, open, cylindrical, one-compartment electrochemical reactor of 6-cm diameter and 400 mL capacity, stirred by a magnetic during the treatment to

enhance the mass transport towards electrodes. The solution pH was fixed to 3 since much higher pH values hamper the development of Fenton-based systems due to the $\text{Fe}(\text{OH})_3$ precipitation, which leads to both the decrease of dissolved iron ion [27]. The solution pH was measured with a Cyber Scan pH 1500 pH-meter from Eutech Instruments. In each run, 250 ml of wastewater was placed in an electrolytic cell and desired amounts of iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) were added before the electrical current was turned on. Then, AAO electrodes were placed in the reactor and solutions were mixed at 350 rpm [28].

RESULTS AND DISCUSSION

Statistical analysis

For experiments design, the Design Expert software (RSM Method, version 7) was applied to minimize the number of experiments. The operating conditions ranges were pH of 2-5, the current density of 25-80 mA/cm^2 , the reaction time of 10-90 min, the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 0.5-5 and volume fraction of H_2O_2 to petrochemical wastewater of 0.25-2.14 ml/l. 46 experiments were designed by the software and carried out as illustrated in Table 1.

The reduced models for describing COD

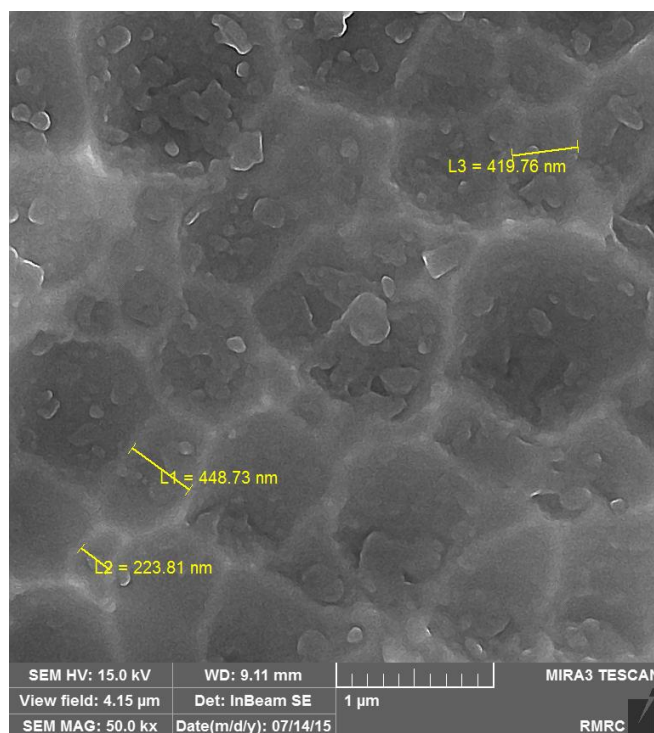


Fig. 1. SEM image of Nano porous anodic aluminum oxide

Table1. Experiments design and obtained results

Run	pH	molH ₂ O ₂		Reaction time	Current density	COD removal (%)	
		molFe ²⁺	Litpw			Exp.	Pred.
1	3.5	2.75	2.14	50	80	45.21	46.16
2	3.5	2.75	1.22	10	80	36.65	35.86
3	2	2.75	1.22	50	80	46.01	43.2
4	3.5	5	0.3	50	52.5	31.26	33.83
5	2	2.75	0.3	50	52.5	38.33	38.61
6	3.5	5	1.22	50	25	26.50	27.05
7	5	2.75	0.3	50	52.5	30.74	31.05
8	3.5	0.5	1.22	50	25	26.54	28.68
9	2	2.75	1.22	10	52.5	37.85	35.23
10	3.5	2.75	1.22	90	25	40.06	40.53
11	2	5	1.22	50	52.5	42.56	44.44
12	3.5	2.75	1.22	50	52.5	47.83	46.62
13	5	2.75	1.22	90	52.5	40.98	42.89
14	3.5	5	1.22	90	52.5	59.06	56.61
15	3.5	2.75	0.3	90	52.5	42.54	42.3
16	5	2.75	2.14	50	52.5	37.41	38.01
17	3.5	0.5	1.22	50	80	34.12	35.58
18	3.5	5	2.14	50	52.5	44.25	44.43
19	3.5	2.75	0.3	50	80	37.51	35.97
20	3.5	2.75	1.22	50	52.5	47.86	46.62
21	3.5	2.75	1.22	90	80	52.64	54.07
22	5	2.75	1.22	50	80	36.48	37.24
23	3.5	2.75	1.22	50	52.5	45.63	46.62
24	3.5	2.75	1.22	10	25	26.59	27.31
25	3.5	0.5	1.22	90	52.5	43.81	41.63
26	3.5	0.5	1.22	10	52.5	29.37	31.37
27	3.5	2.75	2.14	90	52.5	62.95	63.26
28	2	2.75	1.22	90	52.5	52.24	56.73
29	2	2.75	2.14	50	52.5	51.73	49.57
30	3.5	2.75	1.22	50	52.5	43.13	46.62
31	3.5	2.75	0.3	10	52.5	31.26	32.08
32	3.5	5	1.22	10	52.5	28.18	29.43
33	5	0.5	1.22	50	52.5	30.96	32.86
34	3.5	2.75	0.3	50	25	23.49	21.66
35	3.5	2.75	1.22	50	52.5	43.14	46.62
36	2	2.75	1.22	50	25	36.56	37.02
37	3.5	2.75	1.22	50	52.5	48.75	46.62
38	3.5	0.5	1.22	50	52.5	39.62	37.77
39	5	5	1.22	50	52.5	42.56	41.88
40	5	2.75	1.22	10	52.5	31.09	32.95
41	3.5	2.75	2.14	50	25	33.59	36.4
42	3.5	5	1.22	50	80	43.58	43.24
43	3.5	0.5	0.3	50	52.5	33.06	32.45
44	3.5	2.75	2.14	10	52.5	27.17	29.36
45	2	0.5	1.22	50	52.5	40.58	39.42
46	5	2.75	1.22	50	25	24.98	23.1

removal percentage can be presented:

$$\begin{aligned} \text{COD Removal (\%)} = & +46.62 + 9.03A + 5.60B - 4.01C \\ & + 4.81D + 2.57E + 1.25AB - 2.89AC + 5.92AD + 4.23AE \\ & + 1.99BC - 1.14BD + 2.32BE - 1.00CD + 1.00CE + 1.32DE \\ & - 0.91A^2 - 7.45B^2 - 3.19C^2 - 4.13D^2 - 5.15E^2 \quad (4) \end{aligned}$$

Where A, B, C, D and E are pH, H₂O₂/Fe²⁺ molar ratio, volume fraction of H₂O₂ to petrochemical wastewater (ml/l), reaction time (min) and current density (mA/cm²), respectively. R² and adjusted R² are close to one (R²=0.9747 and R² adj.=0.9544). According to the results, 97.47% of the variations for COD removal were explained by the independent

variables in the model. R value is more close to 100% then it proves the high significance of model [29].

The adequacy of developed mathematical models to the experiment was examined by the diagnostic plots such as predicted plot versus actual one (Fig. 2) and normal percent probability graphs (Fig. 3). The predicted plot versus actual one showed that actual values were distributed near the straight line Fig. 2. It indicates that actual values are very close to the predicted ones. These plots show very good agreement between the observed data and the correlated ones obtained from the models [30].

*Effective parameters on the electro-Fenton process
The impact of time*

Fig. 3 shows that reaction time (min) has a positive impact on the progress of the electro-Fenton process. But its effectiveness decreases with increasing time, so after the optimum time, process efficiency does not change with time considerably. That's why optimal reaction time (min) is obtained at almost 2/3 of the total time [31]. Over time the amount of reactive material in the reaction medium decreases and reduces the pollutant removal rate. To achieve perfect efficiency, the system should be given enough time to be able to

produce enough amount of OH ions and take place the act of purification of organic pollutants in the environment. By increasing the time it seems that the system achieves to a chemical equilibrium and the maximum removal occurs at the beginning of this balance and the passage of time do not have much impact on improving the treatment process [32].

The effect of pH on COD

Fig. 5 shows the effect of pH on COD removal. As you can see the effect of this parameter within the acidic range is more than basic and to increase

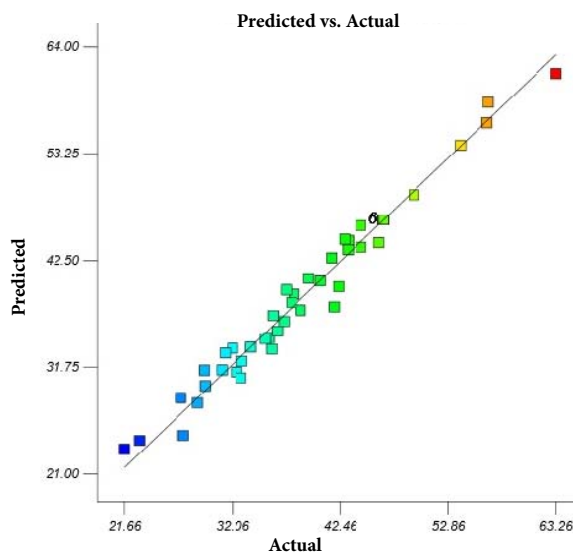


Fig. 2. Predicted vs. actual values plot for COD removal

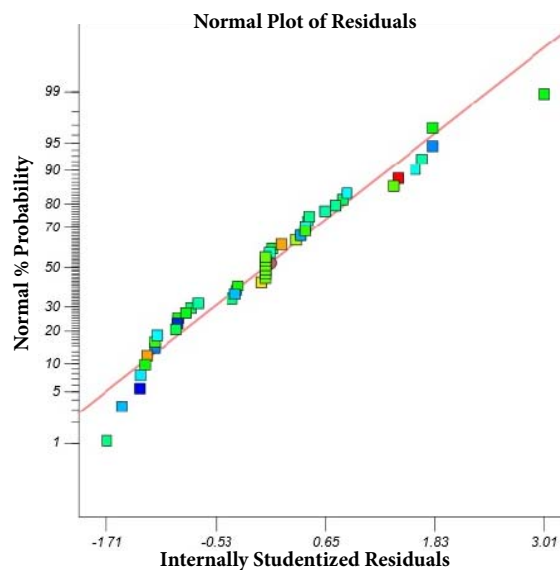


Fig. 3. Normal probability vs. internally studentized residuals values for COD removal

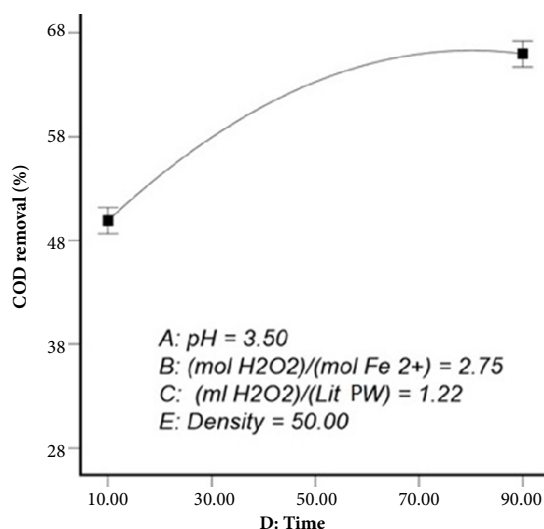


Fig. 4. The effect of time on the reduction of COD parameter

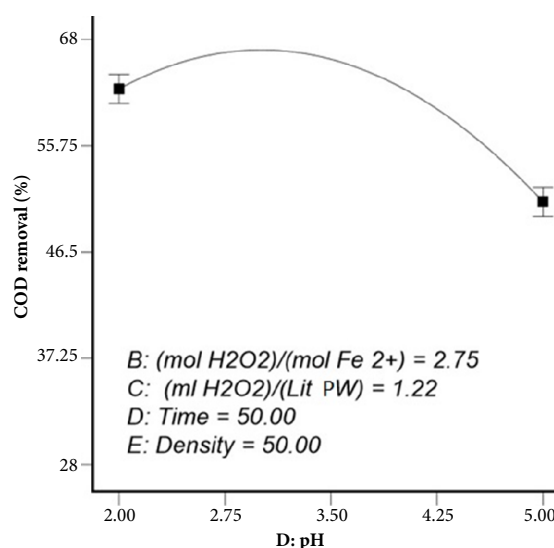


Fig. 5. The effect of pH on the removal of COD parameter

to about 2.75, the effect of this factor increases and then began to decline. With increasing pH, the rate of treatment drops sharply. In fact, this is the optimal operating point that away from it, its impact decreases. Obviously, the Fenton reaction occurs at low pH. At Fenton reactions, the highest efficiency obtains when the pH is around 2–4 [33]. Low pH is suitable for the production of hydrogen peroxide because to convert dissolved oxygen into hydrogen peroxide absorb its required proton of the acidic solution [34]. For pH >4 the oxidation rate significantly decreased mainly because ferrous ions are unstable and they easily form ferric ions and precipitate [35]. On the other hand, at very acidic pH, below pH 3, the electrogenerated hydrogen peroxide turns into an oxonium $H_3O_2^+$ by capturing one proton. $H_3O_2^+$ is electrophilic, leading to the decreasing rate of reaction between H_2O_2 and Fe^{2+} and consequently fewer hydroxyl radicals are produced [36, 37].

Effect of volume fraction on COD removal

The two factors are related to each other so in examining their effects on the COD removal, they are analyzed together. Increasing of $\left(\frac{mlH_2O_2}{LitPW}\right)$ ratio with a fixed volume of wastewater increase the amount of H_2O_2 . The increasing leads to an increase in the ratio of $\frac{molH_2O_2}{molFe^{2+}}$ and thus increase of the reactive material in the reaction medium. As the figures indicate, increasing of reactive material to the optimal point leads to increasing the amount of COD removal and when passes the optimal point, causing wasting reactant materials. Using these

two ratios, the required amount of Fe^{2+} and H_2O_2 is obtained. The Fe^{3+} concentration is a significant parameter in the electro-Fenton process. Fig. 6 represents the influence of molar ratio on the act of purification. Since Fenton's reaction is of first grade, the growth of the reactants concentration will develop the reaction rate therefore, and concentration of hydrogen peroxide is dependent on the rise of the Fe^{2+} amount. As can be seen, at low doses, the efficiency ratio is low and this is because the amount of available material is not sufficient for the production of OH and after enhancement, the filtration rate is added till it comes to the optimal point and after passing through this point we see the opposite effect. This negative influence might be due to the increase of the reactions that scavenged hydroxyl radicals, just like Eq. (5)[38]. In addition, hydroperoxyl radicals (HO_2^\bullet), which is a less oxidizing agent than $^\bullet OH$, would be formed by reaction (6) and(7) as the Fe^{3+} concentration increased [39]. Another reason for the lower removal efficiencies at high Fe^{3+} concentration can be the formation of a yellow precipitate of $Fe(OH)_3$, which is deposited on the electrode surface. This deposited Fe^{3+} cannot be reconverted to Fe^{2+} , so the result is less Fe^{2+} available to react with the H_2O_2 to produce hydroxyl radicals [39].

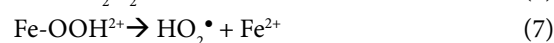
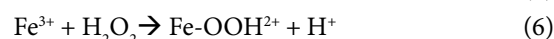


Fig. 7 shows the effect of the volume ratio on the treatment parameter. As can be seen, it has an

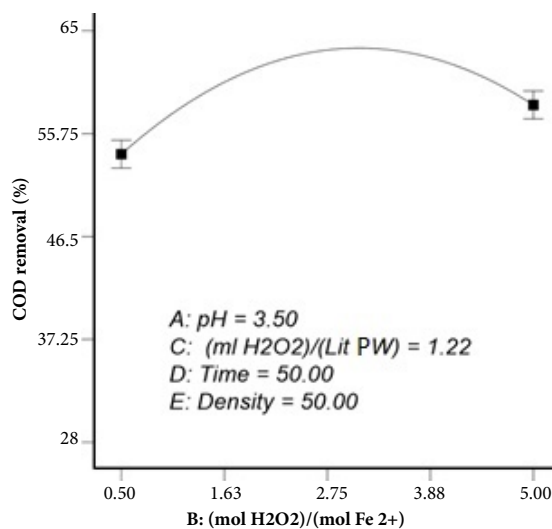


Fig. 6. Effect of $\frac{\text{molH}_2\text{O}_2}{\text{molFe}^{2+}}$ molar ratio on COD removal

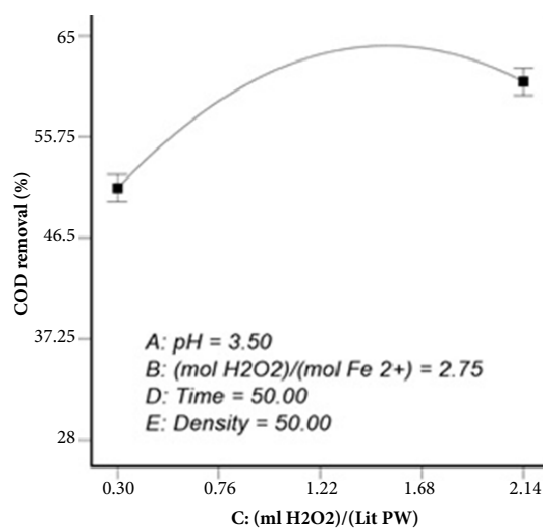
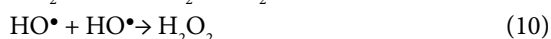
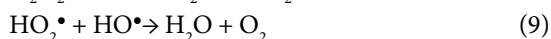
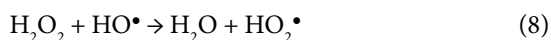


Fig. 7. Effect of volume fraction of H₂O₂ to alcoholic wastewater ($\frac{\text{mlH}_2\text{O}_2}{\text{LitPW}}$) on COD removal

Table 2. Optimum data for both electro-Fenton processes {with the modified electrodes (current research) and traditional electro-Fenton [23]}

Reaction time (min)	Current density (mA/cm ²)	pH	Volume fraction of H ₂ O ₂ to Petrochemical wastewater (ml/l)	H ₂ O ₂ /Fe ²⁺ molar ratio	COD removal (%)		EF type
					Statistical data	Experimental data	
89.51	69.57	2.96	1.93	3.42	65.03	64.15	Current research
78.97	68.65	3.06	2.14	4.99	53.94	51.23	[23]

optimum point. At the small amounts of this ratio, there is no much impact on removal due to the low quantity of hydrogen peroxide in the environment. COD removal can be enhanced by increasing the H₂O₂ concentration. A further increase from optimum point decreases the removal efficiency. At a high level of H₂O₂, the decrease in removal efficiency was due to the hydroxyl radical scavenging effect of H₂O₂ (Eqs. (8) and (9)) and hydroxyl radical recombination (Eq. (10)) [40, 41].



The slope of this graph is greater than the molar ratio graph and by developing a small amount of this ratio we see a significant increase in the amount of treatment. So the hydrogen peroxide has higher efficiency comparing to the iron salts in the experiment environment.

Optimization and validation

Numerical optimization was used to determine the optimum parameters for maximum COD removal. The software automatically gives the

optimum conditions. In this software, numerical optimization is used to achieve the maximum amounts of COD removal. In fact, all variables are targeted to be in a range and COD removal are a goal to be maximized. The found data were shown in Table 2. There are very good agreement between experimental optimum data and statistical ones. Table 2 compares our results with the traditional electro-Fenton data (with plain aluminum electrodes) at the optimum conditions, as well [28]. According to this table, modified AAO electrodes increased 11% COD removal. It follows that the creation of Nano surface in a test environment without changes in operating conditions the system can apply appropriate efficiency. Therefore, special attention given to this issue is justified. By comparing the optimal experimental conditions in the presence of Nanoporosity and lack of it, it is observed that time needed to achieve optimal conditions, decreases. In fact, it seems that the presence of Nanoporous in the environment, accelerate the rate of production of hydroxide ions and purification process. But it is evident that in this case the current density increases and the increase may be due to the fact that reactions related to the

production of iron ions and disinfectant radicals requires high energy consumption and thus increase the current density and it is because of the reaction time is reduced and treatment is fastened. In the case of pH, it is clear that the operation was carried out in the more acidic range. In the case of the reactive substances which present themselves in the parameters of molar ratio and volume ratio, it is observed that there has been a marked decline and this can be one of the major advantages of using Nanoporous materials, because by creating Nano-porosity can save a significant amount of raw materials is used in the process. This impact is likely to be this way, Nanoporous by creating a higher level, helps to decompose hydrogen peroxide with higher efficiency and thereby reducing the consumption of hydrogen peroxide and iron catalyst.

CONCLUSIONS

In this study, the electro-Fenton method was proposed to treat effluent from industrial activities conducted in Arak Petrochemical Company. Finally, the operating conditions were optimized and presented to achieve the best results with the highest amount of COD reduction. The optimum COD removal (65.03%) was obtained at pH of 2.96, reaction time of 89.51 min, current density of 69.57 mA, H_2O_2/Fe^{2+} molar ratio of 3.42 and volume fraction of H_2O_2 to Petrochemical wastewater of 1.93 (ml/l) and it can be seen that the modified electro-Fenton process could optimally remove COD from petrochemical wastewater up to 65.03% while it was around 53.94% in the traditional electro-Fenton, as it is observed, treatment using the second method has been improved by 11%[28]. It seems that the Nano-porosity can be used as an auxiliary agent in order to accelerate the decomposition of hydrogen peroxide and ultimately lead to increase in production of hydroxyl ions. Due to the effectiveness of electro-Fenton operation, this method can be proposed as an easy way to petrochemical wastewater treatment.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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