Short ommunication

Comparison of Electrochemical Treatment of Petroleum Refinery Effluents Using Electrooxidation, Electrocoagulation and Electrophenton Process

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Large amount of water are required for petroleum refinery activity and consequently produced larger volumes of effluents. Wastewater treatment is an important process before discharge these water into drainage system. In this work, several advanced electrochemical petroleum refinery effluents treatment approaches including direct electrochemical oxidation, indirect electrochemical oxidation, electrophenton process and electrocoagulation, were studied by using different electrode materials. Phenol and COD removal were used for estimated the performance of each method. Study showed almost all method could be effectively used for petroleum refinery effluents treatment except the electrocoagulation.

1. INTRODUCTION

Petroleum refinery effluents are wastewater produced by industrial activities including refining crude oil and fuel production. There are many configurations of the refinery due to the different designs of transformation of crude oil into products. Common classification divides it into hydro-skimming unit and complex unit. The effluents usually contain complex composition including heavy oil and toxic organic compound. The composition of petroleum refinery effluents is depending on the different oil types, plant configuration and production mode [1]. Direct discharge these effluents could results important environmental pollution problems [2]. Petroleum refinery effluents are priority pollutants due to their high polycyclic aromatics contents, which are highly toxic and can be persisted in the environment for very long time [3]. The minimum amount of dissolved oxygen in a water

environment for living beings is 2 mg/L. However, the discharge of petroleum refinery effluents into water bodies leads in the excess consumption of oxygen due to the oxidase of the organic materials by bacteria [4]. The depletion of oxygen could result in the dying of higher life forms and produce aesthetically displeasing colours, tastes and odours [5]. Petroleum refinery effluent could aggregate at natural environment and blocking drain pipes and sewer lines. They also could affect the wastewater treatment plants due to the insolubility with water [6]. Therefore, developing an adequate method for petroleum refinery effluent treatment is essential for environmental needs.

Techniques for petroleum refinery effluent treatment include coagulation [7, 8], chemical oxidation [9], adsorption [10], biological approaches [11-13], membrane treatment [12, 14], microwave-assisted catalytic wet air oxidation [15] and electrochemical techniques [16-18]. Generally speaking, the basic ideas of most of these techniques are the transformation of contaminants from one medium to another with low efficiency. Among them, electrochemical treatment methods have been attracting great attention due to many distinctive advantages such as selectivity, cost effectiveness and versatility [19-22]. Electrode material is the key of the performance of electrochemical based petroleum refinery effluent treatment due to the electrode material could alter the oxidation mechanism and anodic reaction. For example, ruthenium oxide has excellent conductivity with good barrier properties. It also can be used as a catalyst for the Cl_2 and O_2 production [23, 24]. Boron doped diamond electrode also has a good electroconducivity as well as extraordinary chemical inertness. Moreover, boron doped diamond electrode has an extremely wide electrochemical window, which can be effectively used for water treatment [25].

Electrocoagulation is a wastewater treatment method, which has shown effective performance to the treatment of soluble or colloidal pollutants [26-28]. The flocculating agent can be generated from the electro-oxidation process without adding chemical coagulant and flocculent. The coagulant can be generated using an appropriate anode material that leads, at appropriate pH, to insoluble metal hydroxide able to remove pollutants by surface complexation or electrostatic attraction [29]. Oxidation using Fenton's reagent is an alternative method for degradation of petroleum refinery effluent treatment [30-32]. The main steps contained in the Fenton process are oxidation, neutralization, flocculation and sedimentation.

In this study, several advanced electrochemical petroleum refinery effluents treatment approaches including direct electrochemical oxidation, indirect electrochemical oxidation, electrophenton process and electrocoagulation, were studied by using ruthenium mixed metal oxide electrode, iron electrodes and boron doped diamond electrode. The detail comparison was carried out.

2. EXPERIMENTS

2.1. Materials

Petroleum refinery effluent samples were provided by the Qingdao Sinopec LLC. Table 1 shows the basic composition information of the refinery effluent. Ruthenium mixed metal oxide electrode, iron electrode and boron doped diamond electrode were purchased from Wuhan Cymenes

Technology Co., Ltd. All chemicals used in the experiments were analytical grade without further purification.

Table 1. Characteristics of petroleum refinery effluent

pH	Conductivity (μS/cm)	Dissolved solids (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Phenol (mg/L)	COD (mg/L)
9.1	1652	878	108	203	140	593

2.2. Electrochemical oxidation of petroleum refinery effluents

Electrochemical oxidation of petroleum refinery effluents were conducted using ruthenium mixed metal oxide electrode according to Yavuz et al. [16] reports. Typically, the experiment was carried out in a parallel plate reactor which has mainly four compartments of total volume of 270 mL. Each compartment contains 4 ruthenium mixed metal oxide anodes and 4 ruthenium mixed metal oxide cathodes. The parameters used in the electrochemical oxidation of petroleum refinery effluents were chosen as follow: electric current: 7000 mA; current density: 25 mA/cm^2; flow rate: 18.51 mL/min; temperature: 20 ^{o}C.

Direct and indirect electrochemical oxidation of petroleum refinery effluents using boron doped diamond electrode were conducted in a thermo-jacketed bipolar trickle tower reactor. For direct anodic oxidation, no addition of large amounts of chemicals to wastewater is required. Direct electrochemical oxidation of petroleum refinery effluents can occur directly at anodes through the generation of physically adsorbed ''active oxygen'' or chemisorbed ''active oxygen''. On the other hand, NaCl was added in the indirect electrochemical oxidation. Organic compounds in NaCl-containing petroleum refinery effluents were eliminated through themediation of Cl$^-$ or ClO$^-$ ions, which formed at the anode. The parameters used in the direct electrochemical oxidation of petroleum refinery effluents were chosen as follow: electric current: 1020 mA; current density: 7 mA/cm^2; flow rate: 22.23 mL/min; temperature: 20 ^{o}C. The parameters used in the indirect electrochemical oxidation of petroleum refinery effluents were chosen as follow: electric current: 485 mA; current density: 2.5 mA/cm^2; flow rate: 17.85 mL/min; temperature: 20 ^{o}C.

2.3. Electrocoagulation and electrophenton process of petroleum refinery effluents

Electrocoagulation and electrophenton process of petroleum refinery effluents were carried out using similar reactor with experiment carried out in direct and indirect electrochemical oxidation of petroleum refinery effluents using boron doped diamond electrode. H$_2$O$_2$ was used in electrophenton process studies. The parameters used in the electrocoagulation of petroleum refinery effluents were chosen as follow: electric current: 150 mA; current density: 1 mA/cm^2; flow rate: 30.71 mL/min; temperature: 20 ^{o}C. The parameters used in the electrophenton process of petroleum refinery effluents

were chosen as follow: H_2O_2: 500 mg/L; electric current: 150 mA; current density: 1 mA/cm^2; flow rate: 30.71 mL/min; temperature: 20 ^{o}C.

2.4. Phenol and COD measurement

Amount of phenol in petroleum refinery effluents was determined according to the standard methods [33]. Amount of COD in petroleum refinery effluents was determined by LAR QuickCODlab. Detection of phenol and COD and phenol were carried out for three times and the average values were used in this study [34].

3. RESULTS AND DISCUSSION

The electrochemical oxidation of the petroleum refinery effluents was firstly studied using ruthenium mixed metal oxide electrode. This electrochemical oxidation requires no electrolyte. After optimization, the best performance of the electrochemical oxidation was under the current density of 25 mA/cm^2 with a flow rate of 18.51 mL/min. Figure 1A shows the phenol and COD degradation profiles of the petroleum refinery effluent along with the electrochemical oxidation using ruthenium mixed metal oxide electrode. It can be seen that almost all of the phenol can be removed after 310 min. It is noteworthy that the content of COD showed a slow decreasing profile with the electrolysis time due to the larger amount of organic and inorganic containments presence in the petroleum refinery effluent. Therefore, the removal of COD requires a longer time than that of the phenol removal. As shown in the figure, after 3 h treatment, more than 85% of COD can be removed. We also noticed the complete removal of COD using ruthenium mixed metal oxide electrode electrochemical oxidation was very hard.

We then studied the direct electrochemical oxidation process using boron doped diamond electrode. The optimum current density was found to be 7 mA/cm^2. Figure 1B shows the profiles of phenol and COD removal using direct electrochemical oxidation treatment. It can be seen that both phenol and COD removal showed a decreasing trends after the treatment started. Almost all of the phenol can be degraded after half hour reaction. In terms of the COD, the complete removal was achieved after one hour. The initial concentration of the phenol is 280 mg/L while only 2.2 mg/L was detected after 90 min reaction. On the other hand, the concentration of the COD is 500 mg/L at initial stage while only 32.5 mg/L can be detected after 1.5 h electrolysis. The indirect electrochemical oxidation process using boron doped diamond electrode was carried out as well. As shown in the Figure 1C, the performance of the indirect electrochemical oxidation process requires longer time than that of the direct electrochemical oxidation process. The complete removal of phenol and COD requires 80 mins and 110 mins, respectively. A good performance of the indirect electrochemical oxidation process can be achieved at low current input. However, there is no clear difference when the comparison of the energy consumption using direct and indirect electrochemical oxidation process. Comprising with the existing reports, the ruthenium mixed metal oxide electrode electrochemical
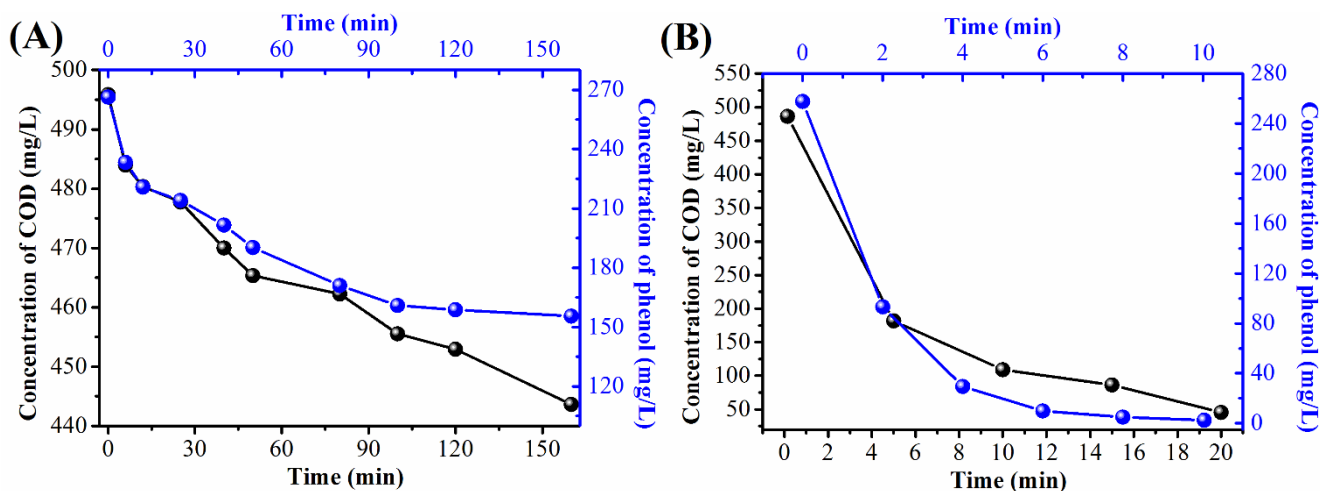
oxidation and boron doped diamond electrode direct electrochemical oxidation showed a similar degradation performance but lower applied current density [33]. The boron doped diamond electrode indirect electrochemical oxidation showed a comparable result compared with the literatures [35, 36].
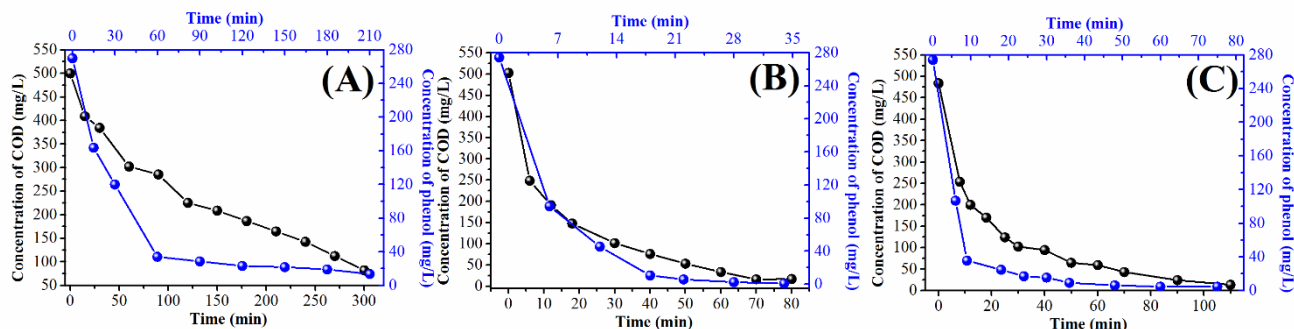
Figure 1. Phenol and COD degradation profiles using (A) ruthenium mixed metal oxide electrode electrochemical oxidation (electric current: 7000 mA; current density: 25 mA/cm^2; flow rate: 18.51 mL/min; temperature: 20 ^{o}C.), (B) boron doped diamond electrode direct electrochemical oxidation (1020 mA; current density: 7 mA/cm^2; flow rate: 22.23 mL/min; temperature: 20 ^{o}C.) and (C) boron doped diamond electrode indirect electrochemical oxidation (electric current: 485 mA; current density: 2.5 mA/cm^2; flow rate: 17.85 mL/min; temperature: 20 ^{o}C).

Iron electrodes were used for electrocoagulation and electrofenton treatment of petroleum refinery effluents. Figure 2A shows the degradation profiles of phenol and COD using electrocoagulation process without the addition of electrolyte. It can be seen that only small amount of phenol and COD can be removed using iron electrode electrocoagulation. Therefore, the electrocoagulation process cannot be effectively used for petroleum refinery effluents treatment. On the other hand, the electrofenton treatment showed a promising performance compared with the iron electrode electrocoagulation. As shown in Figure 2B, after addition of the 500 mg/L H$_2$O$_2$, more than 95% of phenol and COD can be removed from petroleum refinery effluents after 10 min and 20 min, respectively. This performance is higher than many existing reports [37-39]. However, the performance of the electrofenton treatment showed a decline when prolong the reaction time due to the consumption of the H$_2$O$_2$. Continuous feeding of H$_2$O$_2$ is required when the phenol and COD content still reach to the standard for discharge.

The basic mechanisms of the electrochemical oxidation (either direct or indirect) and electrofenton process are similar, which the phenol and DOC were degraded by the electrochemical produced OH$^\bullet$ radicals. When a toxic, non-biocompatible pollutant is treated, the electrochemical conversion transforms the organic substrate into a variety of metabolites; often, biocompatible organics are generated, and biological treatment is still required after the electrochemical oxidation. In contrast, electrochemical degradation yields water and CO$_2$, no further purification being necessary. In electrocoagulation process, the complexation process could be occurred after the generation of coagulant. However, extreme high content of soluble organic compounds and only small amount of suspended substance available in petroleum refinery effluents results an inefficiency removal performance.

Figure 2. Phenol and COD degradation profiles using (A) electrocoagulation process (electric current: 150 mA; current density: 1 mA/cm^2; flow rate: 30.71 mL/min; temperature: 20 ^{o}C) and (B) electrofenton treatment (H$_2$O$_2$: 500 mg/L; electric current: 150 mA; current density: 1 mA/cm^2; flow rate: 30.71 mL/min; temperature: 20 ^{o}C).

Figure 3A shows the comparison of the performances of using different electrode materials and treatment methods toward phenol removal rate. It can be seen that the performance follow the order as: electrophenton process using iron electrode ≥ direct electrochemical oxidation using boron doped diamond electrode ≥ indirect electrochemical oxidation using boron doped diamond electrode ≥ electrochemical oxidation using ruthenium mixed metal oxide electrode ≥ electrocoagulation process. The electrofenton treatment showed a superior performance compared with other methods Figure 3B shows the first-order rate constant of each method, which is 0.4711/min, 0.1641/min, 0.0542/min, 0.0142/min and 0.0035/min for electrofenton process, boron doped diamond electrode direct electrochemical oxidation, boron doped diamond electrode boron doped diamond electrode, ruthenium mixed metal oxide electrode electrochemical oxidation and electrochemical oxidation, respectively. Because the removal performance is depended on the OH$^•$ radicals generated during the electrochemical reaction, the addition of H$_2$O$_2$ in electrofenton process can generate larger number of OH$^•$ radicals, which result a much higher phenol removal performance. The following equation can be described the reaction between H$_2$O$_2$ and Fe^{2+} for hydroxyl radical formation:

$$H_2O_2 + F^{2+} \rightarrow Fe^{3+} + OH^• + OH^-$$
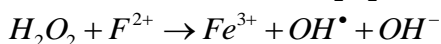
For direct and indirect electrochemical oxidation, the OH$^•$ radicals formation rate was depending on the generation potential, which could be influenced by several parameters, including electrolyte and electrode material. The following formula can be used for explaining the hydroxyl radical formation during the electrochemical oxidation process:

$$H_2O \rightarrow OH^• + e^- + H^+$$
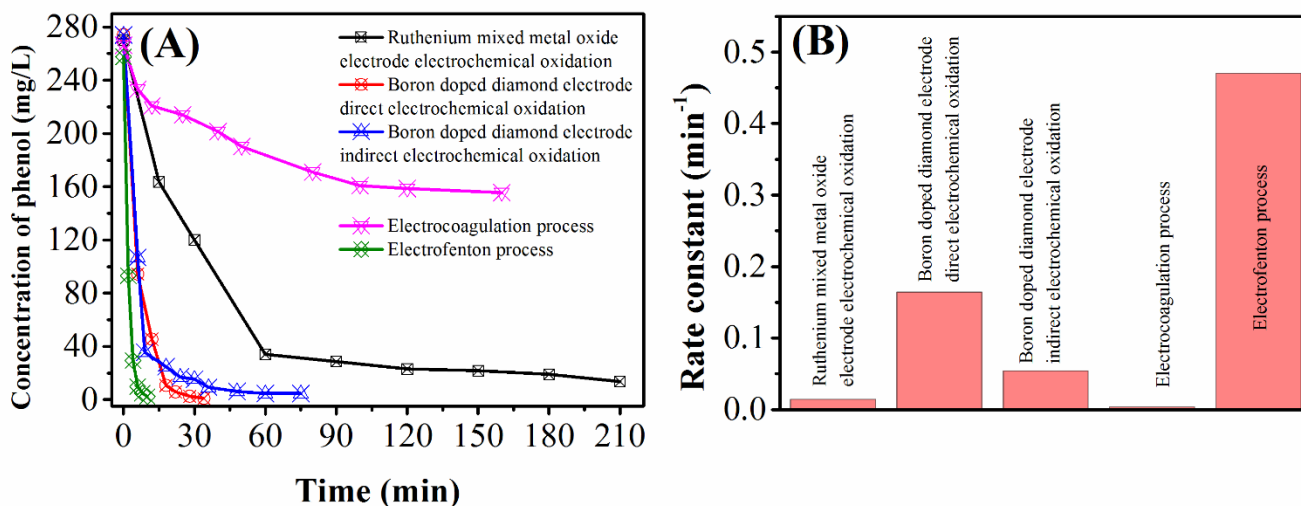
Figure 3. (A) Time coarse variation of phenol concentration with electrode materials employed. (B) Corresponding first-order rate constant.
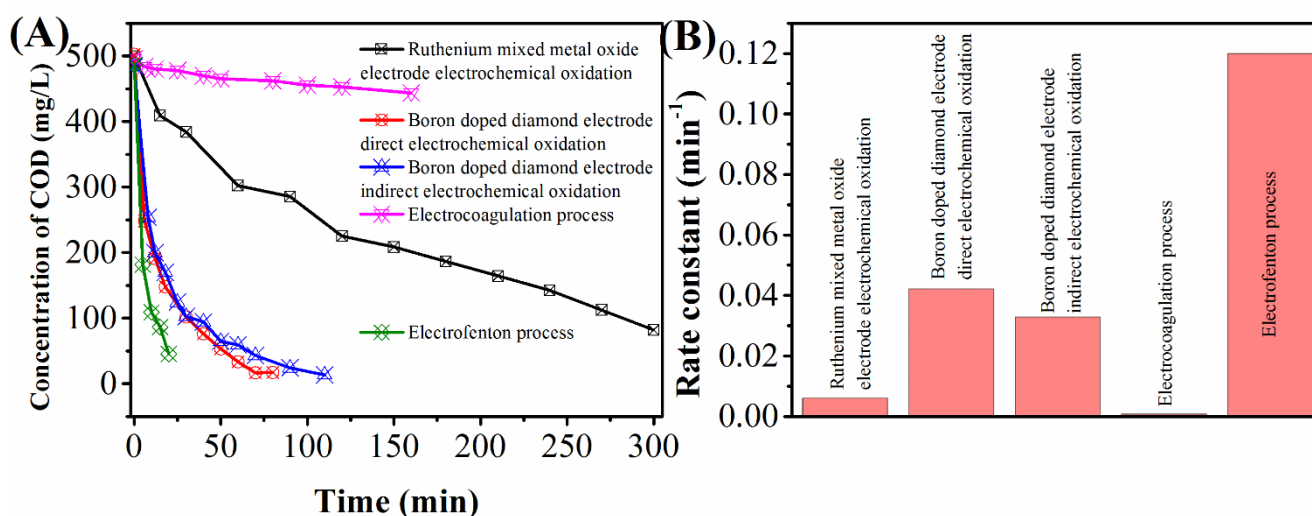

Figure 4. (A) Time coarse variation of COD concentration with electrode materials employed. (B) Corresponding first-order rate constant.

Figure 4A and 4B shows the COD degradation profiles with time depending on the electrode materials and the corresponding first-order rate constants, respectively. The variation of COD had a similar degradation trend compared to the phenol removal results. Therefore, the activity of the proposed electrochemical methods showed similar degradation activities toward phenol and COD. In fact, the COD includes phenol. Therefore, the both studies showed the electrochemical treatments of petroleum refinery effluents not only capable for degradation signal organic compound, but also can be effectively for removing complex organic pollutants. However, the removal of COD is much harder than phenol due to the complex composition of COD in petroleum refinery effluent. The comparison of Figure 4 and Figure 3 proves the removal rate of COD is less than phenol at a given time period.

After the comparison of the phenol and COD removal rate using different electrochemical treatment methods with different electrode, we further considered the energy consumptions of each

proposed electrochemical based methods as the energy consumption is a very important factor in the industrial field. The aim of the developing a favourable method for petroleum refinery effluents treatment requires low energy requirement with high degradation performance. We summarized the cumulative energy consumption of each method and presented in Figure 5. As shown in the figure, the lowest energy consumption was achieved using electrofenton process with 5.22 kWh/g. However, the addition of H_2O_2 requires extra cost, which made this method less attractive. The highest energy consumption was achieved using electrocoagulation process with 42.26 kWh/g. As we already mentioned in the previous discussion, the electrocoagulation process cannot be effectively used for petroleum refinery effluents treatment. The energy consumptions of boron doped diamond electrode direct electrochemical oxidation, boron doped diamond electrode indirect electrochemical oxidation, ruthenium mixed metal oxide electrode electrochemical oxidation were obtained as 11.51 kWh/g, 13.28 kWh/g and 10.56 kWh/g, respectively.
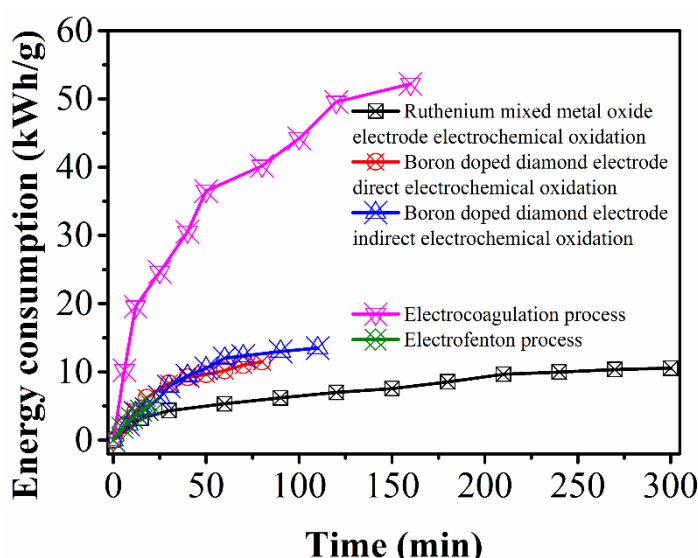
Figure 5. Cumulative energy consumption of different electrochemical based petroleum refinery effluents treatments

4. CONCLUSION

In this work, we studied five different electrochemical based methods for petroleum refinery effluents treatment. Results showed all electrochemical methods except electrocoagulation process can completely remove phenol and COD in petroleum refinery effluent sample. The best performance was observed when applied electrofenton process. The removal of phenol and COD can be accomplished within 10 min and 20 min, respectively. Among the electrochemical oxidation processes, boron doped diamond electrode direct electrochemical oxidation showed a superior performance compared with other two approaches. Besides the treatment performance comparison, the energy consumption of each technique was also discussed. Despite the cost of the H_2O_2, the electrofenton process showed the lowest energy consumption requirement.

References

1. J. Saien and H. Nejati, *J. Hazard. Mater.*, 148 (2007) 491
2. H. Wake, *Estuarine, Coastal and Shelf Science*, 62 (2005) 131
3. B. Mrayyan and M.N. Battikhi, *J. Hazard. Mater.*, 120 (2005) 127
4. F. Attiogbe, M. Glover-Amengor and K. Nyadziehe, *West African Journal of Applied Ecology*, 11 (2007)
5. P. Stepnowski, E. Siedlecka, P. Behrend and B. Jastorff, *Water. Res.*, 36 (2002) 2167
6. X. Xu and X. Zhu, *Chemosphere*, 56 (2004) 889
7. Ş. Demırcı, B. ErdoĞan and R. Özcımder, *Water. Res.*, 32 (1998) 3495
8. M.H. El-Naas, S. Al-Zuhair, A. Al-Lobaney and S. Makhlouf, *Journal of environmental management*, 91 (2009) 180
9. O. Abdelwahab, N. Amin and E.Z. El-Ashtoukhy, *J. Hazard. Mater.*, 163 (2009) 711
10. M.H. El-Naas, S. Al-Zuhair and M.A. Alhaija, *J. Hazard. Mater.*, 173 (2010) 750
11. C.-J.G. Jou and G.-C. Huang, *Advances in Environmental Research*, 7 (2003) 463
12. M.M. Rahman and M.H. Al-Malack, *Desalination*, 191 (2006) 16
13. F. Ma, J.-b. Guo, L.-j. Zhao, C.-c. Chang and D. Cui, *Bioresource technology*, 100 (2009) 597
14. Y.S. Li, L. Yan, C.B. Xiang and L.J. Hong, *Desalination*, 196 (2006) 76
15. Y. Sun, Y. Zhang and X. Quan, *Sep. Purif. Technol.*, 62 (2008) 565
16. Y. Yavuz and A.S. Koparal, *J. Hazard. Mater.*, 136 (2006) 296
17. Y. Yavuz, A.S. Koparal and Ü.B. Öğütveren, *J. Environ. Eng.*, 134 (2008) 24
18. U.T. Un, *Fresenius Environmental Bulletin*, 16 (2007) 1056
19. L. Fu, G. Lai, P.J. Mahon, J. Wang, D. Zhu, B. Jia, F. Malherbe and A. Yu, *RSC Advances*, 4 (2014) 39645
20. L. Fu, G. Lai and A. Yu, *RSC Advances*, 5 (2015) 76973
21. Y. Zheng, A. Wang, H. Lin, L. Fu and W. Cai, *RSC Advances*, 5 (2015) 15425
22. L. Fu, Y. Zheng, A. Wang, W. Cai and H. Lin, *Food chemistry*, 181 (2015) 127
23. A.J. Terezo and E.C. Pereira, *Mater. Lett.*, 53 (2002) 339
24. T. Lister, Y. Tolmachev, Y. Chu, W. Cullen, H. You, R. Yonco and Z. Nagy, *Journal of Electroanalytical Chemistry*, 554 (2003) 71
25. M. Hupert, A. Muck, J. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show and G.M. Swain, *Diamond and Related Materials*, 12 (2003) 1940
26. J.S. Bhullar, Y. Cozakov, N. Varshney, S. Bindroo, G. Subhas, S. Chaudhary, J. Tilak, M. Decker, M.J. Jacobs and V.K. Mittal, *Journal of the American College of Surgeons*, 221 (2015) S93
27. M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M.R. Qtaishat and M. Alkasrawi, *Chem. Eng. J.*, 260 (2015) 749
28. T. Yehya, L. Favier, Y. Kadmi, F. Audonnet, N. Fayad, M. Gavrilescu and C. Vial, *Environmental Engineering and Management Journal*, 14 (2015) 639
29. I. Ben Hariz, A. Halleb, N. Adhoum and L. Monser, *Sep. Purif. Technol.*, 107 (2013) 150
30. S. Wang, *Dyes and Pigments*, 76 (2008) 714
31. A. Özcan and M. Gençten, *Chemosphere*, 146 (2016) 245
32. H. Zazou, N. Oturan, M. Sönmez-Çelebi, M. Hamdani and M. Oturan, *Journal of Materials and Environmental Science*, 6 (2015) 107
33. O. Abdelwahab, N.K. Amin and E.S.Z. El-Ashtoukhy, *J. Hazard. Mater.*, 163 (2009) 711
34. J. Müller, *Proceedings of the Water Environment Federation*, 2001 (2001) 512
35. V. Il'in, V. Kolesnikov and Y.I. Parshina, *Glass and ceramics*, 59 (2002) 242

36. T. Kubritskaya, I. Drako, V. Sorokina and R. Drondina, Surface engineering and applied electrochemistry C/C of elektronnaia obrabotka materialov, (2000) 62
37. A. Oonnittan and M. ET Sillanpaa, *Current Organic Chemistry*, 16 (2012) 2060
38. R. Davarnejad, M. Pirhadi, M. Mohammadi and S. Arpanahzadeh, *Chemical Product and Process Modeling*, 10 (2015) 11
39. M. Azri and D. Zerouali, *Desalination and Water Treatment*, (2015) 1