



Petrochemical wastewater treatment by modified electro-Fenton process with nano iron particles

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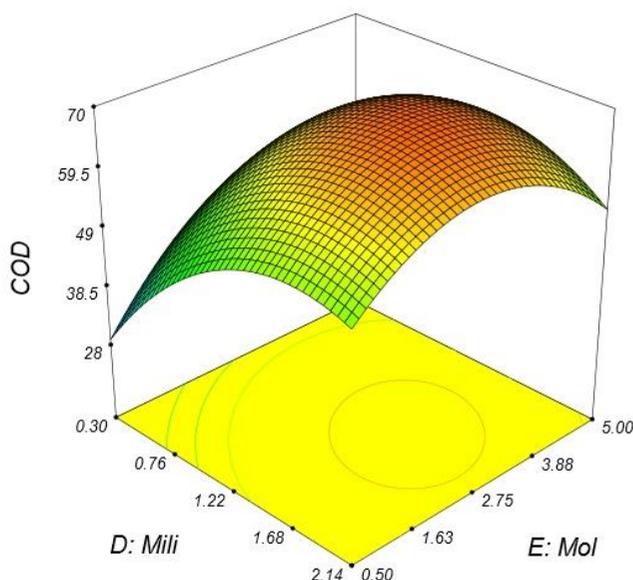
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HIGHLIGHTS

- COD removal from Petrochemical wastewaters by electro-Fenton process was studied.
- Effect of reaction time, current density and pH on process performance was investigated.
- 86.3% removal of COD was obtained during electrolyses, due to formation of hydroxyl radicals.

GRAPHICAL ABSTRACT



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ABSTRACT

Petrochemical manufacturing wastewaters often contain a high concentration of biodegradable compounds that possess either toxicity or activity inhibition to the biological unit. In this paper, COD removal from petrochemical wastewaters by electro-Fenton process was studied. The effect of operating conditions such as reaction time, current density, pH, H_2O_2/Fe^{2+} molar ratio, and H_2O_2 of petrochemical wastewater (PW) (mL/L) on the performance of the process has been studied. The experimental results showed that COD was 75.52% removed by the reaction with hydroxyl radicals generated from electrochemically assisted Fenton's reaction. With our cell design, the higher oxidation rate has been obtained applying a current of 57.01 mA, at pH 2.92 and in the presence of 0.3 mM Fe^{2+} as catalyst and at reaction time of 86.33 minutes.

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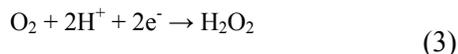
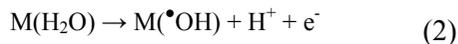
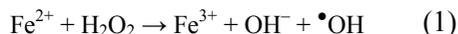
1. Introduction

The production stages of a petroleum industry, such as extraction and refining, are potentially responsible for generating large volumes of effluent to be discarded in the environment [1–3]. The waste generated in oil refineries contains many different Chemical compositions, depending on the complexity of the refinery, the existing processes and the type of oil used [1,4].

Electrochemical advanced oxidation processes (EAOPs) like electro-Fenton (EF) and photo electro-Fenton (PEF) have recently received great attention for the removal of harmful organics in waters because they can generate oxidant hydroxyl radical ($\bullet\text{OH}$) for an effective and fast mineralization of pollutants to CO_2 , water and inorganic ions [5,6]. AOPs are based on the in situ generation of hydroxyl radicals ($\bullet\text{OH}$), a highly powerful oxidizing agent. Among these processes, Fenton and electro-Fenton techniques have attracted attention from investigators around the world [7,8]. These processes are based on the oxidation of ferrous iron to ferric iron by hydrogen peroxide releasing a hydroxyl radical with the capacity to oxidize contaminants [9–11]. As a widely used AOT, Fenton reaction between ferrous iron and hydrogen peroxide could treat wastewater effectively [12,17]. However, high cost of H_2O_2 restricts its large scale application in wastewater treatment. Therefore, the electro-Fenton (EF) process based on cathodically generated hydrogen peroxide (H_2O_2) was developed to overcome high cost of the added H_2O_2 [18–21].

The electro-Fenton process uses electric current for the in situ generation of H_2O_2 by O_2 reduction in the presence of dissolved Fe^{2+} . Furthermore, the overall process does not create secondary pollutants because there is a catalytic cycle with Fe^{3+} species in the medium that revert to Fe^{2+} by different reduction processes, which involve H_2O_2 or organic intermediate radicals, as well as the direct reduction of Fe^{3+} on the cathode. Therefore, the weight of the added ferrous iron (II) is much smaller than it is in the traditional Fenton method [22–24]. In the electrochemical oxidation surfactants and other organic molecules are degraded into CO_2 and water by the reaction with $\bullet\text{OH}$ radicals electro generated by direct oxidation of water [25]. In the electro-Fenton process, organic pollutants are removed by the action of both Fenton's reaction (Eq.1) in the bulk and anodic oxidation at the anode (M) surface when using high oxygen overvoltage anodes, such as dimensionally stable anode (DSA), Pt and BDD anode (Eq.2) [26]. H_2O_2 and

Fe^{2+} can be continuously generated by simultaneous electrochemical reduction of O_2 and Fe^{3+} (Eqs.3 and 4) respectively on the cathode surface [27,28].



This paper presents the EF degradations of petrochemical wastewater solutions using an Iron electrode under comparable conditions. The effect of reaction time, current density, pH, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio, and H_2O_2 of petrochemical wastewater (PW) (mL/L) on the mineralization processes was examined.

2. Experimental

2.1. Chemicals

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 analytical grade and purchased from Shanghai Chemical Reagents Company. All the solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity $> 18 \text{ MX cm}$ at $25 \text{ }^\circ\text{C}$. Their initial pH was adjusted with analytical grade sulfuric acid supplied by Merck. Heptahydrated ferrous sulfate used as catalyst was of analytical grade purchased from Merck.

2.2. Preparation of the $\text{Fe}@/\text{Fe}_2\text{O}_3$

A 0.3 g amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL of distilled water to obtain a ferric solution. A 0.6 g amount of NaBH_4 was dissolved in 40 mL of distilled water to get a NaBH_4 solution. The NaBH_4 solution was dropped to reduce ferric ions into metallic iron. The $\text{Fe}@/\text{Fe}_2\text{O}_3$ was washed with deionized water thoroughly and then dried in nitrogen for further use.

2.2. Electro-Fenton experiments

The electrolyses were 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 lead to both the decrease of dissolved iron ion [29]. 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, electrodes were placed in the reactor and solutions were mixed at 350 rpm. precipitation, which lead to both the decrease of dissolved iron ion [29]. 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, electrodes were placed in the reactor and solutions were mixed at 350 rpm.

3. Results and discussion

3.1. Regression models

In this paper, correlation between the responses and the independent variables were obtained by the following second-order model with a least-squares method:

$$\text{COD} = +68.20 + 9.40A + 5.47B - 7.73C + 7.68D + 4.28E + 0.63AB + 1.75AC + 4.02AD + 1.90AE + 2.50BC + 0.000BD - 1.12BE + 4.88CD + 0.000CE - 5.00DE - 5.72A^2 - 11.45B^2 - 11.29C^2 - 11.02D^2 - 11.28E^2$$

A, B, C, D and E are reaction time, current density, pH, $\text{mLH}_2\text{O}_2/\text{L PW}$ and $\text{molH}_2\text{O}_2/\text{molFe}^{2+}$, respectively. The negative sign in the equation represents the depressing effect of parameters and positive signal parameter represents the incremental effect on the response variables. For example, pH has reduction and time has increasing effect on the response variable.

To compare the predicted values and experience can be used Figure 1. The slope of the graphs is much closer to one so the accuracy of the models was higher. Charts obtained good correlation between experimental results with predicted values to show statistical method.

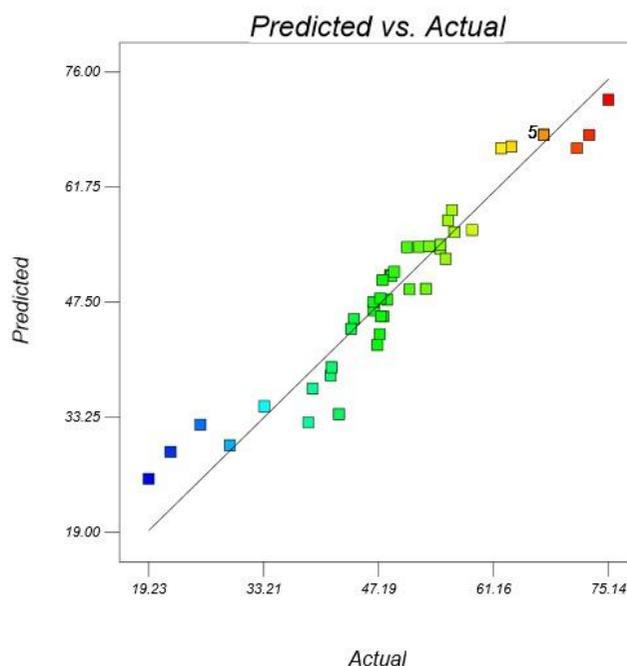
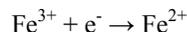
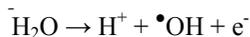


Fig. 1. Comparing observed values with predicted values when performing a purification

3.2. Three-dimensional curves regression

To explain the conflict between the parameters of the regression model used three-dimensional curves. The response curves have been obtained of a quadratic equation mentioned above. All the curves have a clear peak response. As a result, there are optimum conditions for maximum response values based on the design operating conditions and the optimum condition for the removal of COD was found. Figures 5, 8, 10 and 11 show that the reaction time has a positive impact on the development of electro-Fenton process but by increasing the time its impact is reduced so after the optimum time, the efficiency of process does not significantly change with time for this reason, the optimal response is obtained almost 2/3 of the total time [30]. Current density has a positive impact on the process electro-Fenton. In the process electro-Fenton, $\bullet\text{OH}$ formation rates applied in the purification process is controlled by the current density; increased density improves efficiency up to the optimal value.

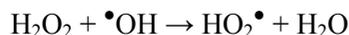
Increasing the current density will help produce hydroxyl radicals at the anode surface and Fe^{2+} ions generated of Fe^{3+} ions at the cathode surface. This will help to increase the efficiency of chain reactions of Fenton process [31,32]. Fe^{3+} to Fe^{2+} continuous transformation is a significant advantage of electro-Fenton in comparison with Fenton's method.



Figures 4, 7, 9 and 11 are indicative of the impact of this parameter.

pH in the electro-Fenton process plays an important role due to the control of hydroxyl radical production and concentration of Fe^{2+} in solution [33]. Electro-Fenton seen high activity at pH 3.5. When the pH increases the production of Fe^{2+} ions can be avoided so amount of reaction catalyst reduces. At pH 4.5 compared to pH 3 hydroxyl radical production becomes less also hydrogen peroxide is unstable at pH above 5 and may itself be decomposed into water and oxygen. It was also reported that the pH should be in the range of 2 to 4 to hydroxyl radical production becomes stable because high potential of the oxidation is observed in this range of pH. On the other hand, when $\text{pH} < 2$ is, hydrogen peroxide can not be parsed by Fe^{2+} to OH. In this case, hydrogen peroxide by attracting one proton to turns to H_2O_2 . That produced H_2O_2 forward reaction between hydrogen peroxide and Fe^{2+} to lower rates [34, 35]. Effect of pH is shown in Figures 3, 6, 9 and 10.

In order to maximize the impact of the process it is necessary that the ratio of should be kept at optimum level. As can be seen in the diagrams increase this ratio to be higher than optimum point, reduce the efficiency of the removal and it may be that the Fenton reaction mechanism will be changed and side reactions will happen. It seems that excess hydrogen peroxide has a negative effect on hydroxyl radical and the process drives to the following reaction [36]:



The reaction proceeds to production of the hydroperoxyl radical that has weak oxidation power compared with the hydroxyl radical [37]. At below you can see the corresponding reactions.

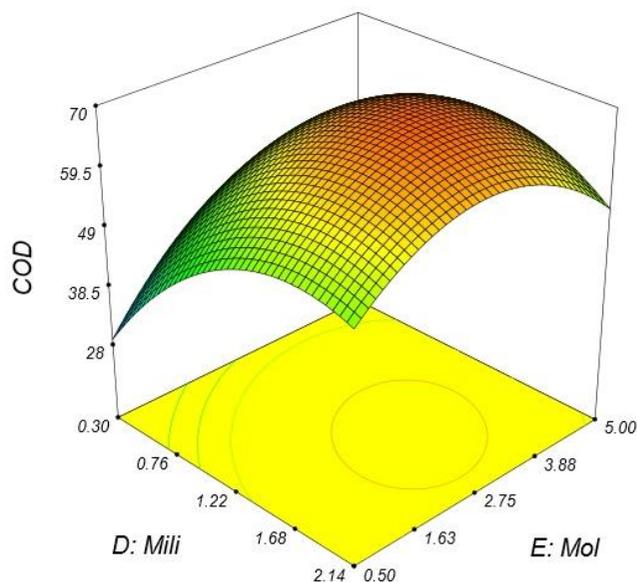
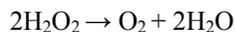


Fig. 2. Simultaneous effect of $\text{mLH}_2\text{O}_2/\text{LPW}$ and $\text{molH}_2\text{O}_2/\text{molFe}^{2+}$ on COD reduction

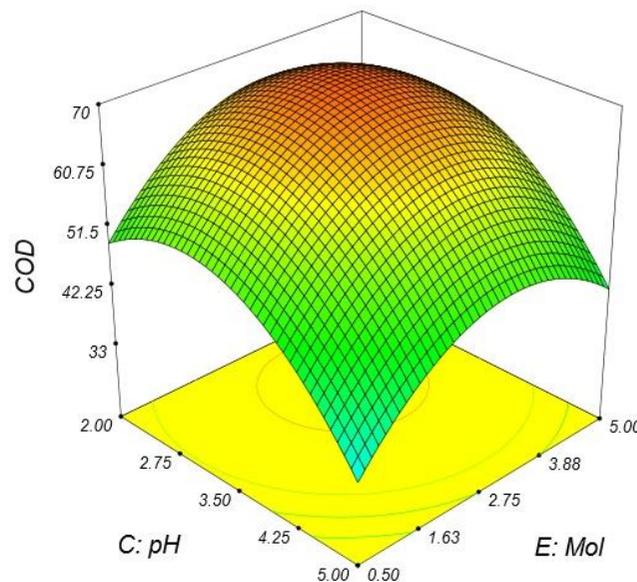
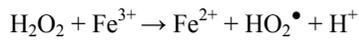
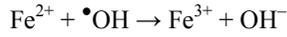


Fig. 3. Simultaneous effect of pH and $\text{molH}_2\text{O}_2/\text{molFe}^{2+}$ on COD reduction..

The result of $\text{mLH}_2\text{O}_2/\text{LPW}$ are shown in Figures 2, 6, 7 and 8.

The molar ratio of $\text{molH}_2\text{O}_2/\text{molFe}^{2+}$ should also be kept at the optimum value because if this ratio is reduced extra Fe^{2+} will reduce the removal efficiency. Here is a competition between Fe^{2+} and biomaterials for reaction with the hydroxyl radical [38]. In addition produced Fe^{2+} can react with hydrogen peroxide and generate Fe^{2+} and hydroperoxyl radical [39]. The mentioned reactions are as follows:



The effect of this parameter is given in Figures 2, 3, 4 and 5.

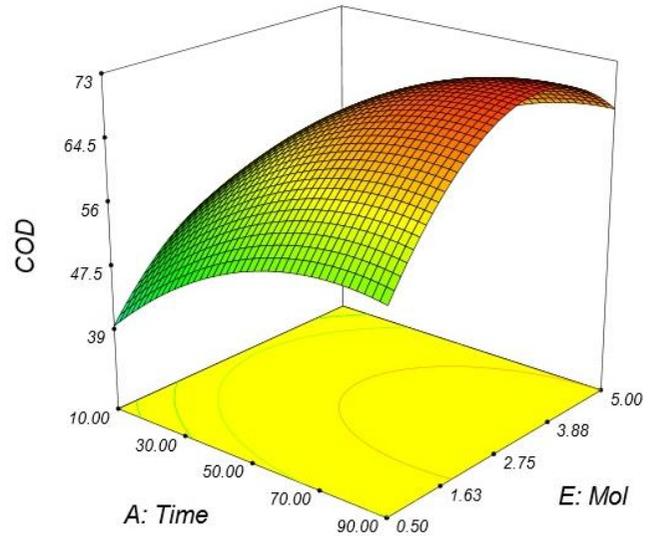


Fig. 5. Simultaneous effect of time and $\text{molH}_2\text{O}_2/\text{molFe}^{2+}$ on COD reduction

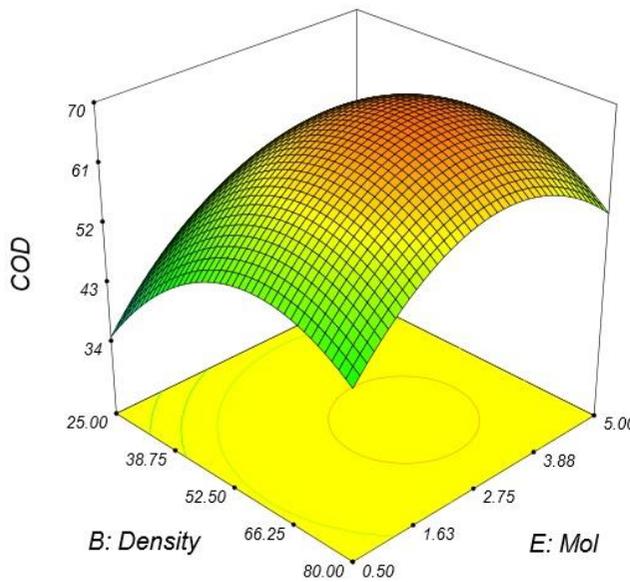


Fig. 4. Simultaneous effect of current density and $\text{molH}_2\text{O}_2/\text{molFe}^{2+}$ on COD reduction

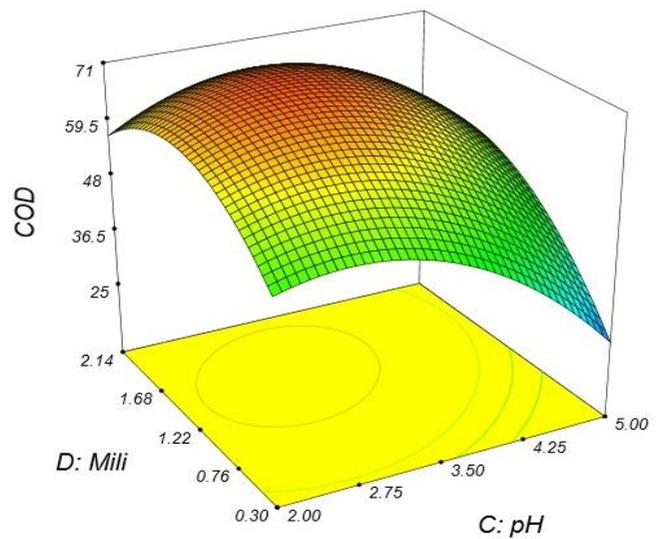


Fig. 6. Simultaneous effect of $\text{mLH}_2\text{O}_2/\text{LPW}$ and pH on COD reduction

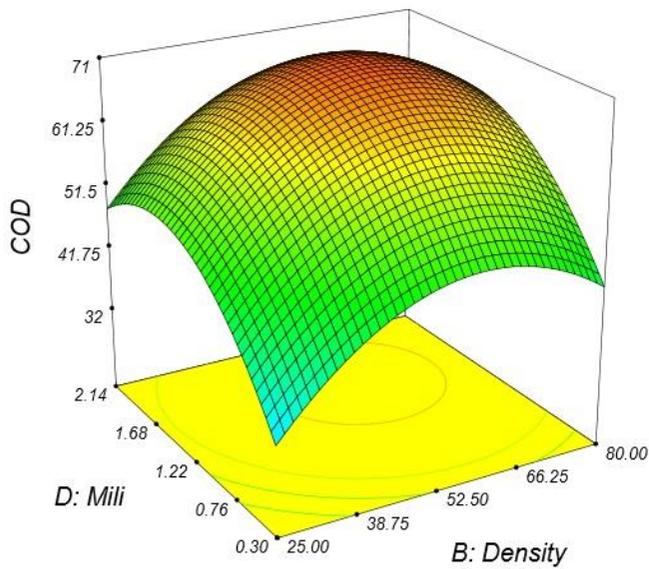


Fig. 7. Simultaneous effect of $\text{mLH}_2\text{O}_2/\text{LPW}$ and current density on COD reduction.

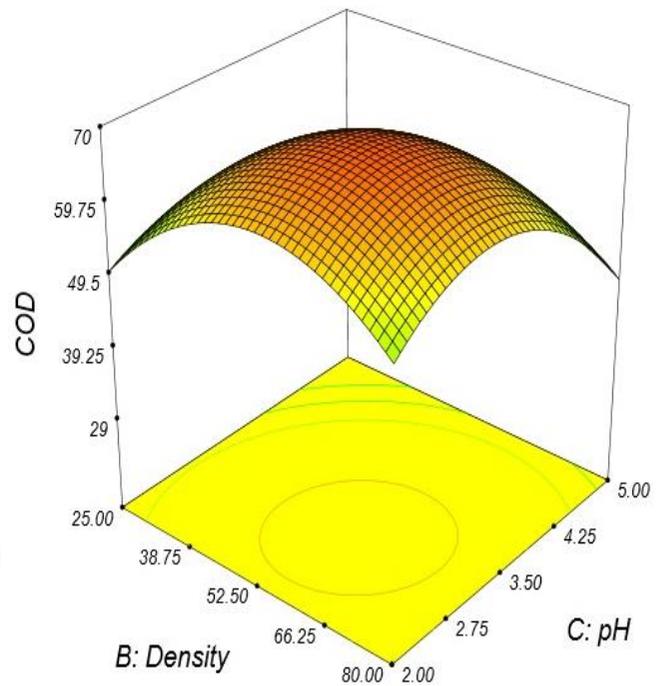


Fig. 9. Simultaneous effect of pH and current density on COD reduction

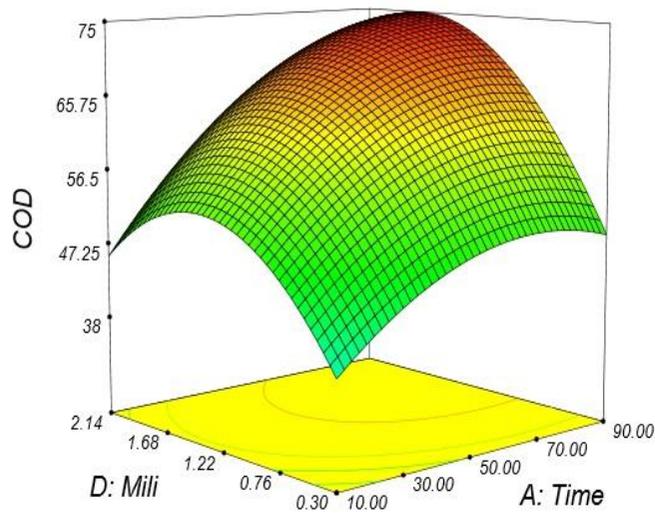


Fig. 8. Simultaneous effect of $\text{mLH}_2\text{O}_2/\text{LPW}$ and time on COD reduction .

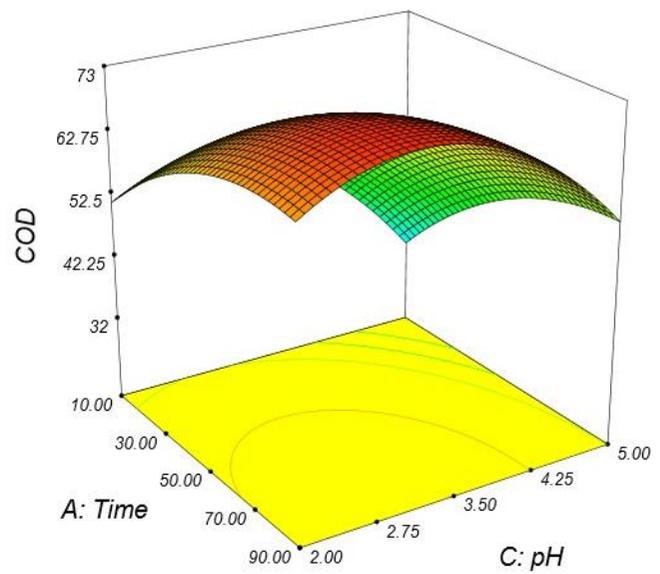


Fig. 10. Simultaneous effect of time and pH on COD reduction.

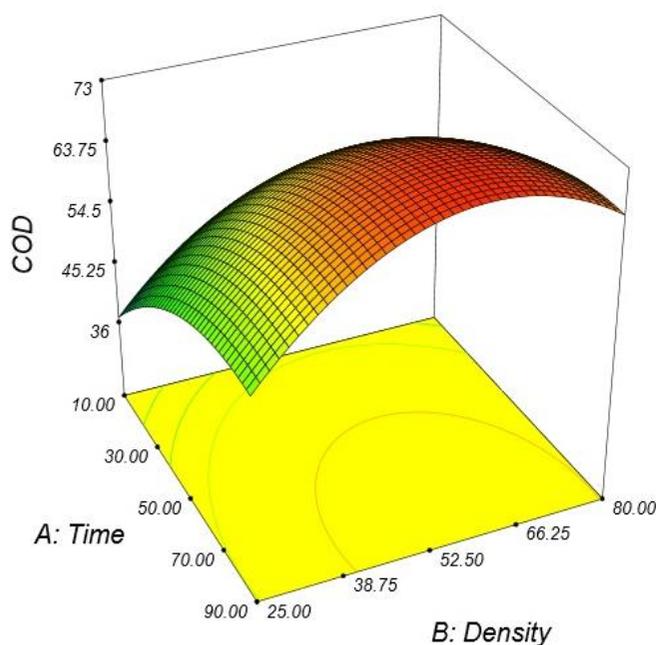


Fig. 11. Simultaneous effect of Time and current density on COD reduction

4. Conclusions

In this study COD removal from petroleum industry by electro-Fenton process was investigated. The effect of various parameters such as reaction time (10–90 min), current density (25–80 mA/m²), pH(2–5) were investigated. 86.3% removal of COD has been obtained during electrolyses, due to the formation of hydroxyl radicals in the bulk from Fenton reaction via in situ electro generated Fenton's reagent or at the anode surface from water oxidation. There was a slight increase of the H₂O₂ electro generation with the decreasing pH, but the current efficiencies declined significantly due to the enhanced parasitic reactions at anode in acid solution. Therefore, the electro-Fenton presents promising applications for wastewater treatment because of its high and stable electrochemical activity, as well as feasibility for scaling up.

References

- [1] J.V.F.L. Cavalcanti, C.A.M. Abreu, M.N. Carvalho, M.A.M. Sobrinho, M. Benachour, O.S. Baraúna, Removal of effluent from petrochemical wastewater by adsorption using organoclay, in: V. Patel (Ed.), *Petrochemicals*, Intech, Rijeka, 2012, pp. 277–294.
- [2] Y. Yavuz, A.S. Kopalal, Ü. Ögütveren, Treatment of petroleum refinery waste-water by electrochemical methods, *Desalination* 258 (2010) 201–205.
- [3] J.H.B. Rocha, M.M.S. Gomes, N.S. Fernandes, D.R. da Silva, C.A. Martínez-Huitle, Application of electrochemical oxidation as alternative treatment of produced water generated by Brazilian petrochemical industry, *Fuel Process. Technol.* 96 (2012) 80–87.
- [4] A. Coelho, A.V. Castro, M. Dezotti, G.L. Sant'Anna Jr., Treatment of petroleum refinery sourwater by advanced oxidation processes, *J. Hazard. Mater.* 137 (2006) 178–184.
- [5] E. Brillas, I. Sirés, M.A. Oturan, *Chem. Rev.* 109 (2009) 6570–6631.
- [6] I. Sirés, E. Brillas, *Environ. Int.* 40 (2012) 212–229.
- [7] H.J. Lewerenz, C. Heine, K. Skorupska, N. Szabo, T. Hannappel, T. Vo-Dinh, S.A. Campbell, H.W. Klemm, A.G. Muñoz, Photo electrocatalysis: principles, nanoemitter applications and routes to bio-inspired systems, *Energy Environ. Sci.* 3 (2010) 748–760.
- [8] Z. Liu, X. Zhang, S. Nishimoto, M. Jin, D.A. Tryk, T. Murakami, A. Fujishima, Highly ordered TiO₂ nanotube arrays with controllable length for photo electrocatalytic degradation of phenol, *J. Phy. Chem. C* 112 (2007) 253–259.
- [9] J. Shang, S. Xie, T. Zhu, J. Li, Solid-state, planar photoelectrocatalytic devices using a nanosized TiO₂ layer, *Environ. Sci. Technol.* 41 (2007) 7876–7880.
- [10] Y. Xu, Y. He, X. Cao, D. Zhong, J. Jia, TiO₂/Ti rotating disk photoelectrocatalytic (PEC) reactor: A combination of highly effective thin-film PEC and conventional PEC processes on a single electrode, *Environ. Sci. Technol.* 42 (2008) 2612–2617.
- [11] G. Dai, J. Yu, G. Liu, Synthesis and enhanced visible-light photoelectrocatalytic activity of p–n junction BiOI/TiO₂ nanotube arrays, *J. Phy. Chem. C* 115 (2011) 7339–7346.
- [12] G. Jiang, Z. Lin, L. Zhu, Y. Ding, H. Tang, Preparation and photoelectrocatalytic properties of titania/carbon nanotube composite films, *Carbon* 48 (2010) 3369–3375.
- [13] A. Wang, Y.Y. Li, A.L. Estrada, Mineralization of antibiotic sulfamethoxazole by photoelectro-Fenton treatment using activated carbon fiber cathode and under UVA irradiation, *Appl. Catal. B: Environ.* 102 (2011) 378–386.
- [14] S.J. Yuan, G.P. Sheng, W.W. Li, Z.Q. Lin, R.J. Zeng, Z.H. Tong, H.Q. Yu, Degradation of organic pollutants in a photoelectrocatalytic system enhanced by a microbial fuel cell, *Environ. Sci. Technol.* 44 (2010) 5575–5580.
- [15] X. Zhao, J. Qu, H. Liu, C. Hu, Photoelectrocatalytic degradation of triazinecontaining azo dyes at c-Bi₂MoO₆ film electrode under visible light irradiation (k

- > 420 nm), *Environ. Sci. Technol.* 41 (2007) 6802–6807.
- [16] G. Jiang, Z. Lin, L. Zhu, Y. Ding, H. Tang, Preparation and photoelectrocatalytic properties of titania/carbon nanotube composite films, *Carbon* 48 (2010) 3369–3375.
- [17] A. Wang, Y.Y. Li, A.L. Estrada, Mineralization of antibiotic sulfamethoxazole by photoelectro-Fenton treatment using activated carbon fiber cathode and under UVA irradiation, *Appl. Catal. B: Environ.* 102 (2011) 378–386.
- [18] S.J. Yuan, G.P. Sheng, W.W. Li, Z.Q. Lin, R.J. Zeng, Z.H. Tong, H.Q. Yu, Degradation of organic pollutants in a photoelectrocatalytic system enhanced by a microbial fuel cell, *Environ. Sci. Technol.* 44 (2010) 5575–5580.
- [19] X. Zhao, J. Qu, H. Liu, C. Hu, Photoelectrocatalytic degradation of triazinecontaining azo dyes at c-Bi₂MoO₆ film electrode under visible light irradiation ($k > 420$ nm), *Environ. Sci. Technol.* 41 (2007) 6802–6807.
- [20] X. Zhao, Y. Zhu, Synergetic degradation of rhodamine B at a porous ZnWO₄ film electrode by combined electro-oxidation and photocatalysis, *Environ. Sci. Technol.* 40 (2006) 3367–3372.
- [21] M. Panizza, M. Delucchi, G. Cerisola, Electrochemical degradation of anionic surfactants, *J. Appl. Electrochem.* 35 (2005) 357–361.
- [22] P.V. Nidheesh, R. Gandhimathi, Removal of Rhodamine B from aqueous solution using graphite-graphite electro-Fenton system, *Desalin. Water Treat.* (2013).
- [23] A. Ozcan, Y. Sahin, A.S. Koparal, M.A. Oturan, A comparative study on the efficiency of electro-Fenton process in the removal of prophan from water, *Appl. Catal. B: Environ.* 89 (2009) 620–626.
- [24] P.V. Nidheesh, R. Gandhimathi, Comparative removal of Rhodamine B from aqueous solution by electro-Fenton and electro-Fenton-like processes, *Clean Soil, Air, Water* 41 (2013) 1–6.
- [25] L. Ciriaco, C. Anjo, J. Correia, M.J. Pacheco, A. Lopes, Electrochemical degradation of ibuprofen on Ti/Pt/PbO₂ and Si/BDD electrodes, *Electrochim. Acta* 54 (2009) 1464–1472.
- [26] C. Flox, C. Arias, E. Brillas, A. Savall, K. Groenen-Serrano, Electrochemical incineration of cresols: a comparative study between PbO₂ and boron-doped diamond anodes, *Chemosphere* 74 (2009) 1340–1347.
- [27] M.A. Rodrigo, P. Caizares, A. Sanchez-Carretero, C. Sez, Use of conductive diamond electrochemical oxidation for wastewater treatment, *Catal. Today* 151 (2010) 173–177.
- [28] E. Brillas, S. Garcia-Segura, M. Skoumal, C. Arias, Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond anodes, *Chemosphere* 79 (2010) 605–612.
- [29] E. Tsantaki, T. Velegraki, A. Katsaounis, D. Mantzavinos, Anodic oxidation of textile dyehouse effluents on boron-doped diamond electrode, *J. Hazard. Mater.* 207–208 (2012) 91–96.
- [30] M. Panizza, M.A. Oturan, Degradation of alizarin red by electro-Fenton process using CLEAN g a graphite-felt, *Electrochim. Acta* 56 (2011) 7084–7087.
- [31] B. Marselli, J. Garcia-Gomez, P.A. Michaud, M.A. Rodrigo, Ch. Cominellis, Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes, *J. Electrochem. Soc.* 150 (2003) D79–D83.
- [32] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chem. Rev.* 109 (2009) 6541–6569.
- [33] J. Rodriguez, M.A. Rodrigo, M. Panizza, G. Cerisola, Electrochemical oxidation of acid yellow 1 using diamond anode, *J. Appl. Electrochem.* 39 (2009) 2285–2289.
- [34] X. Florenza, A.M.S. Solano, F. CC.A. Martinez-Huitl, E. Brillas, S. Garcia-Segura, Degradation of the azo dye acid red 1 by anodic oxidation and indirect electrochemical processes based on Fenton's reaction chemistry. Relationship between decolorization, mineralization and products, *Electrochim. Acta* 142 (2014) 276–288.
- [35] I. Sirés, E. Brillas, G. Cerisola, M. Panizza, Comparative depollution of mecoprop aqueous solutions by electrochemical incineration using BDD and PbO₂ as high oxidation power anodes, *J. Electroanal. Chem.* 613 (2008) 151–159.
- [36] M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, *Electrochim. Acta* 51 (2005) 191–199.
- [37] M. Panizza, G. Cerisola, Electrocatalytic materials for the electrochemical oxidation of synthetic dyes, *Appl. Catal. B – Environ.* 75 (2007) 95–101.
- [38] N. Oturan, E. Brillas, M.A. Oturan, Unprecedented total mineralization of atrazine and cyanuric acid by anodic oxidation and electro-Fenton with a bo-

- ron-doped diamond anode, *Environ. Chem. Lett.* 10 (2012) 165–170.
- [39] G.D. Fang, D.D. Dionysiou, S.R. Al-Abed, D.M. Zhou, Superoxide radical driving the activation of per-sulfate by magnetite nanoparticles: implications for the degradation of PCBs, *Appl. Catal. B: Environ.* 129 (2013) 325–332.