DEGRADATION OF DEXAMETHASONE USING ANODIC OXIDATION, SOLAR LIGHT AND PERSULFATE IN ENVIRONMENTAL MATRICES

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ABSTRACT

The scope of this work was to investigate the electrochemical oxidation of dexamethasone (DEX), an anti-inflammatory drug, over boron-doped diamond (BDD) anode with the synergy of sodium persulfate (SPS). Na_2SO_4 was utilized as the electrolyte in various water matrices, including secondary treated wastewater, bottled water, ultrapure water spiked with humic acid and inorganic ions (bicarbonate, chloride). The occurrence of chloride in UPW favored reaction rate, while humic acid had practically no effect. Persulfate was found to be activated electrochemically progressively promoting DEX degradation at greater SPS concentrations. The simultaneous application of solar light and electrochemistry to activate persulfate resulted in no kinetic enhancement.

KEYWORDS

Anodic oxidation; BDD; dexamethasone; hybrid process; persulfate

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1. INTRODUCTION

According to some studies, dexamethasone, an anti-inflammatory drug, is one of the most commonly used glucocorticoids for the treatment of many conditions, including rheumatic problems, a number of skin diseases, severe allergies, asthma and nausea [1,2]. The massive and uncontrolled discharge of pharmaceuticals into the aqueous environment leads to severe environmental problems. Several studies reported that conventional treatment applied in the wastewater treatment plants is not effective on the removal of pharmaceuticals, suggesting that their upgrade on advanced oxidation processes are essential to achieve high efficiency of these organic pollutants [3].

Advanced oxidation processes (AOPs) are based on hydroxyl radical production by different ways. These radicals are highly reactive and lead to complete mineralization. Amongst the various AOPs, electrochemical oxidation has been a promising technology for the degradation of micropollutants since the development of boron-doped diamond (BDD) as the electrode of the anode. This non-active material exhibits great activity and stability [4].

A major disadvantage of this process is the large surface area of the electrodes that is required. To enhance the efficiency of the process the addition of oxidants, such as persulfate, could promote the production of extra reactive oxygen species. Persulfate has a long half-life, ease of storage and transportation and can be activated via transition metals, ultraviolet irradiation and electrochemical techniques.

In the present study, the combined electrochemical oxidation on a BDD anode and sodium persulfate (SPS) process for the degradation of dexamethasone is investigated. Emphasis was given to the operating conditions of the process, while the effect of solar irradiation on the combined process was tested, as well as the use of a different cathode, carbon cloth.

2. METHODOLOGY

The experimental set up of the electrochemical reactor consists of two electrodes, a BDD as the anode and Ti (unless otherwise mentioned) as the cathode. To assess the influence of operating conditions on DEX degradation, experiments were performed in an open cell of 150 mL liquid capacity, which was stirred continuously with a magnetic stirrer to ensure the homogeneous mixture of the reagents in the solution.

In those cases where the reactor was irradiated, a solar simulator (Newport LCS- 100) equipped with a 100 W xenon, ozone- free lamp was employed.

To monitor the concentration of DEX, high performance liquid chromatography (HPLC, Alliance 2695, Waters) was employed and a UV/Vis detector (Waters 2996) set at 240 nm.

3. RESULTS AND DISCUSSION

To evaluate the effect of operating conditions, preliminary experiments were carried out at 0.02-0.2 A/m^2 current density on 0.5 mg/L DEX degradation in UPW with 0.1 M Na_2SO_4. As can be seen in Figure 1, conversion increases with increasing current density and nearly complete removal can be achieved within 45 min at 0.2 A/m^2. This increase is attributed to the greater formation of hydroxyl radicals occurring at higher current densities.

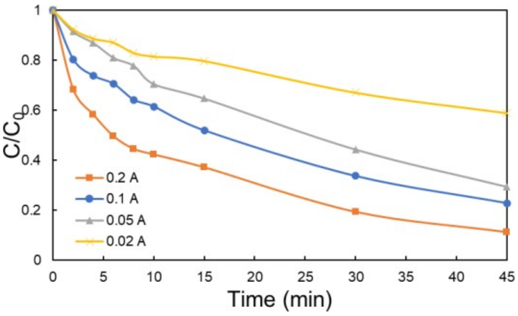

Figure 1. Effect of current density on the degradation of 0.5 mg/L DEX at inherent pH.

Various water matrices were tested, including wastewater (WW), bottled water (BW), ultrapure water (UPW) spiked with 10 and 20 mg/L humic acid (to simulate the natural organic matter of waters) and UPW spiked with different concentrations of bicarbonate and chloride, on the degradation of 0.5 mg/L DEX at 0.2 A/m^2 current density with 0.1 M Na_2SO_4. Interestingly, DEX degradation in complex matrices is faster than in UPW (Figure 2); on the assumption that degradation obeys to a pseudo-first order kinetic expression, the apparent rate constant computed from the data of Figure 2 is 0.065 min^{-1} in WW and 0.043 min^{-1} in UPW.

The addition of NaCl in the range of 50- 250 mg/L enhances DEX degradation. The presence of chloride during BDD anodic oxidation results in the formation of active chlorine species that complement hydroxyl radicals in the degradation of DEX. On the other hand, bicarbonate at concentrations 50-250 mg/L slightly slow down the rate of oxidation of DEX. This is probably due to the fact that bicarbonate scavenges hydroxyl radicals.

Regarding the presence of humic acid, an analogue of the natural organic matter, it seems to have little effect on DEX degradation. As seen in Figure 2, the addition of 10 mg/L or 20 mg/L HA in UPW leads to about 90% removal of DEX within 45 min with similar apparent rate constants of 0.045 and 0.041 min^{-1} respectively.

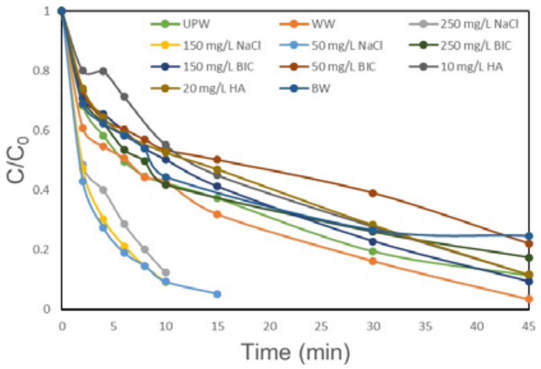

Figure 2. Effect of water matrix on the degradation of 0.5 mg/L DEX at inherent pH. BIC: bicarbonate; HA: humic acid.

Treatment performance may also be affected by effluent pH, experiments were performed in UPW at initial pH values of 3 and 9. As Figure 3 shows, degradation of 0.5 mg/L DEX is favored at acidic conditions.

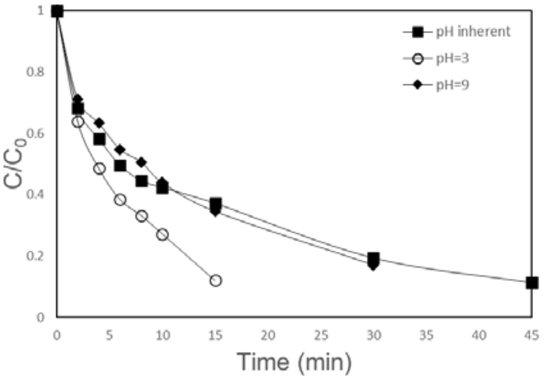

Figure 3. Effect of initial pH on the degradation of 0.5 mg/L DEX in UPW.

Further experiments were conducted to investigate the electrochemical activation of SPS. As seen in Figure 4, the addition of 150 mg/L SPS in UPW enhances the reaction rate and degrades DEX in only 15 min possibly due to the formation of additional reactive oxygen species (i.e. sulfate and hydroxyl radicals).

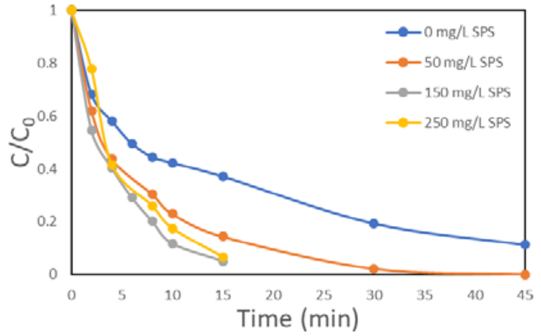

Figure 4. Effect of SPS on the degradation of 0.5 mg/L DEX at inherent pH at 0.2 A/m^2 current density.

Moreover, the effect of simulated solar radiation on the combined method was investigated and the results are summarized in Figure 5. The combined application of solar irradiation and BDD for SPS activation resulted in complete removal after 10 min of reaction. To evaluate whether the simultaneous application of solar light and BDD results in a synergistic effect relative to the respective individual processes (SPS+Solar and SPS+BDD), the extent of synergy (S) can be quantified as follows:

$$S\ (\%) = 100 * [(k_{combined} - \Sigma k_i)/k_{combined}]$$

where k_i is the rate constant of the individual process.

The computed apparent rate constants are 0.18, 0.179 and 0.034 min^{-1} for the SPS+BDD+Solar, SPS+BDD and SPS+Solar processes, respectively and this gives a slightly negative S value, thus implying that there is no synergy between the individual processes. On a quantitative basis, synergy occurs when S>0, a single additive effect occurs when S=0, while negative values may be characteristic of an antagonistic effect between the processes.

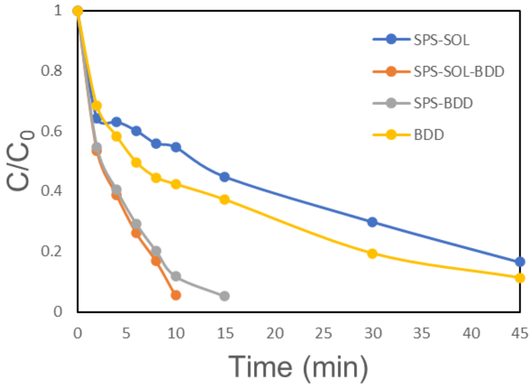

Figure 5. Comparison of various processes for the degradation of 0.5 mg/L DEX in UPW and inherent pH.

Experiments were also performed replacing Ti with carbon cloth as the cathodic material. As seen in Figure 6, complete decomposition of 0.5 mg/L DEX in UPW was achieved in just 15 min of treatment with BDD anode and carbon cloth cathode. The addition of 150 mg/L SPS does not seem to affect the process. Interestingly, carbon cloth acts as adsorbent since about 30% removal takes place at zero current density.

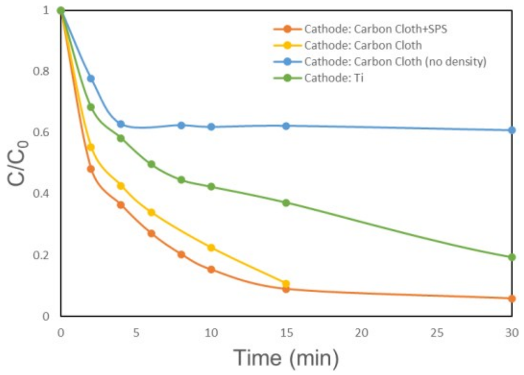

Figure 6. Comparison of different cathodes on the degradation of 0.5 mg/L DEX at inherent pH with 0.1 M Na2SO4.

4. CONCLUSIONS

In a nutshell, this work demonstrates the efficient application of BDD anodic oxidation for the degradation of DEX. The process is favored at increased current densities and increasing matrix complexity, where there may be some kind of synergy between the organic and inorganic water matrix components, oxidants and the anode surface. Sodium persulfate seems to be activated electrochemically, thus enhancing the removal of DEX. The simultaneous application of electrochemical oxidation and solar irradiation in the presence of persulfate has no positive effect. Interestingly, replacing Ti with carbon cloth as the cathode on the degradation of DEX showed good enhancement on the process.

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