Chemosphere 117 (2014) 309–315

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Application of electrochemical technology for removing petroleum hydrocarbons from produced water using lead dioxide and boron-doped diamond electrodes

Boutheina Gargouri [a], Olfa Dridi Gargouri [a], Bochra Gargouri [b], Souhel Kallel Trabelsi [a], Ridha Abdelhedi [a], Mohamed Bouaziz [a,b,*]

[a] Laboratoire d'Electrochimie et Environnement, Ecole Nationale d'Ingénieurs de Sfax, BP"1173", 3038-Sfax, Université de Sfax, Tunisia
[b] Institut Supérieur de Biotechnologie de Sfax, 3038, BP"1175", 3038-Sfax, Université de Sfax, Tunisia

HIGHLIGHTS

- Produced Petroleum water (PW) is a serious environmental problem.
- Remediation of industrial PW by electrochemical oxidation is performed.
- Different current densities was carried out using PbO_2 and BDD anodes.
- The BDD anode showed a better performance than PbO_2 to the treatment of PW.

ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form 16 July 2014
Accepted 20 July 2014

Handling Editor: E. Brillas

Keywords:
Produced water
Electrochemical oxidation
Petrochemical pollution
Cytotoxicity

ABSTRACT

Although diverse methods exist for treating polluted water, the most promising and innovating technology is the electrochemical remediation process. This paper presents the anodic oxidation of real produced water (PW), generated by the petroleum exploration of the Petrobras plant-Tunisia. Experiments were conducted at different current densities (30, 50 and 100 mA cm^{-2}) using the lead dioxide supported on tantalum (Ta/PbO_2) and boron-doped diamond (BDD) anodes in an electrolytic batch cell. The electrolytic process was monitored by the chemical oxygen demand (COD) and the residual total petroleum hydrocarbon [TPH] in order to know the feasibility of electrochemical treatment. The characterization and quantification of petroleum wastewater components were performed by gas chromatography mass spectrometry. The COD removal was approximately 85% and 96% using PbO_2 and BDD reached after 11 and 7 h, respectively. Compared with PbO_2, the BDD anode showed a better performance to remove petroleum hydrocarbons compounds from produced water. It provided a higher oxidation rate and it consumed lower energy. However, the energy consumption and process time make useless anodic oxidation for the complete elimination of pollutants from PW. Cytotoxicity has shown that electrochemical oxidation using BDD could be efficiently used to reduce more than 90% of hydrocarbons compounds. All results suggest that electrochemical oxidation could be an effective approach to treat highly concentrated organic pollutants present in the industrial petrochemical wastewater and significantly reduce the cost and time of treatment.

1. Introduction

Petroleum effluents are hazardous compounds, whose discharge into the environment adversely affects the ecosystem. They are pollutants that are caused mainly by the increasing global energy demand required by the greater exploration and exploitation of the raw materials in crude oil. Produced water (PW) is considered as one of the largest waste streams in the petroleum, oil and gas industry. The drilling and extraction operations aiming to maximize the production of oil may be counterbalanced by the huge production of contaminated water with pollutants, such as heavy metals and organic compounds (Wake, 2005; Santos et al., 2006; Ahmaduna et al., 2009). In addition, PW is a serious environmental problem, whose discharge is directly poured into

* Corresponding author at: Institut Supérieur de Biotechnologie de Sfax, BP "1175", 3038, Université de Sfax, Tunisia. Tel.: +216 98 667 581; fax: +216 74 674 364.
E-mail address: mohamed.bouaziz@fsg.rnu.tn (M. Bouaziz).

http://dx.doi.org/10.1016/j.chemosphere.2014.07.067
0045-6535/

the sea in offshore areas. Actually, being loaded with hazardous compounds that remain soluble in water, PW is regarded as the most harmful pollutant that affects life directly. So, there is an urgent need to develop efficient and economical methods to simultaneously remove organic and inorganic pollutants from such effluents. Due to their toxicity and potential carcinogenic effect, they may cause irreparable damage not only to human health but also to the environment (Diya'uddeen et al., 2011; Rocha et al., 2012; Da Silva et al., 2013).

Several alternative treatments of PW have been studied by several research groups around the world (Ahmaduna et al., 2009; Ramalho et al., 2010; Rocha et al., 2012). Yet, the physico-chemical and bioremediation methods utilized for the degradation of these compounds have shown various operational problems, such as generation of toxic gases, phase transfer of pollutants, residual sludge production, demand for large territorial areas and the impossibility of destroying refractory compounds (Cañizares et al., 2011). During recent years, electrochemical methods have been proved as both an efficient and viable alternative for the treatment of wastewater practicability in various industrial wastewaters treatment, like refinery wastewater (Dos Santos et al., 2014). This is due to its unique ability to oxidize or reduce contaminants in the water near the well-controlled electrode (Hamza et al., 2009; Martínez-Huitle and Brillas, 2009; Yavuz et al., 2010; Méndez et al., 2012) and its attractive characteristics, such as versatility, energy efficiency, amenability of automation and environmental compatibility (free-chemical reagents).

The electrochemical treatment has various advantages, among which wide application, simple equipment, easy operation, no consumption of chemical, lower temperature requirements and lack of sludge formation can be mentioned (Chen, 2004; Martínez-Huitle and Ferro, 2006). Among these electrochemical methods, the anodic oxidation is useful to directly destroy organic pollutants by reaction with hydroxyl radical ($HO^{\cdot}$) formed at the anode surface from water oxidation (Belhadj-Tahar and Savall, 1998):

$$H_2O \rightarrow HO^{\cdot}_{ads} + H^+ + e^- \quad (1)$$

Over the past years, the application of anodic oxidation to water remediation has received great attention owing to the use of special electrodes. Moreover, the total mineralization to CO_2 and H_2O as well as the optimal faradic efficiency was strictly obtained by using high oxygen over-potential anodes, such as Tin dioxide SnO_2 (Ramalho et al., 2010), lead dioxide PbO_2 (Belhadj-Tahar and Savall, 1998; Weiss et al., 2008) and boron-doped diamond BDD, which brought about different removal organic matter efficiencies (Michaud et al., 2003; Zhao et al., 2010; Da Silva et al., 2013). Non-active anodes, as BDD, is a new anode material and possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous medium (Panizza and Cerisola, 2009; Da Silva et al., 2013; Dos Santos et al., 2014).

In this context, BDD anodes have a great potential for the electrochemical applications in the treatment of wastewater. This is due to their extraordinary chemical inertness and their ability to mineralize a wide range of recalcitrant organic compounds (Dos Santos et al., 2014; Urtiaga et al., 2014). This is explained by the very high over-voltage of oxygen production and the generation of hydroxyl radicals, a very powerful oxidant (Gomes de Lima et al., 2009; Panizza and Cerisola, 2009, 2010b; Sales et al., 2013). The BDD electrode is often used as anode material for petroleum wastewater treatment (Dos Santos et al., 2014).

Nevertheless, none of the previously done works reports the electrochemical treatment of the petroleum wastewater on the PbO_2 anodes. The main objective of the present work is to study the electro-oxidation process in treating petroleum PW using Ta/PbO_2 and BDD anodes to remove petroleum hydrocarbons. Effectiveness was measured in terms of the reduction in total petroleum hydrocarbon [TPH], COD and petroleum hydrocarbons (C10–C40) by GC/MS analysis. Besides, the toxicity of the water after treatment was tested using cell culture.

2. Experimental

2.1. Produced water samples and chemicals

The waste analyzed in this study was continuously produced as a by-product during crude oil extraction in secondary extraction wells. Since there was no actual way for the deposition of this waste, it was disposed in closed reservoirs at a rate of 10–15 m^3 per day per well. PW samples were supplied by Petrobras plant "SEREPT" an industry for research and exploitation of petroleum located in the southwest of Tunisia–Sfax. The oil was separated from the produced water in that terminal. Its pH was around 6.9 and its electric conductivity around 1540 $\mu S\ cm^{-1}$. It contained 4.38 $g\ L^{-1}$ of total dissolved solids, 59 $mg\ L^{-1}$ of phenol and 56.7 $mg\ L^{-1}$ of oils and greases. Chemical oxygen demand (COD) was about 19842 ppm. Table 1 lists the average composition of the produced water as received in the terminal, according to the physicochemical parameters.

The chosen chemicals were of the highest-quality commercially-available ones, and they were used without further purification. NaCl was purchased from Chemi-Pharma and used as a supporting electrolyte for increase effluent conductivity. Besides, H_2SO_4 and NaOH (Merck, Germany) were used for the pH adjustment. All the solutions were freshly prepared with ultra pure water.

Cytotoxicity using cell lines HeLa was carried out to get information about the toxicity of the initial and treated produced water under optimum experimental conditions.

2.2. Extraction procedure of hydrocarbon

The analyses of hydrocarbons were carried out after dichloromethane extraction. The aqueous phase sample was removed and put in a sealed flask for sub-sequent analysis. Then, it was concentrated to approximately 3 mL using a rotary evaporator under reduced pressure in a water bath. Afterwards, it was dissolved in equal volume of dichloromethane and further cleaned through a column filled with florisil (SUPELCLEAN LC-FLORISIL, USA) and then analyzed by gas chromatography–mass spectrometry apparatus.

After the evaporation of the solvent, the amount of residual TPH was determined by gravimetric methods after dichloromethane evaporation by simple distillation at 60 °C (Mishra et al., 2001).

2.3. Cytotoxicity experiments

2.3.1. HeLa cell culture

The continuous human cell lines HeLa (epithelial cervical cancer cell line) was investigated for cytotoxicity of petrochemical waste-

Table 1
Main physical and chemical characteristics of produced wastewater.

Characteristics	Values
pH	6.9
COD ($mg\ O_2\ L^{-1}$)	19842
BOD_5 ($mg\ L^{-1}$)	475
Phenol ($mg\ L^{-1}$)	59
Oil and greases ($g\ L^{-1}$)	56.7
Electrical conductivity ($\mu S\ cm^{-1}$)	1540
Total petroleum hydrocarbons ($g\ L^{-1}$)	11.22