

**Treatment of *ex-situ* soil-washing fluids polluted with petroleum by anodic oxidation,  
photolysis, sonolysis and combined approaches**

Elisama Vieira dos Santos<sup>1</sup>, Cristina Sáez<sup>2</sup>, Pablo Cañizares<sup>2</sup>, Djalma Ribeiro da Silva<sup>3</sup>,

Carlos A. Martínez-Huitle<sup>3,\*</sup>, Manuel A. Rodrigo<sup>2,\*</sup>

<sup>1</sup> School of Science and Technology, Federal University of Rio Grande do Norte, 59078-970 Natal,  
Brazil

<sup>2</sup> Department of Chemical Engineering. Enrique Costa Building. Campus Universitario s/n. 13071  
Ciudad Real. Spain

<sup>3</sup> Institute of Chemistry, Federal University of Rio Grande do Norte, 59078-970 Natal, Brazil

\*author to whom all correspondence should be sent: [carlosmh@quimica.ufrn.br](mailto:carlosmh@quimica.ufrn.br)

**Abstract**

In this research, the treatment of soil spiked with petroleum was studied using a surfactant-aided soil-washing (SASW) process followed by sonolysis (US), photolysis and boron doped diamond electrolysis (BDD-electrolysis) for washing liquid treatment. Results clearly demonstrate that SASW is a very efficient approach in the treatment of soil, removing completely the petrochemical compounds by using dosages about 5 g of extracting surfactant (sodium dodecyl sulfate (SDS)) per Kg of soil. The main characteristics of the effluents produced in this soil remediation technology as well as the efficiency of the treatment (US, photolysis and BDD-electrolysis) depend on the dosage of SDS. Depollution of the effluents (degradation and mineralization of the organic matter) is related to the reduction in size of micelles formed by SDS and petroleum, and it depends on the treatment used. US and photolysis were inefficient decontamination processes, while BDD-electrolysis favors the complete depletion of micelles. However, the intensification of the efficiency was attained by synergic degradation effects when UV light irradiation and US were coupled with BDD-electrolysis, US/BDD-electrolysis and photo/BDD-electrolysis, respectively. Sulfate (coming

from SDS) ions play an important role during the BDD-electrolysis, US/BDD-electrolysis and photo/BDD-electrolysis because persulfate and persulfate radicals are produced (by sulfate activation applying US or photolysis), improving the efficiency of the processes.

**Keywords:** Petroleum, Soil washing, Sonolysis, Photo-electrolysis, Sono-electrolysis, Diamond electrode.

## 1. Introduction

Recently, an increasing interest in the remediation of soil and water polluted with petroleum has been attained [1-3]. Petroleum refining industries convert crude oil into more than 2500 petroleum products including gasoline, kerosene, aviation fuel, diesel fuel, lubricating oils, etc. World oil demand is expected to rise to 107 thousand barrels per day over the next two decades, and oil will account for 32 % of the world's energy supply by 2030 [4]. Nevertheless, the petrochemical activities by industries have generated serious environmental problems in water and soil ecosystems. In the former, the petrochemical wastewaters generated contain many chemicals, such as benzene, volatile phenol, sulfides, ammonia, suspended solids, cyanides, nitrogen compounds and heavy metals. Meanwhile, hydrophobic organic compounds (HOCs) such as petroleum hydrocarbons, polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAH) are extremely difficult to remove from the later [5]. The persistence of HOCs in soils is a matter of significant public, scientific and regulatory concerns because of their potential toxicity, mutagenicity, carcinogenicity and ability to be bioaccumulated in the food chain [5,6]. Most of them are persistent in the natural environment due to their slow degradation by natural attenuation or by (photo) chemical/biological processes [5,7,8].

Low solubility in water, high octanol/water partition coefficient, a high organic carbon/water partition coefficient and volatility influence on the accumulation, mobility and availability of HOCs in the soil [8,9] as well as the efficiency of their removal during the treatment. Therefore, several soil treatments have been developed in the last years, however, these processes have at least one important drawback such as high costs (thermal treatments), high perturbation of the soil texture (thermal treatments), low efficiency (pump and treat), long treatment time requirements (biodegradation processes), or selectivity toward target pollutants (volatile organic compounds for venting, hydrophilic organic compounds for pump and treat) [5]. In this frame, more efficient, less expensive and ecofriendly approaches were technologically advanced in the last years [5,10]. Soil washing (*ex-situ* process) or soil flushing (*in-situ* process) procedures were developed using

extracting agents (surfactants, biosurfactants, cyclodextrins (CDs), cosolvents) in order to enhance the solubility, desorption and biodegradation of soil pollutants [5]. After that, a treatment stage of the oil washing/soil flushing solutions is carried out [10-19].

Nevertheless, the effluents obtained after the soil depollution are difficult to be treated due to the higher organic load (pollutants and extracting agents) and generally, a partial decontamination is attained [5]. For this reason, the main objectives of the present research are to evaluate the efficacy of single technologies (BDD-electrolysis, sonolysis (US) and photolysis) to depollute soil washing fluid obtained from petroleum decontamination of soils by Surfactant-Aided Soil Washing (SASW) [14-20] as well as the study of the intensification of the efficiency on the degradation of this effluent by coupling US and photolysis with BDD-electrolysis (US/BDD-electrolysis and photo/BDD-electrolysis).

## **2. Materials and methods**

### **2.1. Chemicals**

Petroleum (American Petroleum Institute (API) gravity  $> 30$ , it consists basically of alkanes, and approximately 15 to 25% of cycloalkanes) and hexane were obtained from Sigma-Aldrich (Spain). Sodium dodecyl sulfate (SDS) and sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) were obtained from Panreac. Deionized water (Millipore Milli-Q system) was used to prepare all solutions.

### **2.2. Preparation of simulated soil**

Spiking soil samples with organic compounds is the most frequently contamination method used in the lab-scale studies [5,21], for this reason, a model soil was chosen and it was polluted with petroleum. The model soil used in this work was kaolinite. Petroleum-contaminated clay samples were prepared by mixing raw clay minerals and crude oil. Samples of polluted soil were prepared by dissolving a known amount of petroleum in hexane and then mixing this petroleum/hexane solution with soil. The spiked clay was aerated for 24 h to evaporate the hexane and, in this way;

the petroleum was homogeneously distributed on the clay surface. The resulting petroleum concentration in the soil was around 1000 mg/kg-soil. Kaolinite was provided by Manuel Riesgo Chemical Products (Madrid, Spain), and it is not reactive and has low hydraulic conductivity, low cation exchange capacity and no organic content, and for this reason, it is frequently used as a model of low-permeability soils. Properties of this synthetic clay soil were provided by the commercial supplier, and are detailed in [Table 1](#).

### 2.3. Analytical techniques

The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. The organic removal was monitored through the COD content during the treatment by single technologies (BDD-electrolysis, US and photolysis) and coupled electrochemical approaches (US/BDD-electrolysis and photo/BDD-electrolysis) using a HACH DR2000 analyzer. Zeta potential (z-potential) was also measured for the clarified liquid using a Zetasizer Nano ZS (Malvern, UK). Measurements of pH were carried out with an InoLab WTW pH-meter. The particle size was monitored during the treatment approaches with a Mastersizerhydro 2000SM (Malvern). The anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{ClO}^-$  and  $\text{ClO}_3^-$ ) present in the target wastewater were characterized using ion chromatography by means of a Shimadzu LC-20A system [\[18\]](#).

### 2.4. *Ex-situ* soil washing procedure

*Ex-situ* soil washing [\[5\]](#) with surfactant fluid solution was carried out in a stirred tank operated in batch mode. The tank volume was 1 dm<sup>3</sup>. Low-permeability soil (1000 g) polluted with 1000 mg petroleum per kg of soil and 0.8 dm<sup>3</sup> of solubilizing agent (containing deionized water, 500 mg/dm<sup>3</sup> of NaHCO<sub>3</sub>, and different concentrations of SDS surfactant ranging from 100 to 5000 mg/dm<sup>3</sup> were mixed in the reactor for 6 h at a stirring rate of 120 rpm). Thus, the same tank then acted as a settler (during 24 h) to separate the soil from the effluent. These effluents consisted of

complex aqueous mixtures of petroleum, surfactant and sodium hydrogen carbonate, with emulsified micro drops and soluble species. As it will be discussed below, only two kinds of effluents will be treated by BDD-electrolysis, US, photolysis, US/BDD-electrolysis and photo/BDD-electrolysis technologies and their characteristics are reported in Table 2.

## **2.5. Bulk treatment of the soil washing effluents by BDD-electrolysis, photolysis, US, US/BDD-electrolysis and photo/BDD-electrolysis**

Three different treatment approaches were employed as follows: BDD-electrolysis (application of electric current), photolysis (UV irradiation) and US (ultrasound irradiation). Ultrasound or photocatalysis processes combined with BDD-electrolysis are considered as emerging and interesting integrated technologies with clear advantages over conventional technology for removing organic pollutants from water [17,18,22-24]. Photolysis and photo/BDD-electrolysis were performed by using a UV lamp VL-215MC (Vilber Lourmat),  $\lambda = 254$  nm, intensity of  $930 \text{ W/cm}^2$  and energy 4.43–6.20 eV irradiating 15W directly to the quartz cover. [17]. US and US/BDD-electrolysis were carried out by employing an ultrasound generator UP200S (Hielscher Ultrasonics GmbH, Germany) equipped with a titanium glass horn of 40 mm diameter, length 100 mm, emitting 24 kHz and maximum ultrasonic power 200W [18]. Electrochemical oxidation experiments were carried out in a bench-scale plant with a single-compartment electrochemical flow cell. BDD and steel electrodes were used as anode and cathode, respectively [14]. Characteristic of BDD are as follows:  $\text{sp}^3/\text{sp}^2$  ratio: 225; boron content: 500 ppm; width of the diamond layer:  $2.68 \mu\text{m}$  [14,24]. For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor; the SASW effluent was stored in a thermo-regulated glass tank ( $1 \text{ dm}^3$ ) and circulated through the cell using a peristaltic pump at a flow rate of  $200 \text{ dm}^3/\text{h}$ . The electrical current was applied using a DC Power Supply (FA-376 PROMAX). Temperature was kept constant by means of a water bath. The applied current density used in this

work was chosen according the existing literature about the treatment of other pollutants [14,16,18,25].

The energy consumption per m<sup>3</sup> of treated effluent was estimated and expressed in kWh, using the average cell voltage registered during the electrolysis:

$$\text{Energy consumption} = [(V \times I \times t)/(1000 \times V_s)] \quad (1)$$

where  $t$  is the time of electrolysis (h);  $V$  and  $I$  are the average cell voltage (V) and the electrolysis current (A), respectively; and  $V_s$  is the sample volume (m<sup>3</sup>).

### 3. Results and Discussions

The soil washing process by using surfactant is an *ex-situ* process that improves the removal of contaminants sorbed to soil [5]. This process (usually known as SASW) transfers the pollution from the soil to a washing liquid, which becomes wastewater and consequently, it needs for further treatment in order to complete the depollution process [14,18-20]. For petroleum with a low solubility in water, the washing fluid dosed should contain surfactants, being SDS one of the most commonly used, because of the typically high efficiencies attained and its low hazardousness [5,14,26]. Then, samples of the polluted soil (0.2 Kg) were treated by SASW process using different SDS concentrations (ranging from 100 to 5000 mg dm<sup>-3</sup>). After that, contamination of effluent was determined (in terms of TOC) in order to establish the decontamination of soil by SASW process. Fig. 1 shows the organic matter removal from soil, as a function of SDS/soil ratio, after the washing treatment of the spiked soil studied. As observed, when higher amounts of SDS are used, higher organic matter removals are expected, but higher concentrations of SDS remaining in the soil [5,14,25,26]. This indicates that, the characteristics of wastewater strongly depend on the surfactant/soil ratio. However, only two kinds of the effluents were studied in this work, as shown in Table 2. In comparing the two effluents, it can be observed that the effluent 2 (with a higher concentration of surfactant in the washing fluid) has a much higher COD and TOC than effluent 1,

and similar behavior is observed for turbidity. Based on the results obtained, higher doses are more effective [5,14,18,25] because these favor a more complete depollution of soil, but the washing effluents generated must be treated. In this context, the efficacy of BDD-electrolysis, US, photolysis and coupled electrochemical approaches (US/BDD-electrolysis and photo/BDD-electrolysis) were evaluated by treating washing effluents with lower and higher TOC contents (when lower and higher SDS were used, see Table 2).

Fig. 2 shows COD decay, as a function of time, during the treatment of washing fluid via BDD-electrolysis, photolysis, US and combined approaches (US/BDD-electrolysis and photo/BDD-electrolysis) at different concentration of SDS (Figs. 2a and 2b) by applying 30 mA/cm<sup>2</sup>. As can be observed, partial degradation of the organic matter in the waste was attained with photolysis and US, obtaining about 30% and 23%, respectively, when lower SDS concentration was used to extract the petrochemical compounds from soil. Conversely, minor COD decays were obtained when 5000 mg/dm<sup>3</sup> of SDS were employed to extract petrochemical contaminants from soil. This findings indicate that the raw pollutants were not completely degraded but partially oxidized [18,20]. This leads to the formation of reaction intermediates due to the break-up of the molecules or even to the simple attack to any functional group by direct action of these irradiation techniques or by means of the oxidant agents generated [18-20]. Meanwhile, BDD-electrolysis favors a quasi-complete elimination of organic matter (97%) after 600 min of treatment under similar experimental conditions when lower or higher concentrations of surfactant were used during SASW process [16-18].

On the other hand, the combination of BDD-electrolysis with US or photolysis is expected to show other advantages as compared to the single processes [27,28]. In fact, complete COD removals (100%) were achieved after 350 min, at US/BDD-electrolysis and photo/BDD-electrolysis when lower concentration of SDS (100 mg/dm<sup>3</sup>) was used by applying 30 mA/cm<sup>2</sup>. Conversely, when 5000 mg/dm<sup>3</sup> of SDS were employed to extract petrochemical contaminants from soil, the treatment times increased, even when complete elimination is achieved. However, in general, this



behavior indicates that, organic pollutants are efficiently removed from washing fluid, and their by-products formed during the application of these oxidative processes [14,19,20].

As well-known, the COD is an important feature that can be taken into account, but this parameter is not indicative of the mineralization of the pollutants. Therefore, the TOC efficiency must be monitored before the discharge of the effluent into water bodies to achieve the legal limits according to environmental laws.

Fig. 3 shows the TOC decay of soil washing during treatment by BDD-electrolysis, photolysis, US, US/BDD-electrolysis and photo/BDD-electrolysis at different concentration of SDS (Figs. 3a and 3b). Results clearly showed that, US and photolysis achieved lower TOC removal efficiencies at both SDS concentration conditions (Figs. 3a and 3b). Even when, at 5000 mg/dm<sup>3</sup> (Fig. 3b), the photolysis approach showed inefficient performances to depollute the washing effluent. Conversely, total mineralization of the waste is obtained when BDD-electrolysis and coupled technologies were used, regardless of the initial composition of the effluent. Nevertheless, the differences between these technologies are greater in terms of the mineralization rate, in the case of the washing-fluid obtained with a lower SDS/soil ratio (Fig. 3a) than those achieved at higher SDS concentrations (Fig. 3b). This behavior may be due to the size of particles, micelles formed and the synergic effect obtained by the combination of both advanced oxidation processes, such as electrolysis plus US or photocatalysis [22,23]. In the last case, BDD-electrolysis can be electrochemically produced many oxidants from the ions present in the effluent, such as hydroxyl radicals, chlorine, persulfate, peroxocarbonate and peroxophosphate. Some of these species are strong oxidants but they can be activated and transformed into more aggressive species. Activation of oxidants, that is, the formation of highly reactive species from poorly reactive oxidants can be attained by combination of oxidants or by UV light or ultrasounds irradiation [23]. Therefore, the combination of technologies promotes the formation of strong radicals during the treatment, increasing its mineralization efficacy. Additionally, it is important to indicate that, TOC removal

rate of organic matter is influenced by the mass transport effects (Fig. 3a and 3b) because the organic load in solution is very different at both effluents.

Another feature is that, the size of micelles is completely different [14], and this is a very interesting point, scarcely studied in the literature. Because of that, this paper does not only focus on the oxidation of a single washing fluid but it takes into account different colloids dispersions which can be obtained when petroleum and SDS are combined (Figs. 4a and 4b). In comparing the two effluents, it can be observed that the effluent 1 (with a lower concentration of surfactant in the washing fluid) has a lower COD and TOC, but the size of particles is higher and the superficial charge is more positive. In fact, when lower SDS concentrations were used, higher micelles can be performed (Fig. 4a). On the contrary, the micelles have a minor mean size when higher SDS concentrations were used (Fig. 4b). This behavior is related to the superficial area that influence the number of SDS molecules forming the micelles. As it can be observed Figs. 4a and 4b, size particle decreases during the treatment with US and photolysis, but no complete depletion of particles is achieved, regardless of the wastewater used. During BDD-electrolysis of effluent 1, the decrease of particle sizes shows an apparent exponential behavior with slopes of (204-89)/60 min; but the complete depletion of particles is achieved at 600 min. Conversely, the combination of BDD-electrolysis with US and photocatalysis results in a complete depletion of particles during treatment effluent 1 and 2 (Fig. 4), but in the case of photo/BDD-electrolysis, it occurs in short times of treatment (360 min). This performance indicates that the petroleum/surfactant micelles are drastically attacked during the first stages to form smaller particles with more negative surface charge. In this point, it is important to take in mind that it is used an anionic surfactant and thus, the expected superficial charge of micelles is negative. After this initial rapid reduction in size of the micro-drops, size continues decreasing till the end of the test, although at a lower rate.

Comparing the kinetic constants estimated for the raw COD (parameter that represents only the complete degradation of organic matter) and TOC (it provides information on the mineralization process), significant differences can be observed (Fig. 5). In terms of petroleum and SDS

elimination (degradation and mineralization), these figures indicate a very strong effect of process type. Synergistic effects, for degradation of organic matter and mineralization, are clearly observed during the treatment of soil-washing fluids using US/BDD-electrolysis and photo/BDD-electrolysis (Fig. 5) [23]. In the case of US/BDD-electrolysis, the phenomena of ultrasound and cavitation (the secondary effect of ultrasound) [29] as well as the activation of oxidants [23] in solution are the responsible on the intensification effect on the single BDD-electrolysis for removing organic matter. In the case of ultrasound phenomenon, the radicals generated from transient cavitation ( $\bullet\text{H}$ ,  $\bullet\text{O}$ ,  $\text{HO}_2\bullet$  and  $\bullet\text{OH}$ ) induce degradation reactions, while ultrasound waves favor the production of oxidants (equation 3) [18,29]:



and the activation of several oxidants previously produced by BDD-electrolysis (equations 4 to 7) [18,23]:



However, photo/BDD-electrolysis demonstrated to be the most efficient technology. In this case, it was found that in addition to the well-known UV light based processes; combination with electrochemical technology allows the formation of powerful radicals during the treatment [18,22] as indicated in equations 8 to 11.



Comparing depollution procedures of the two wastes, the treatment of the effluent polluted with high concentrations of SDS is more efficient, in terms of oxidation and mineralization, than the

effluent polluted with low concentrations of petroleum and SDS. Then, in consideration of the fact that, the effect on the depollution intensification is very significant when US or UV light are coupled with BDD/electrolysis [18], it is certainly due to the activation of oxidants produced during the treatment [22,23,29,30].

At this point, it is worth taking into account that, the main difference between the wastes is the concentration of SDS. Then, the oxidation of SDS can lead to the formation of sulfates, which are precursors in the production of persulfates during the electrochemical treatments (equation 12), as previously suggested [14]:



Micelles obtained during the soil washing approach with SDS solution consist of microdrops of petroleum surrounded by SDS molecules with negative sulphonic group facing the water [31]. It explains that surface charge of micelles is negative (Figs. 6a and 6b). The higher the concentration of SDS molecules in the micelles the more negative is the resulting charge (Fig. 6b) [14]. Then, in consideration of the fact that, the changes in the surface charge of micelles can give information about the mechanisms of oxidation (attack to the micelles), z-potential was monitored during the treatments. These changes are shown in Fig. 6 during the tests where the effluent 1 (less concentration of petroleum and SDS) exhibited a superficial charge of  $-29$  mV, while the value of the effluent 2 (high concentration of petroleum and SDS) was about  $-69$  mV. Then, the decrease in the z-potential towards more negative values observed during the treatment of the effluent 1 suggests that the decrease in size of the micelles is followed by a reorientation of the SDS (SDS micelles formed in solution can be randomly oriented and partially disordered, when  $\bullet\text{OH}$  radicals are produced by BDD-electrolysis (equation 13), these strong oxidants promote the fragmentation of SDS structure; resulting in an increased aggregation packing density of SDS and its subsequent restructuring via the orientation of SDS molecules oriented from the microdrops of petroleum with the polar head groups extended into the aqueous environment (compacted micelles) due to the decreased electrostatic repulsions [31]), making the new smaller particles, more negative.



A change in the opposite direction is attained during the treatment of the washing fluid produced with a higher SDS/soil ratio and the treatment leads to the particles less negative than those contained in the raw washing fluid. The type of change depends only on the waste treated. Likewise, the z-potential of the particles obtained at the final of treatment remains in the same range for both SASW process, in all cases, with values between  $-40$  and  $-50$  mV. Another feature is that, less negative z-potential value is attained by the electrolytic treatment, which may indicate a more efficient depletion of the SDS from the micelles [14].

Fig. 7 shows the changes in the turbidity during the application of treatment technologies to the two soil-washing fluids polluted with petroleum with different concentrations of surfactant SDS by applying  $30 \text{ mA/cm}^2$  (Fig. 7a and Fig. 7b). As can be observed, the initial point of the effluent 2, higher concentration of petroleum and SDS is used, then, significant values of turbidity are achieved; indicating that concentration of micelles is also high. Concerning to the application of photolysis and US, the concentration of colloids is little affected. However, when US/BDD-electrolysis and photo/BDD-electrolysis are applied, the concentration of colloids is completely depleted, being the process significantly efficient for higher initial concentrations of turbidity. Moreover, it should be noted that the removal rates during US/BDD-electrolysis and photo/BDD-electrolysis technologies were different, indicating that the oxidation mechanisms involved, when photolysis and US are coupled, may differ.

From results reported in Fig. 3, it can be noted that, a complete removal of the organic matter is achieved by using US/BDD-electrolysis and photo/BDD-electrolysis in different concentration of SDS. This behavior suggests that the sulfonic group in SDS structure [5,31], after disruption of the micelle, is dissolved in the supporting electrolyte as sulfate. To confirm it, sulfate accumulation in washing effluent was determined when all technologies were used (Fig. 8). Evaluating single technology notes that a significant concentration of sulfate is released in solution when BDD-electrolysis is used in comparison with photolysis and US. Conversely, US/BDD-

electrolysis and photo/BDD-electrolysis promote a more significant sulfate release in the washing effluent. Both technologies favor synergistic effects to improve the mass transfer to favor the formation of radicals in the bulk solution from oxidants produced electrochemically at BDD surface [22,23]. These results confirm that UV light irradiated during photo/BDD-electrolysis clearly enhanced the oxidation rate. It is comparing integrated technology is observed that photo/BDD-electrolysis is more efficient thanks the formation of persulfates. Higher SDS concentrations in the waste may lead to higher concentrations of  $S_2O_8^{2-}$  from  $SO_4^{2-}$  ions (equation 12) on BDD surface, after SDS breaking structure. Activation by light irradiation promotes the formation of highly active species by light decomposition of peroxy compounds [23,32]. These contribute to complete the degradation of remaining petroleum as well as part of the organic surfactant. Hydroxyl radicals formed from water discharge on BDD surface (equation 13) are also considered the responsible species for the electrochemical combustion of organic pollutants in the emulsion, as can observed previous studies [27,28,30,32-36].

Regarding the other oxidants that can be electrochemically generated by advanced oxidation technologies during washing effluent treatment; the concentrations of active chlorine species were monitored. Fig. 9 shows maximum concentrations of  $Cl^-$ ,  $ClO^-$  and  $ClO_3^-$  measured during the treatment. As can be observed, the occurrence of chlorates and perchlorates was scarcely found and they do not behave as final products but as intermediates. These oxidants can also contribute to the mineralization of organic pollutants contained in the effluents [12,14,36]; however, their concentrations are relatively minor to the sulfate concentration produced that can promote the production of persulfate.

In order to evaluate the efficiency of depollution systems, we compare the results obtained by estimating the energy consumptions as a function of percentage of COD removal. Fig. 10 shows the energy consumption required for each one of the treatments with different concentrations of SDS surfactant by applying  $30 \text{ mA cm}^{-2}$ . As can be observed, higher energy consumptions were spent by photolysis and US processes with lower efficacy to remove organic pollutants from

washing liquid. Conversely, higher elimination of organic matter was achieved (more than 90% of COD removals) by using BDD-electrolysis and the coupled methods (US/BDD-electrolysis and photo/BDD-electrolysis) with modest energy requirements. However, it is important to indicate that, in the case of US/BDD-electrolysis, if higher COD removals are required, the electrical consumption increases significantly. Meanwhile, BDD-electrolysis and photo/BDD-electrolysis showed similar energy consumptions, but the intensification of the depollution was considerably improved at photo/BDD-electrolysis, showing the feasibility of this process as a green alternative to treat wastewaters.

#### 4. Conclusions

- The combination of soil washing fluid containing surfactant was considered an efficient technology from the removal of petroleum pollutants from soils. Dosages of 5.0 g/Kg of soil favor 92% of depletion of the petroleum. Characteristic of effluents obtained by SASW process depends strongly on the dose of surfactant used.
- The intensification of the efficiency was attained by synergic degradation effects when photo/BDD-electrolysis was used because the irradiation influences significantly the oxidants electrochemically produced (persulfate) by light activation approach, producing more oxidant species (radicals).
- TOC and COD decays during the application of US/BDD-electrolysis and photo/BDD-electrolysis treatments indicate that the micelles are attacked, and subsequently, the surfactant and petroleum are released and are rapidly mineralized by strong oxidants species in the effluent ( $\bullet\text{OH}$ ,  $\text{SO}_4\text{-}\bullet$ ,  $\text{S}_2\text{O}_8^{2-}$ ).
- The intensification of photolysis approach is efficiently attained when it is combined with BDD-electrolysis, and it consumes lower electrical energy.

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## References

- [1] G. Li, S. Guo, J. Hu, The influence of clay minerals and surfactants on hydrocarbon removal during the washing of petroleum-contaminated soil. *Chem. Eng. J.* 286 (2016) 191–197.
- [2] R. Lopez-Vizcaino, C. Saez, P. Canizares, M.A. Rodrigo, The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment. *Sep. Purif. Technol.* 88 (2012) 46–51
- [3] R. Lopez-Vizcaino, J. Alonso, P. Canizares, M.J. Leon, V. Navarro, M.A. Rodrigo, C. Saez, Removal of phenanthrene from synthetic kaolin soils by electrokinetic soil flushing. *Sep. Purif. Technol.* 132 (2014) 33–40.
- [4] K. S. L. de Figueredo, C. A. Martínez-Huitle, A. B. R. Teixeira, A. L. S. de Pinho, C. A. Vivacqua, Djalma R. da Silva, Study of produced water using hydrochemistry and multivariate statistics in different production zones of mature fields in the Potiguar Basin – Brazil, *J. Pet. Sci. Eng.* 116 (2014) 109–114.
- [5] C. Trelu, E. Mousseta, Y. Pechaud, D. Huguenot, E. D. van Hullebusch, G. Esposito, M. A. Oturan, Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review, *J. Hazard. Mater* 306 (2016) 149–174.



- [6] E. V. dos Santos, S. F. M. Sena, D. R. da Silva, S. Ferro, A. De Battisti, C. A. Martínez-Huitle, Scale-up of electrochemical oxidation system for treatment of produced water generated by Brazilian petrochemical industry, *Environ. Sci. Pollut. Res* (2014) 21:8466–8475.
- [7] A. F. Almansoor, H. A. Hasan, M. Idris, S. R. S. Abdullah, N. Anuar, Potential application of a biosurfactant in phytoremediation technology for treatment of gasoline-contaminated soil. *Ecol. eng.* 84 (2015) 113–120.
- [8] F.-R. Ahmaduna, A. Pendashteh, L. Chuah Abdullah, D. R. Awang Biak, S. Siavash Madaeni, Z. Zainal Abidin, Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.*, 170 (2009) 530–551.
- [9] E. Mousset, N. Oturan, E. D. vanHullebusch, G. Guibaud, G. Esposito, M. A. Oturan, Treatment of synthetic soil washing solutions containing phenanthrene and cyclodextrin by electro-oxidation. Influence of anode materials on toxicity removal and biodegradability enhancement. *Appl. Catal., B* 160–161 (2014) 666–675.
- [10] B.H. Diya'uddeen, W.M.A.W. Daud, A.R. Abdul Aziz, Treatment technologies for petroleum refinery effluents: A review, *Process Saf. Environ. Protect.*, 89 (2011) 95–105.
- [11] D. Huguenot, E. Mousset, E. D. van Hullebusch, M. A. Oturan, Combination of surfactant enhanced soil washing and electro-Fenton process for the treatment of soils contaminated by petroleum hydrocarbons. *J. Environ. Manage.* 153 (2015) 40-47.
- [12] P. R. F. da Costa, D. R. da Silva, C. A. Martínez-Huitle, S. Garcia-Segura, Fuel station effluent treatment by electrochemical technology. *J. Electroanal. Chem.* 763 (2016) 97–103.
- [13] M.R.G. Santos, M.O.F. Goulart, J. Tonholo, C.L.P.S. Zanta, The application of electrochemical technology to the remediation of oily wastewater. *Chemosphere* 64 (2006) 393–399.
- [14] E.V. dos Santos, C. Saez, C.A. Martinez-Huitle, P. Canizares, M.A. Rodrigo, The role of particle size on the conductive diamond electrochemical oxidation of soil-washing effluent polluted with atrazine, *Electrochemistry Communications*, 55 (2015) 26-29.

- [15] R. López-Vizcaíno, C. Sáez, P. Cañizares, M.A. Rodrigo, The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment, *Sep. Purif. Technol.* 88 (2012) 46–51.
- [16] F.L. Souza, C. Saez, M.R.V. Lanza, P. Canizares, M.A. Rodrigo, Removal of herbicide 2,4-D using conductive-diamond sono-electrochemical oxidation, *Sep. Purif. Technol.*, 149 (2015) 24-30.
- [17] M.J. Martín de Vidales, C. Saez, J.F. Perez, S. Cotillas, J. Llanos, P. Canizares, M.A. Rodrigo, Irradiation-assisted electrochemical processes for the removal of persistent organic pollutants from wastewater, *J. Appl. Electrochem.*, 45 (2015) 799-808.
- [18] F.L. Souza, C. Saez, P. Canizares, A.J. Motheo, M.A. Rodrigo, Coupling photo and sono technologies to improve efficiencies in conductive diamond electrochemical oxidation, *Environmental. Appl. Catal., B*, 144 (2014) 121-128.
- [19] C.C. Lai, Y.C. Huang, Y.H. Wei, J.S. Chang, Biosurfactant-enhanced removal of total petroleum hydrocarbons from contaminated soil, *J. Hazard. Mater.* 167(2009) 609–614.
- [20] J.M. Rosas, F. Vicente, A. Santos, A. Romero, Soil remediation using soil washing followed by Fenton oxidation. *Chem. Eng. J.* 220 (2013) 125-132.
- [21] U. C. Brinch, F. Ekelund, C. S. Jacobsen, Method for spiking soil samples with organic compounds, *Appl. Environ. Microbiol.* 68 (2002) 1808–1816.
- [22] C. A. Martínez-Huitle, M. A. Rodrigo, I. Sires, O. Scialdone, Single and Coupled Electrochemical Processes and Reactors for the Abatement of Organic Water Pollutants: A Critical Review. *Chem. Rev.* 115 (2015) 13362–13407.
- [23] I. Sirés, E. Brillas, M. A. Oturan M. A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review. *Environ. Sci. Pollut. Res.* 21 (2014) 8336–8367.
- [24] S. Garcia-Segura, E. Vieira Dos Santos, C.A. Martínez-Huitle, Role of  $sp^3/sp^2$  ratio on the electrocatalytic properties of boron-doped diamond electrodes: A mini review, *Electrochem. Commun.*, 59 (2015) 52–55.

- [25] E. V. dos Santos, C. Sáez, C. A. Martínez-Huitle, P. Cañizares, M. A. Rodrigo, Removal of oxyfluorfen from ex-situ soil washing fluids using electrolysis with diamond anodes, *J. Environ. Manage.*, 171 (2016) 260–266.
- [26] O. Atteia, E.D.C. Estrada, H. Bertin, Soil flushing: a review of the origin of efficiency variability, *Rev. Environ. Sci. Biotechnol.* 12 (2013) 379–389.
- [27] X. Wang, J. Jia, Y. Wang, Enhanced photocatalytic–electrolytic degradation of Reactive Brilliant Red X-3B in the presence of water jet cavitation. *Ultrason. Sonochem.* 23 (2015) 93–99.
- [28] H. Park, C. D. Vecitis, M. R. Hoffmann, Solar-Powered Electrochemical Oxidation of Organic Compounds Coupled with the Cathodic Production of Molecular Hydrogen. *J. Phys. Chem. A* 112 (2008) 7616–7626.
- [29] S. Chakma, V. S. Moholkar, Mechanistic analysis of sono-photolysis degradation of carmoisine, *J. Ind. Eng. Chem.* 33 (2016) 276–287.
- [30] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, *Appl. Catal. B*, 166-167 (2015) 603-643.
- [31] Handbook of Carbon Nano Materials, World Scientific Series on Carbon Nanoscience: Vol. 7 & 8, Edited by Francis D'Souza and Karl M Kadish (2015) USA.
- [32] D. Medeiros de Araújo, S. Cotillas, C. Sáez, P. Cañizares, C. A. Martínez-Huitle, M. A. Rodrigo, Activation by light irradiation of oxidants electrochemically generated during Rhodamine B elimination, *J. Electroanal. Chem.*, 757 (2015) 144-149.
- [33] C. Ramírez, A. Saldana, B. Hernández, R. Acero, R. Guerra, S. Garcia-Segura, E. Brillas, J. M. Peralta-Hernández, Electrochemical Oxidation of Methyl Orange Azo Dye at Pilot Flow Plant using BDD Technology. *J. Ind. Eng. Chem.* 19 (2013) 571–579.
- [34] S. Fierro, E. Passas-Lagos, E. Chatzisyneon, D. Mantzavinos, Ch. Comninellis, Pseudo-Potentiostatic Electrolysis by Potential Buffering Induced by the Oxygen Evolution Reaction. *Electrochem. Commun.* 11 (2009) 1358–1361.

[35] H. Huang, Y. Zhan, G. Liu, X. Wang, H. Lu, L. Xiao, Q. Feng, D. Y.C. Le, Efficient degradation of gaseous benzene by VUV photolysis combined with ozone assisted catalytic oxidation: Performance and mechanism. *Appl. Catal., B*, 186 (2016) 62–68.

[36] D. Medeiros de Araújo, C. Sáez, C. A. Martínez-Huitle, P. Cañizares, M. A. Rodrigo, Influence of mediated processes on the removal of Rhodamine with conductive-diamond electrochemical oxidation, *Appl. Catal. B*, 166–167 (2015) 454-459.

## Tables

**Table 1.** Properties of kaolinite: a low permeable model soil.

<i>Mineralogy</i>		<i>Particle size distribution</i>	
Kaolonite	100%	Gravel	0%
Fe <sub>2</sub> O <sub>3</sub>	0.58%	Sand	4%
TiO <sub>2</sub>	0.27%	Silt	18%
CaO	0.10%	Clay	78%
K <sub>2</sub> O	0.75%	Specific gravity	2.6%
SiO <sub>2</sub>	52.35%	Hydraulic conductivity	1×10 <sup>-8</sup> (cm/s)
Al <sub>2</sub> O <sub>3</sub>	34.50%	Organic content (%)	0%
Others	11.42%	pH	4.9

**Table 2.** Characteristic of the effluents produced by soil washing method.

	<i>Effluent 1</i>	<i>Effluent 2</i>
Surfactant/soil ratio (mg of SDS per kg of soil)	0.08	4.00
COD (mg/dm <sup>3</sup> )	487	2943
TOC (mg/dm <sup>3</sup> )	359	1298
Mean particle size (µm)	237	59
z-potential (mV)	-29	-68
Turbidity (NTU)	398	958

**Figure 1.** Elimination of organic matter load as a function of surfactant/soil ratio.

**Figure 2.** Relative COD of soil washing during treatment via (▲) BDD-electrolysis, (◇) photolysis, (○) US, (◆) US/BDD-electrolysis and (■) photo/BDD-electrolysis at different concentration of SDS (a) 100 and (b) 5000 mg/dm<sup>3</sup> by applying 30 mA/cm<sup>2</sup> at 25°C.

**Figure 3.** TOC decay of the soil washing during treatment via (▲) BDD-electrolysis, (◇) photolysis, (○) US, (◆) US/BDD-electrolysis and (■) photo/BDD-electrolysis at different concentration of SDS (a) 100 and (b) 5000 mg/dm<sup>3</sup> by applying 30 mA/cm<sup>2</sup> at 25°C.

**Figure 4.** Mean size particle of soil washing: (▲) BDD-electrolysis, (◇) photolysis, (○) US, (◆) US/BDD-electrolysis and (■) photo/BDD-electrolysis at different concentration of SDS (a) 100 and (b) 5000 mg/dm<sup>3</sup>.

**Figure 5.** Kinetic constants (k) in the oxidation and mineralization of effluents produced by soil washing by BDD-electrolysis, photolysis, US, US/BDD-electrolysis and photo/BDD-electrolysis. COD (empty symbols) and TOC (full symbols). At different concentration of SDS (▲,●) 100 and (Δ,○) 5000 mg/dm<sup>3</sup>. Conditions: 30 mA/cm<sup>2</sup> and 25°C.

**Figure 6.** Changes in the z-potential during (▲) BDD-electrolysis, (◇) photolysis, (○) US, (◆) US/BDD-electrolysis and (■) photo/BDD-electrolysis at different concentration of SDS (a) 100 and (b) 5000 mg/dm<sup>3</sup> by applying 30 mA/cm<sup>2</sup> at 25°C.

**Figure 7.** Turbidity profiles during the (▲) BDD-electrolysis, (◇) photolysis, (○) US, (◆) US/BDD-electrolysis and (■) photo/BDD-electrolysis at different concentration of SDS (a) 100 and (b) 5000 mg/dm<sup>3</sup> by applying 30 mA/cm<sup>2</sup> at 25°C.

**Figure 8.** Maximum sulfate concentration during treatment applied (■) 100 and (●) 5000 mg/dm<sup>3</sup> of SDS. Conditions: 30 mA/cm<sup>2</sup> and 25°C.

**Figure 9.** Evolution of ionic chlorinated species ( $=[\text{Cl}^-] + [\text{ClO}^-] + [\text{ClO}_3^-]$ ) during treatment via BDD-electrolysis, photolysis, US, US/BDD-electrolysis and photo/BDD-electrolysis at different concentration of SDS 100 (empty symbols) and 5000 (full symbols) mg/dm<sup>3</sup>. Conditions: 30 mA/cm<sup>2</sup> and 25°C.

**Figure 10.** Energy consumption requirements, as a function of COD removal, during the treatment of the soil washing via (▲) BDD-electrolysis, (◇) photolysis, (○) US, (◆) US/BDD-electrolysis and (■) photo/BDD-electrolysis at different concentration of SDS (a) 100 and (b) 5000 mg/dm<sup>3</sup> by applying 30 mA/cm<sup>2</sup> at 25°C.



## Figures

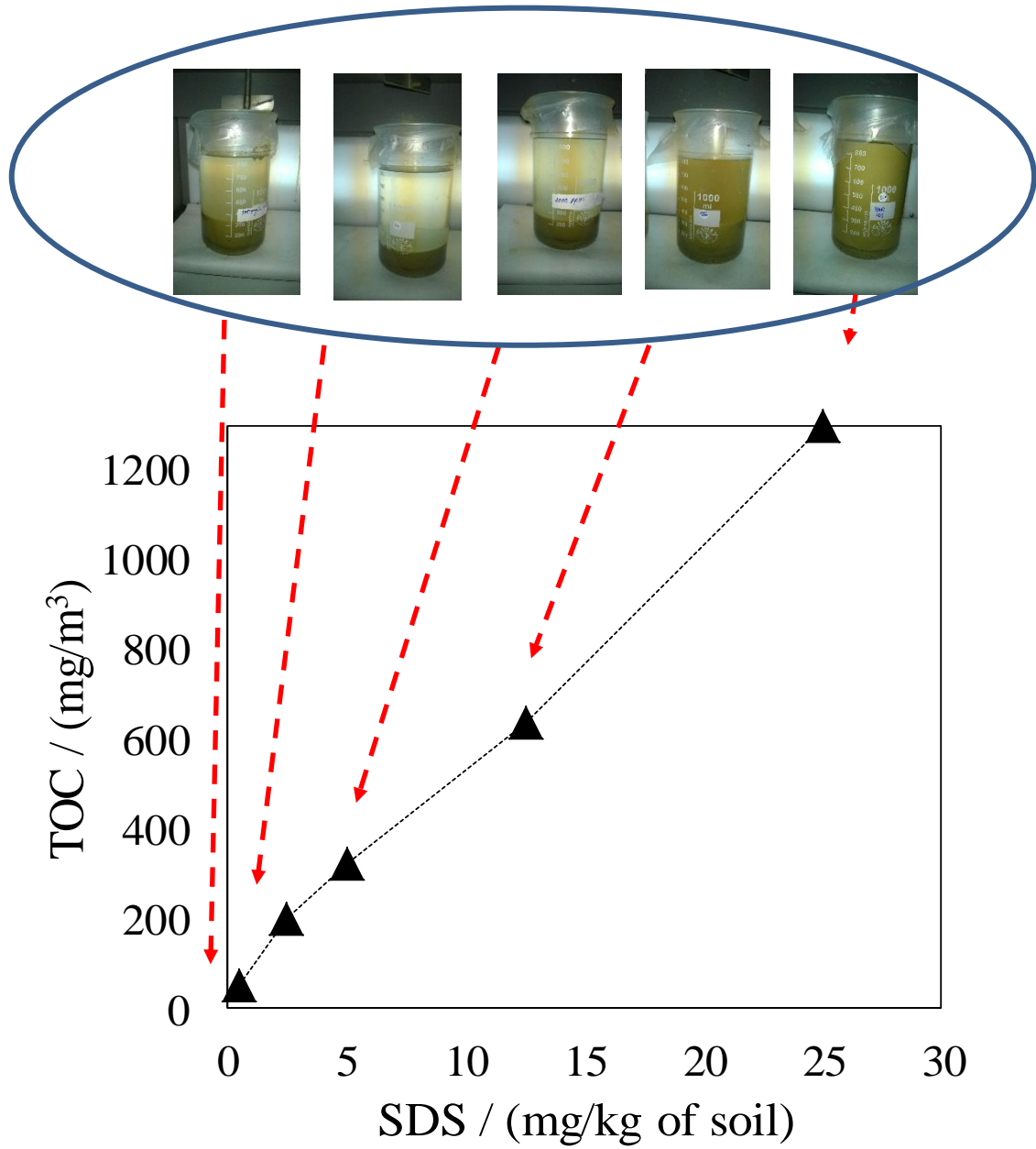


Figure 1

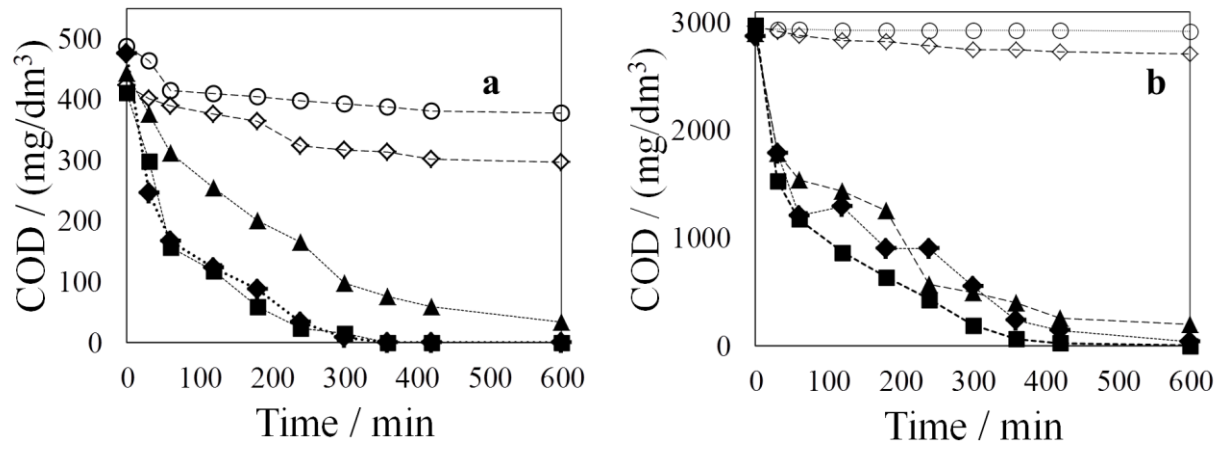


Figure 2.

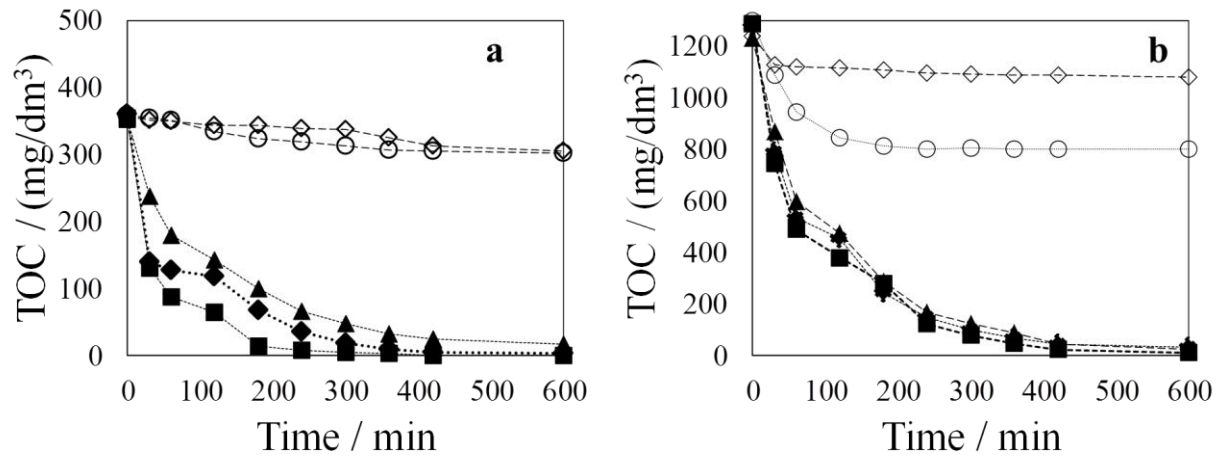


Figure 3.

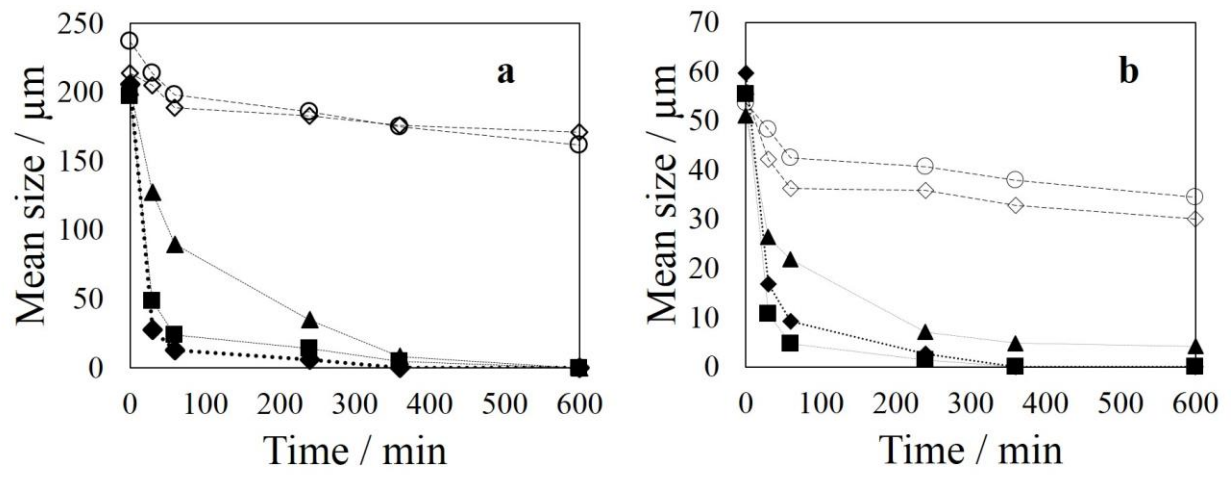
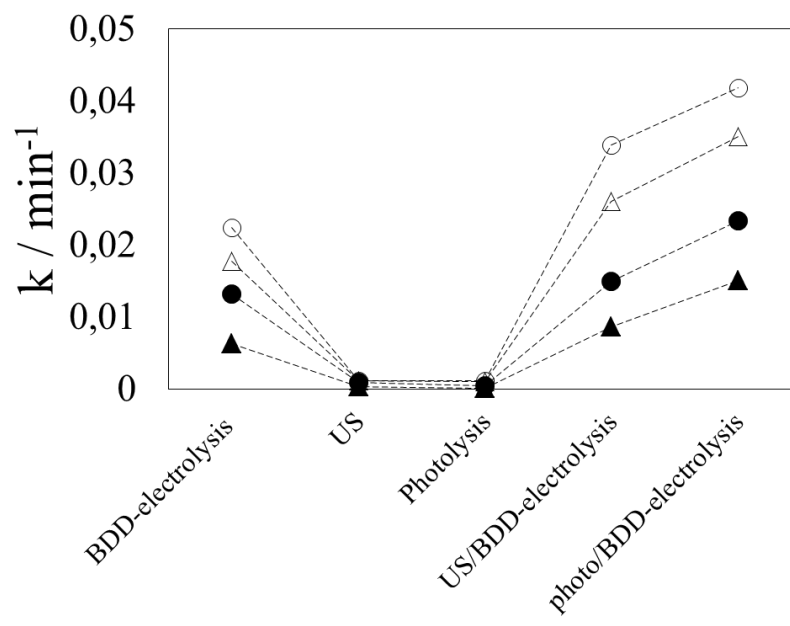


Figure 4.



**Figure 5.**

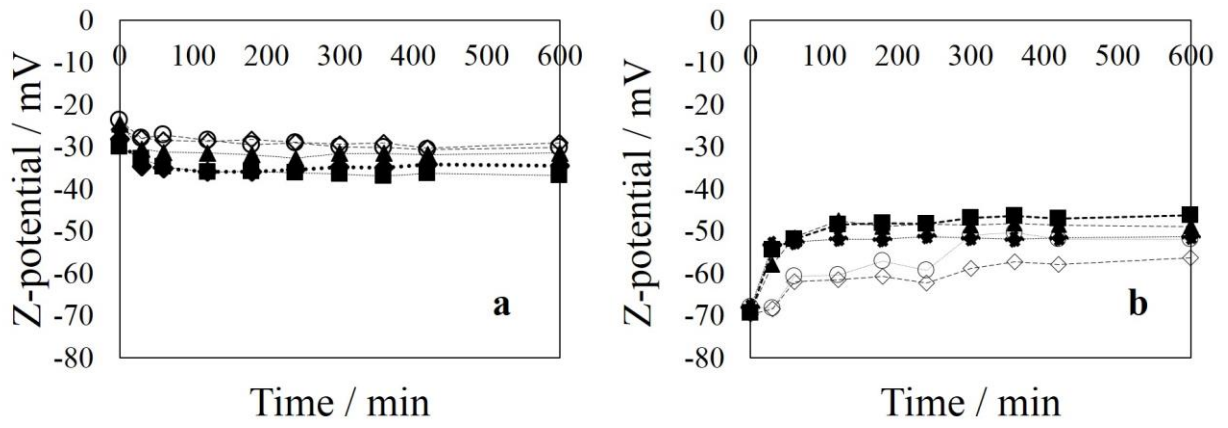


Figure 6.

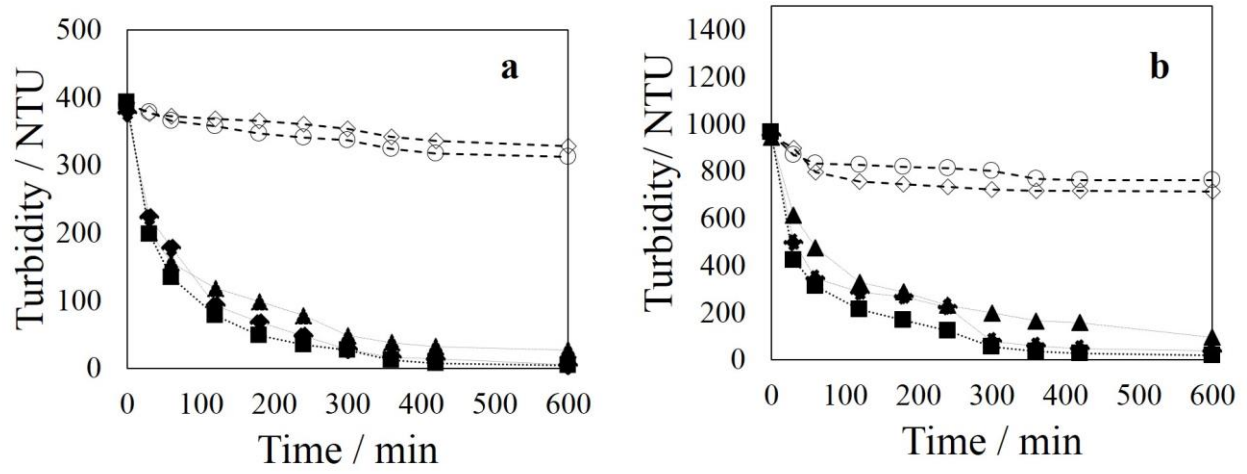
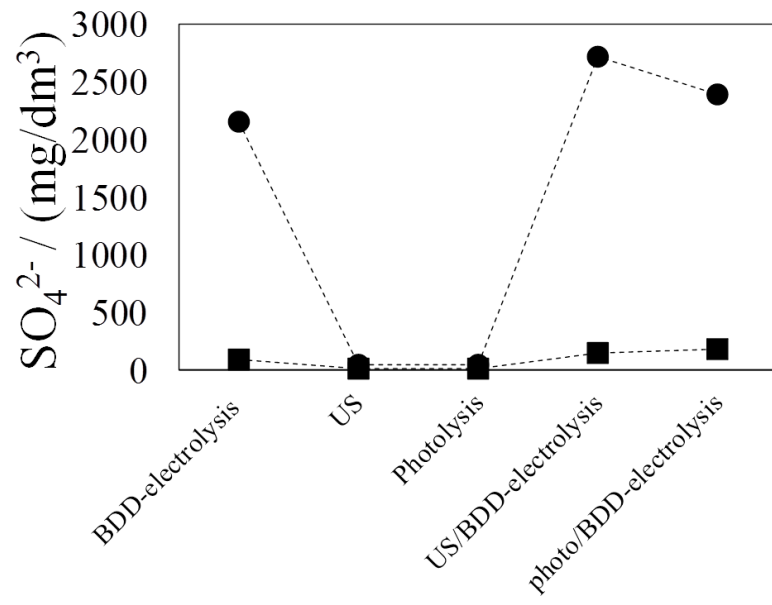
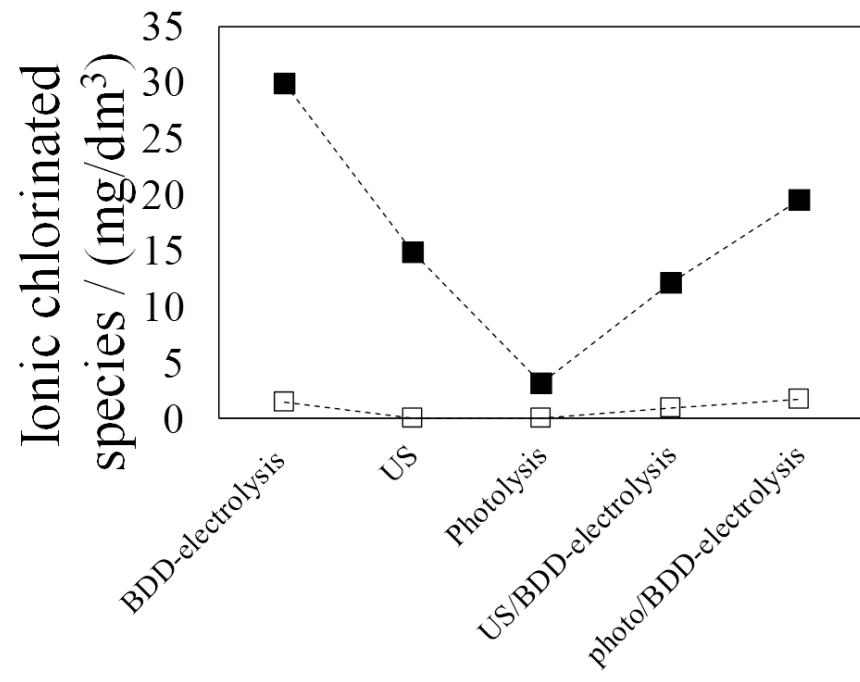


Figure 7.



**Figure 8.**





**Figure 9.**

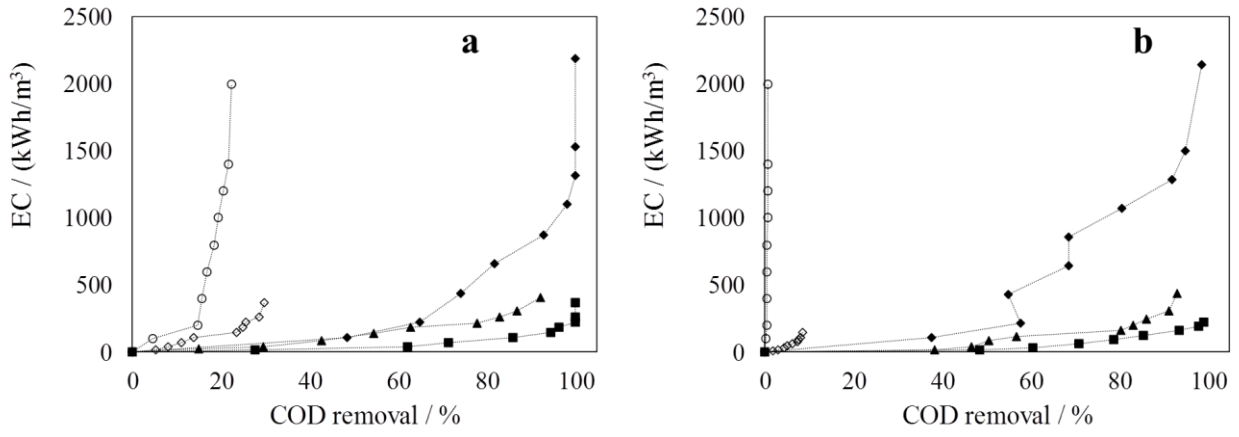


Figure 10.