

Irradiated-assisted electrochemical processes for the removal of persistent pollutants from real wastewater

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Abstract

In this work, it is studied the treatment of real wastewater (intensified with two target compounds) using electro-irradiated technologies. Two types of effluents coming from an organic-synthesis pharmaceutical industry and the outlet of a municipal wastewater treatment plant were intensified with metoprolol (β -blocker) and caffeine (stimulant), respectively. Conductive diamond electrochemical oxidation (CDEO), photolysis, sonolysis and all possible combinations among these technologies were evaluated for the treatment of both wastes. Results demonstrate that complete oxidation of the target compounds, as well as mineralization of the organic compounds contained in the matrixes, can be attained by all electro-irradiated technologies and no salt addition was needed to obtain an efficient treatment. Single irradiated technologies were inefficient in the oxidation but their combination with CDEO improves significantly the efficiency of the process showing clear synergistic effects. However, due to the large energy requirement of ultrasound irradiation, this combination is only cost-effective in the case of ultraviolet irradiation.

Key Words: Electrochemical oxidation, real wastewater, sonoelectrolysis, photoelectrolysis, caffeine, metoprolol.

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1. Introduction

A broad spectrum of chemicals are required for the manufacturing of each pharmaceutical specialty, including solvents, catalyst, raw materials, intermediates and side manufacture materials. Most of them are not natural but anthropogenic products. This fact implies that wastewater generated in these industries contains a wide range of substances that, very often, exhibit a recalcitrant nature and cannot be easily removed by the conventional treatments applied (they are defined as persistent organic pollutants, POPs), first in industrial facilities and later in municipal wastewater treatment plants (WWTP) [1]. As a consequence, their occurrence in environment is a factor of increasing concern nowadays [2-4], in particular because of the acute consequences that may be associated to public health [1, 5-7]. Because of this occurrence in environment, new treatment approaches are needed, and application of advanced oxidation processes (AOPs) is considered by many researchers as a promising alternative [8-11].

An efficient strategy to avoid the occurrence of these anthropogenic species in environment needs for two different stages: the treatment of the industrial wastes, for which these chemicals are strongly concentrated (and hence their removal is very efficient) [12, 13] and the later treatment of the effluents of municipal wastewater treatment plants, in which they are diluted with domestic wastes and mixed with many other types of pollutants [14, 15]. Both represent two different boundary chemical matrixes, with a noteworthy difference in terms of treatability.

Among the various AOPS, conductive diamond electrochemical oxidation (CDEO) has demonstrated very important prospects, because of its high efficiency and robustness [16-18]. However, the main drawback of this technology is the tight control of the transfer of the organic mass to the anodic surface, especially in the treatment of diluted wastes. To improve the process efficiency, recently two modifications have been proposed:

- ultrasound (US) can be irradiated to the system entailing an increase in the turbulence (due to implosion of microbubbles) and, consequently, minimizing mass transfer limitations [19-21], or
- ultraviolet (UV) light radiation can be coupled with electrochemical process in order to increase the generation and/or activation of oxidizing agents in the bulk [22-26].

Up to now, degradation studies of POPs by CDEO in water and wastewater have been typically conducted in synthetic medium with POP concentration ranging from $\mu\text{g dm}^{-3}$ to mg dm^{-3} . Although the experiments tried to reproduce real conditions, they only can be understood as a previous stage of the research [27] and its validation with real wastewater is necessary. The ionic conductivity of real wastewater can vary depending on the typology of the effluent, and thus on the inorganic salts contained. However, in order to apply electrochemical technology efficiently it should be enough to guarantee an efficient treatment without the addition of salts as supporting electrolyte. Although the accumulation of salts can be seen as a not acute problem, it is not a minor problem because of its persistence and hence, salt additions should be avoided, even despite their positive effect on the performance of electrochemical processes. Likewise, there are other two important factors which should be accounted in the treatment of real wastewater [28-32]:

- the oxidation of inorganic salts present in the medium during the treatment can significantly affect the efficiency of the process because of the “oxidation cocktail generated” and it may lead to different behaviours with the different organics contained in the treated waste.
- the presence of different types of chemicals may lead to competition in the oxidation processes.

Hence, it is clear that many efforts have to be done during the next years in the scale-up of wastewater electrolytic treatment processes, not only to determine if the technology could be applied at the full scale but also to state the feasibility of this technology to remove refractory pollutants in very complex real wastewater. In this way, a new approach in the study of the degradation of POPs in real wastewater consists of adding or spiking a given concentration of pollutant in a real medium [33-39] in order to make easier the monitoring of POP degradation during the treatment and to be able to corroborate the feasibility of electrochemical oxidation to deplete POP independently of the aqueous matrix.

With this background, the goal of this work is to study the removal of persistent pollutants from real wastewater, in order to carry out a key step in the scale-up of CDEO. To do this, two effluents with very different organic and inorganic content have been selected: the effluent of an organic-synthesis pharmaceutical and the real wastewater coming from the secondary treatment of a WWTP. To evaluate the feasibility of CDEO to remove complex organic molecules from real matrix, both wastewater have been intensified with chemicals that are generally found in high concentration in these type of effluents: metoprolol (β -blocker) in the pharmaceutical wastewater and caffeine (stimulant) in the urban treated wastewater (unlike many other psychoactive substances, caffeine can be present in relatively high concentration in urban wastewater [40]). Finally, the effect of coupling irradiation processes (UV light and US) and CDEO in the treatment of POPs in the two real wastewater has been evaluated.

2. Materials and methods

2.1. Chemicals

Metoprolol tartrate (2:1) salt $((C_{15}H_{25}NO_3)_2 \cdot C_4H_6O_6)$ and caffeine ($C_8H_{10}N_4O_2$) were analytical grade (> 99.0 % purity) and supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany). The anhydrous sodium sulfate was analytical grade and purchased from Fluka. Sulfuric acid and sodium hydroxide, which were used to adjust the pH of the solution, were analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Real wastewater

Industrial real effluent was collected from an organic-synthesis pharmaceutical manufacturing plant. Its main characteristics are shown in Table 1. As it can be observed, the effluent is complex with respect to composition and has a high organic load. The value of conductivity measured is due to the occurrence of chloride, sulfate and sodium borohydride salts.

Municipal effluents were collected from secondary treatment of a WWTP located in Ciudad Real (Spain). An exhaustive characterization of these effluents was conducted (Table 2). In this case, it is important to note the low concentration of organic mass ($TOC \approx 13 \text{ mg dm}^{-3}$) and the relatively high concentration of chloride and sulfate, which were above 110 and 80 mg dm^{-3} , respectively (but very low if they are compared with studies carried out with synthetic wastewater with a high concentration of inorganic salts used as supporting electrolyte [41-43]).

2.3. Analytical procedures

The carbon concentration was monitored using a Multi N/C 3100 Analytik Jena TOC analyzer. Measurements of pH and conductivity were conducted with an InoLab WTW pH-meter and a GLP Crison conductimeter, respectively.

The concentrations of metoprolol, caffeine and the generated intermediates were measured by HPLC–UV (Agilent 1100 series). The detection wavelengths used were 223 and 205 nm for metoprolol and caffeine, respectively. The column temperature was 25 °C. The volume injection was set at 20 µL, and a Phenomenex Gemini 5 µm C18 analytical column was used. Solvent A was composed of 25 mM of a formic acid water solution, and Solvent B was acetonitrile. A linear gradient chromatographic elution was obtained by initially running 10 % of Solvent B and ascending to 100 % in 40 min. The samples extracted from the electrolyzed solutions were filtered with 0.20 µm Nylon filters before analysis.

Ionic species (NH_4^+ , NO_3^- , NO_2^- , SO_4^{2-} , Cl^- , ClO_2^- , ClO_3^- , and ClO_4^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column (anionic species) or Shodex IC YK-421 column (cationic species); mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, $1 \cdot 10^{-3} \text{ dm}^3 \text{ min}^{-1}$ (concentration accuracy: ± 0.5 %).

2.4. Electrochemical cells

The electrolysis were conducted in a compartment electrochemical flow cell working under batch-operation mode [44]. A conductive diamond electrode (p-Si-boron doped diamond) was used as the anode and stainless steel (AISI 304) as the cathode. Both electrodes were circular (100 mm in diameter) and had a geometric area of 78 cm^2 and an electrode gap of 9 mm. The boron doped diamond films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si <100> wafers ($0.1 \Omega \text{ cm}$, Siltronix).

The ultrasound generator was a UP200S (Hielscher Ultrasonics GmbH, Germany) equipped with a titanium glass horn of 40 mm diameter, length 100 mm, emitting at 24

kHz and a maximum ultrasonic power of 200 W. The output, which can be both continuous or pulsed, is varied adjusting the percentage of cycle duty ranging from 10 to 100%.

The ultraviolet lamp (low-pressure Hg vapor lamp) was a Filtered Lamp Vilber Lourmat VL-215.MC with a power of 4 W. The wavelength used was 254 nm (UV-C).

2.5. Experimental procedures

Wastewater was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (flow rate $21.4 \text{ dm}^3 \text{ h}^{-1}$). The mass transfer coefficient (K_m) of the electrochemical cell within the fluid dynamic conditions used ($21.4 \text{ dm}^3 \text{ h}^{-1}$, 298 K) was $2.8 \cdot 10^{-6} \text{ m s}^{-1}$ and was calculated using a standard $\text{Fe}(\text{CN})_6^{3+}/\text{Fe}(\text{CN})_6^{2+}$ current limit test [45]. A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point ($25 \text{ }^\circ\text{C}$).

The cell voltage did not vary during electrolysis, indicating that the conductive diamond layers did not undergo appreciable deterioration or a passivation phenomenon. Prior to use in galvanostatic electrolysis assays, the electrode was polarized for 10 min using a $0.035 \text{ M Na}_2\text{SO}_4$ solution at 30 mA cm^{-2} to remove impurities from the electrode surface.

2.6. Synergy coefficient and energy efficiency

The synergy coefficient (%) is used to evaluate the effect of the coupling of different processes. It can be calculated according to Eq. 1 where k_{comb} is the kinetic constant calculated for the combined process (photoelectrolysis, sonoelectrolysis or sono-photoelectrolysis) and k_{single} is the kinetic constant calculated for the single processes involved in the evaluated process (CDEO, photolysis and/or sonolysis).

$$\text{Synergy coefficient (\%)} = \frac{k_{\text{comb}} - \sum k_{\text{single}}}{\sum k_{\text{single}}} \cdot 100 \quad [1]$$

On the other hand, the energy efficiency can be calculated according to Eq. 2, taking into account the TOC removal, the applied power and the reaction time (t) related to each evaluated technology.

$$\text{Energy efficiency (mg(Wh)}^{-1}) = \frac{\Delta\text{TOC}}{\Delta\text{Power}\cdot t} \quad [2]$$

3. Results and discussion

In the first case-study evaluated in this work, an effluent coming from the secondary treatment of a WWTP has been intensified with 100 mg dm⁻³ of caffeine (as target pollutant). As stated before, the real wastewater contain sulfate, chloride and nitrates (see Table 2) and no extra salts were added.

Figure 1 shows the profiles of caffeine concentration (part a) and TOC (part b) obtained during the treatment of this wastewater by photoelectrolysis (conductive diamond photoelectrochemical oxidation, CDPEO), sonoelectrolysis (conductive diamond sonoelectrochemical oxidation, CDSEO) and sono-photoelectrolysis (conductive diamond sono-photoelectrochemical oxidation, CDSPEO), and these results are compared with those obtained with the application of the single technologies: sonolysis, photolysis and CDEO.

With the application of the single irradiated processes (sonolysis and photolysis), both removal of compound and mineralisation are not observed, indicating that not only the intensified chemical, but also all the organics contained in the wastewater matrixes are not affected by UV or US irradiation. However, a different behaviour is observed in the case of CDEO, which allows an efficient mineralization in addition to the total removal of the pollutant (down to the detection limit of the chromatographic technique used, HPLC 0.01 ppm) in less than 10 hours.

With respect to the coupling of CDEO with the irradiated processes, it can be observed that at the beginning of the experiments ($t < 100$ min) the curves are overlapped, indicating that the caffeine removal efficiency obtained by the different technologies is very similar. From 100 minutes on, differences among the processes become evident and CDSEO behaves around 10-13 % more efficient than the rest of technologies. This may indicate that ultrasound improves the mass transfer to the anodic surface when the concentration of reactants is particularly low and the process is tightly controlled by mass transfer [19-21, 46, 47], because ultrasound irradiation improves the turbulence originated by the implosion of microbubbles in the aqueous medium [48, 49]. On the other hand, the improvement observed when applying UV light can be explained in terms of the generation and/or activation of electrogenerated oxidants (from sulfate and chloride ions contained in the real wastewater), which exhibit a higher oxidizing power [22-26, 50, 51]. In this case, in contrast to the results observed for a single electrolytic process, the effect of these radicals can be extended to the bulk, improving significantly the removal efficiency.

In terms of mineralization (Figure 1b), the effect of electro-irradiated techniques is less significant, except for CDSEO, with an average effectiveness of $0.0045 \text{ dm}^3 (\text{Ah})^{-1}$ versus 0.0031 or $0.0039 \text{ dm}^3 (\text{Ah})^{-1}$ of other technologies [49]. The simultaneous use of both radiation techniques (CDSPEO) has an antagonistic effect that could be explained in terms of the potential combination of oxidizing radical species, massively generated in the reaction medium, that is to say, oxidants react among them and do not attack the organic matter [52, 53].

Focusing on the second case study (industrial wastewater), Figure 2 shows the profiles of metoprolol (part a) and TOC depletion (part b) obtained during the treatment by electro-irradiated technologies of the effluent of an organic-synthesis pharmaceutical industry, which was intensified with 100 mg dm^{-3} of metoprolol. As in the study carried out with caffeine, mineralization is not attained with the single irradiated technologies, but for this waste, sonolysis is able to attack slightly metoprolol molecule. That is, the break-up of the molecule or even to the simple attack to any functional group by direct action of these irradiation techniques (or by means of the oxidizing agents generated) takes place. Thus, the pollutant is not **completely** degraded but partially oxidized, leading to the formation of reaction intermediates, which are not easily degraded to carbon dioxide by any of the irradiation technologies. On contrary, electrochemical oxidation is able to deplete around 50 % of metoprolol and to attain around 50 % of mineralization after 480 min of electrolysis (24 Ah dm^{-3} of electrical charge passed). The higher electrical charges required to attain a fixed removal of metoprolol in comparison with CDEO of caffeine in WWTP-wastewater (99 % of caffeine removal after 480 min of electrolysis) are related to the higher organic concentration of the pharmaceutical wastewater. However, as expected, the harsh oxidation conditions of electrochemical process seem to lead to the simultaneous oxidation of the different organics contained in the real wastewater, indicating that CDEO is an efficient technology for the treatment of POPs in real wastewater, regardless the reaction media. In addition, it is important to remark that higher efficiencies were obtained in comparison to the results achieved in synthetic media in previous studies of this research group [54].

By coupling irradiated techniques to electrochemical oxidation, an improvement in the efficiency of the process is obtained, especially in the case of CDSEO. However, this improvement is lower than that reported in literature for the removal of POPs by CDSEO in synthetic medium with Na_2SO_4 as supporting electrolyte [48, 52, 55]. This fact can be explained considering that, in this case, there is a higher amount of organics in the medium and, consequently, the mass transfer limitations are lower and the improvement attained by the effect of ultrasonic irradiation is less pronounced. A synergistic effect seems to be observed by CDSPEO, suggesting that the electrogenerated oxidants react rapidly with the organics present in the reaction medium.

Figure 3 focuses on the comparison of the synergy coefficients calculated according to Eq. 1, for the treatments conducted by the electro-irradiated technologies in terms of compound and TOC removal.

As it can be observed, in both cases (urban and industrial wastewater), the application of the electro-irradiated technologies entails a synergistic effect with respect to the addition of the single technologies in terms of compound removal, mainly due to the generation and/or activation of oxidants. This behavior is even more remarkable when it is taken into account that the concentration of ionic species in these types of water is much lower than the typically used on the studies of synthetic wastewater with addition of an electrolyte (see Tables 1 and 2) [41-43].

Likewise, it is important to note the high synergy coefficient achieved by CDSPEO in the treatment of industrial wastewater polluted with metoprolol (> 250%). This fact can be explained in terms of the higher concentration of organics available to be oxidized in the industrial effluent, which prevents the combination of generated oxidizing radicals, as it is presumed to occur in urban wastewater [52, 53]. However, the coefficient calculated in

terms of TOC removal is lower in all cases, being even negative in the study of CDSPEO in urban wastewater (part a).

According to Eq. 2, energy efficiencies can be compared for the electrochemical technologies studied in this work. Figure 4 shows the values of this parameter calculated for the treatment of urban and industrial real wastewater polluted with caffeine (part a) and metoprolol (part b), respectively.

In the case of urban wastewater, the coupling of UV-light irradiation to CDEO entails a slight decrease of the energy efficiency, but in the case of industrial wastewater the value is higher. However, the coupling of US irradiation originates an important decrease in both cases, due to the high power consumption associated to this technique. For this reason, the application of CDSEO and CDSPEO just seems advisable if entails a high synergistic effect or with lower values of power and application periods of the US irradiation [48, 52].

Figure 5 shows the pseudo-first order kinetic constants calculated for the different electrochemical technologies studied [56, 57]. In all cases the kinetic constant seems to be higher with the application of the electro-irradiated technologies than with CDEO, mainly in terms of pollutant removal. However, the joint application of UV-light and US irradiation (CDSPEO) entails a negative effect with respect to CDPEO and CDSEO technologies for the treatment of urban wastewater polluted with caffeine in contrast to what it is observed in the study of industrial wastewater. This observation can be related to the lower concentration of organic matter available to be oxidized in the urban water, and thus to the potential combination of oxidizing radical species (antagonistic effect).

The degradation rate is much higher in the study carried out with industrial effluent (both in terms of pollutant and TOC removal). This seems to indicate a higher presence of oxidants in this type of wastewater. At this point it is important to remind that according to literature, the pseudo-first order kinetic constant in electrochemical processes can be explained by Eq. 3, where a clear influence of the concentration of oxidants on the value of the kinetic constant is seen [58].

$$K = k' \cdot [\text{Oxidants}] + K_m \cdot A \cdot n \cdot F \quad [3]$$

where k' is first order kinetic constant, K_m is the mass transfer coefficient, A is the anodic area, n is the number of electrons exchanged and F is the Faraday constant.

During the operation of the different technologies, reaction intermediates were monitored by HPLC in order to try to help to explain the differences observed in evolution of the removals of the targeted model-chemicals and TOC. Those coming from the oxidation of metoprolol or caffeine are followed in this work and compared to intermediates species detected during the treatment of synthetic solutions of caffeine and metoprolol in Na_2SO_4 or NaCl medium carried out in previous works of our research group [59, 60].

The first important observation is the much lower generation of intermediates in the treatment of intensified effluents as compared to the treatment of synthetic wastewater, both in terms of number of intermediates and concentration. Thus in the case of caffeine oxidation, only one intermediate was observed during treatment of the intensified wastewater and it corresponds to one intermediate found in the electrolysis of caffeine with NaCl as supporting electrolyte but not with Na_2SO_4 . Thus, it should be related to the attack of generated ClO^- by oxidation of Cl^- to the molecule [28]. The maximum concentration measured is five times lower than in the removal of caffeine in synthetic wastewater. Regarding the test with metoprolol, no intermediates associated to the oxidation of this chemical was found. Differences can be explained in terms of the lower

presence of ionic species in real medium (see Tables 1 and 2). This becomes an additional advantage versus the studies that need the addition of inorganic salts for the application of an electrochemical technique.

4. Conclusions

From this work, the following conclusions can be drawn:

- CDEO attains an efficient removal of refractory pollutants from real wastewater matrixes (industrial and urban effluents). The addition of salts to increase conductivity is not necessary and mineralization of all compounds contained in the wastewater matrixes is also obtained.
- Single irradiated technologies (sonolysis and photolysis) are not efficient in the oxidation of metoprolol or caffeine. However, coupling these irradiation technologies with CDEO entails, in most cases, a synergistic effect and hence a clear enhancement in the performance of the electrochemical processes.
- The huge demands of energy of US irradiation technologies make their combination with CDEO not very attractive. Opposite, the combination of UV irradiation is a much more interesting process in terms of energy consumption.

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Table 1. Characteristics of the industrial effluent.

Parameter	Value
pH	6
Conductivity (mS cm ⁻¹)	0.2
COD (mg dm ⁻³)	4980
TOC (mg dm ⁻³)	1600
Chemicals in high concentration	CH ₂ Cl ₂ , CCl ₃ COOH, THF, CF ₃ COOH, CH ₃ (CO)CH ₃ , CH ₃ C(O)N(CH ₃) ₂ , CH ₃ CH ₂ CN

*COD: chemical oxygen demand.

TOC: total organic carbon.

Table 2. Characteristics of the effluent from the WWTP secondary treatment.

Parameter	Value
Cl ⁻ (mg Cl dm ⁻³)	110-180
NO ₃ ⁻ (mg N dm ⁻³)	3-12
SO ₄ ²⁻ (mg S dm ⁻³)	80-105
NH ₄ ⁺ (mg N dm ⁻³)	10-28
Conductivity (mS cm ⁻¹)	1.2
Turbidity (NTU)	10-11
Total suspended solids (mg dm ⁻³)	7-10
TOC (mg dm ⁻³)	12-14
COD (mg O ₂ dm ⁻³)	35-42

Figure captions

Figure 1. Concentration (a) and TOC (b) profiles observed in the treatment of urban wastewater polluted with caffeine by the different evaluated technologies. Operating conditions: $[\text{Caffeine}]_0 = 100 \text{ mg dm}^{-3}$, $j = 30 \text{ mA cm}^{-2}$. Ultrasound: continuous mode, 200 W; ultraviolet light: 254 nm, 4 W. (▲) Sonolysis, (■) Photolysis, (□) CDEO, (Δ) CDSEO, (◇) CDPEO, (○) CDSPEO.

Figure 2. Metoprolol (a) and TOC (b) profiles observed in the treatment of industrial wastewater polluted with metoprolol by the different evaluated technologies. Operating conditions: $[\text{Metoprolol}]_0 = 100 \text{ mg dm}^{-3}$, $j = 30 \text{ mA cm}^{-2}$. Ultrasound: continuous mode, 200 W; ultraviolet light: 254 nm, 4 W. (▲) Sonolysis, (■) Photolysis, (□) CDEO, (Δ) CDSEO, (◇) CDPEO, (○) CDSPEO.

Figure 3. Synergy coefficients calculated for the application of electro-irradiated technologies in the treatment of urban wastewater polluted with caffeine (a) and industrial effluents polluted with metoprolol (b) in terms of compound (■) and TOC (■) removal.

Figure 4. Energy efficiency calculated for the evaluated electrochemical technologies in the treatment of urban wastewater polluted with caffeine (a) and industrial effluents polluted with metoprolol (b).

Figure 5. Kinetic constants calculated for the evaluated electrochemical technologies in the treatment of urban wastewater polluted with caffeine (a) and industrial effluents polluted with metoprolol (b) in terms of compound (■) and TOC (■) removal.

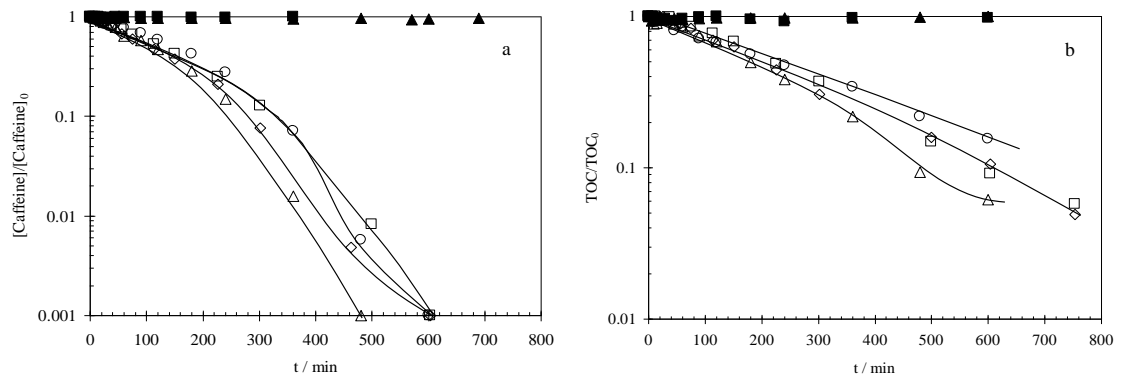


Figure 1

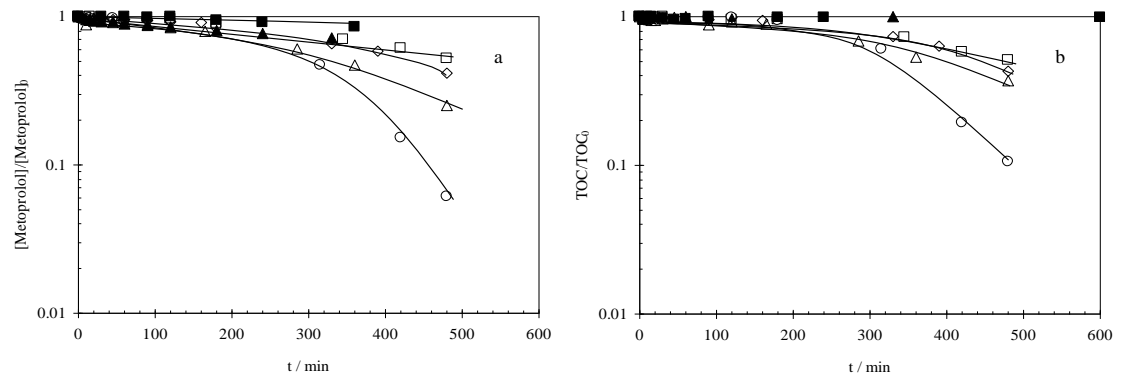


Figure 2

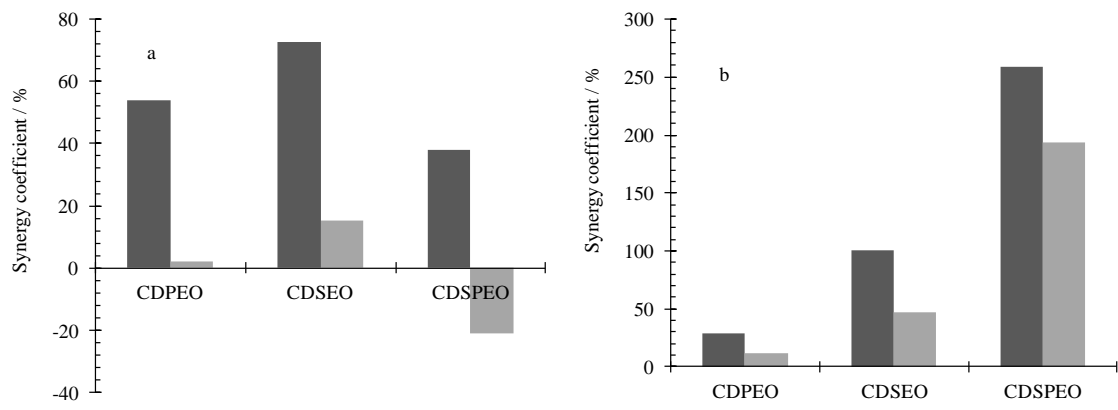


Figure 3.

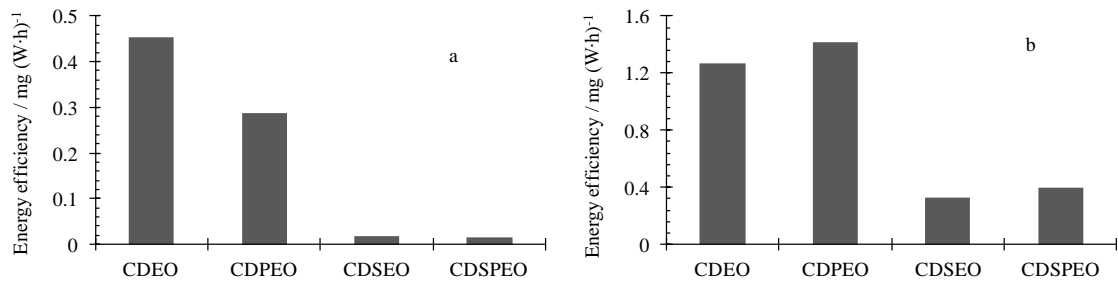


Figure 4.

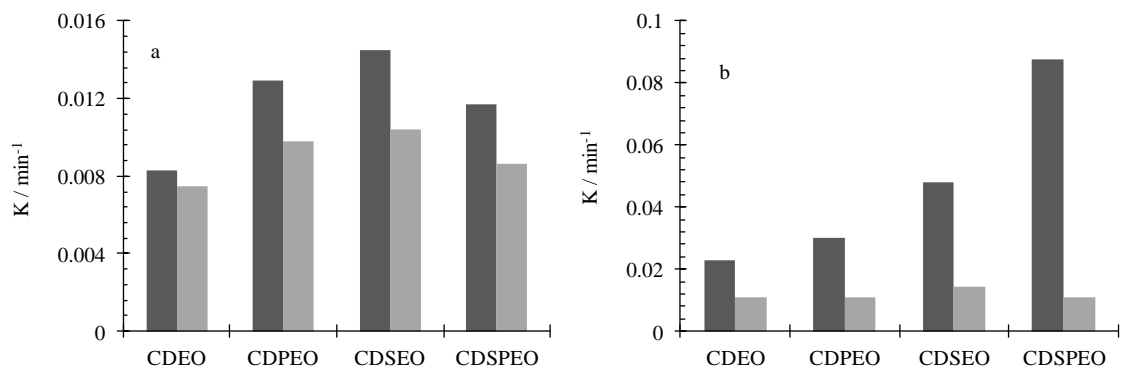


Figure 5.