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Research Paper

Removal of carbamazepine from MBR effluent by electrochemical oxidation (EO) using a $Ti/Ta_2O_5\text{-}SnO_2$ electrode

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ABSTRACT

This study aims at investigating the electrochemical oxidation (EO) of carbamazepine (CBZ) synthetic solutions and real membrane bioreactor (MBR) effluent using newly developed $Ti/Ta_2O_5\text{-}SnO_2$ electrodes to enhance CBZ removal. The characterization of the prepared $Ti/Ta_2O_5\text{-}SnO_2$ electrodes was performed by using scanning electron microscope, energy dispersive X-ray spectroscope, atomic force microscope, and cyclic voltammetry analyses. The main operating parameters influencing the CBZ removal efficiency in synthetic solutions using $Ti/Ta_2O_5\text{-}SnO_2$ electrodes were evaluated including the applied current density, initial CBZ concentration, pH, and temperature. The optimum removal of CBZ (20 mg L^{-1}) and TOC reached 75.5%, and 71.1%, respectively, after 8 h of electrolysis, under current density of 9 mA cm^{-2}, pH 6, temperature of 30 °C, and using 0.1 M Na_2SO_4 as supporting electrolyte. Increasing current density and temperature influenced the CBZ removal, unlike pH which did not have significant influence on CBZ removal. The performance of $Ti/Ta_2O_5\text{-}SnO_2$ electrode was compared with conventional Ti/PbO_2 electrode in terms of CBZ removal efficiencies and stability of the electrodes. The results showed that under the same operating conditions, the CBZ removal efficiency of Ti/PbO_2 electrode was slightly higher than of $Ti/Ta_2O_5\text{-}SnO_2$ (77.9 and 71.7%, respectively). Nonetheless, the use of this newly developed electrode is more energy-efficient as it required the lowest energy consumption of 60.3 kWh m^{-3} to achieve optimum CBZ removal, in addition to fact that no heavy metals were leached (unlike the PbO_2 electrode). Furthermore, a complete degradative removal of real MBR effluents spiked with CBZ was achieved when electrolyzed under the optimized conditions of CBZ synthetic solutions. Overall, the EO based on the use of $Ti/Ta_2O_5\text{-}SnO_2$ electrode was found to be a reliable approach to remove CBZ from contaminated waters, with promising potential for integration with MBR technology to remediate CBZ.

1. Introduction

Pharmaceutically active compounds (PhACs) have gained a great deal of attention among researchers in recent years as emerging micropollutants with long-term potential threats to aquatic environment and human health [1–4]. These PhACs are introduced to aquatic ecosystems primarily from the effluents of wastewater treatment plants (WWTPs). In addition, direct and unsafe discharge of untreated wastewaters from agriculture, industries and hospitals are also reported to contribute to the release of PhACs into the aquatic ecosystems [2,3,5–7].

Carbamazepine, which is used for the treatment of epilepsy, depression, trigeminal neuralgia and wide variety of mental disorders, is one of the frequently identified PhAC in various aquatic environments [2,3,7]. The world-wide annual consumption of CBZ is more than 1000 tons and about 28% of it ends up in WWTPs as unmetabolized forms [3,5]. In Finland, the annual consumption of CBZ is around 3.3 tons, with comparatively more concentrations in winter seasons than in summer at WWTP effluents [8]. CBZ is highly recalcitrant to biodegradation in conventional activated sludge processes and photo-degradation (more than 100 days) [2]. In fact, many researchers have documented difficulties in removing CBZ, with biodegradation removal of only less than 10% [3,4,6,8]. Thus, it is crucial to apply highly efficient degradation technologies for the removal of CBZ in order to achieve the highest mineralization or generate non (or less) toxic intermediates.

In this context, MBRs have been studied for the removal of various PhACs including CBZ by many researchers [9–11]. However, a relatively low removal (0–28%) of CBZ was reported in MBR processes when treating synthetic and real wastewaters [2,9,11]. Thus, biodegradation and membrane filtration alone are not efficient enough for the removal of CBZ. Therefore, in order to meet the future legislations

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regarding the stringent limits of PhACs from WWTP effluents, MBR process integrated with various advanced oxidation processes (AOPs) has gained increasing interest.

AOPs are oxidation-based technologies applied in aqueous phase in order to destruct organic pollutants via the in-situ generated highly reactive oxygen species, mainly hydroxyl radicals ($\cdot$OH) [12]. They are promising and environmentally friendly methods for the treatment of wastewaters contaminated with a wide range of recalcitrant PhACs. Among the various AOPs, EO processes are of growing interest for water and wastewater decontamination due to their low cost and high efficiency [3]. In EO processes, dissolved organic pollutants are mainly oxidized by (i) direct anodic oxidation on the anode surface by charge transfer, and (ii) reaction with physio and/or chemisorbed hydroxyl radical ($\cdot$OH) generated from water oxidation (Eq. (1)) [13,14]. Hydroxyl radicals are extremely reactive oxidants (2.8 V (vs. SHE)) with the life time of less than a second, which makes their detection very challenging [15]. The subsequent oxidation mechanism of organic compounds depends on the behavior of anodes, which are divided as "non-active" and "active" [13–16]. In both cases, firstly, water molecules splitted and leading to the formation of OH at the anode oxide surface (MO_x) (Eq. (1))[17].

$$H_2O + MO_x = MO_x(\cdot OH) + H^+ + e^- \tag{1}$$

At 'active' anodes, OH radicals are chemisorbed (strongly adsorbed), thus allow only selective oxidation of organics (R), which involves intermediate step of higher oxide formation (Eqs. (2) and (3))[14,16].

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{2}$$

$$MO_{x+1} + R \rightarrow MO_x + RO \tag{3}$$

On the other hand, at 'non-active' anodes, the formation of higher oxide is excluded and OH radicals are physisorbed without interaction on the anode surface [14,16]. Moreover, 'non-active' anodes with high O_2-overpotential towards water oxidation allow good electrochemical stability and can generate many strong (OH) radicals predominantly leading to the complete combustion of organics (Eq. (4)) [15–17].

$$MO_x(\cdot OH) + R = MO_x + CO_2 + H_2O + zH^+ + ze^- \tag{4}$$

The major problems of EO process are the polarization and passivation of electrodes, related either to the poor mass transfer, corrosive environment, formation of polymer films or the inevitable formation of oxide interlayers due to the considerable porosity in supported catalyst films, [14,15,18]. In any cases, those phenomena result in the attenuation of the efficiency and service life of electrodes.

Various anodes such as PbO_2, and more recently, boron-doped diamond (BDD) have shown an interesting electro-degradation efficiency for CBZ [2,3,6]. Nevertheless, the higher cost of BDD electrodes and the possible leaching of lead (Pb) from PbO_2 coated electrodes tend to compromise their applicability in large-scale applications [19,20]. In fact, PbO_2 is one of the widely studied anode on the electrochemical degradation of PhACs [2,6,21,22]. PbO_2 anodes are inexpensive, relatively easy to prepare, has low electrical resistivity, and has a large surface area [23]. In this context, Ti/Ta_2O_5-SnO_2 (SnO_2 semi-conductor doped with Ta_2O_5) are eco-friendly electrodes, which were proven to be efficient in the oxidation of some organic compounds [18,24].

The main aim of the current research is to evaluate the efficiency of this novel electrode to remove persistent CBZ drug from synthetic solutions and the real MBR effluent. First, the EO of synthetic solution loaded with CBZ was investigated by monitoring and optimizing the major influencing factors including current density, pH, and temperature, under various initial concentrations of CBZ. In addition, the degradation efficiency and stability of Ti/Ta_2O_5-SnO_2 were compared with Ti/PbO_2 electrodes. Furthermore, optimized operating conditions in EO process were applied for the treatment of real MBR effluent spiked with CBZ. This study is the first research work on the EO of CBZ using novel Ti/Ta_2O_5-SnO_2 electrodes in synthetic solutions and real wastewaters.

2. Materials and methods

2.1. Reagents and materials

All the reagents and materials used were of analytical grade. CBZ (meets USP testing specifications), Titanium foil (99.7% trace metal basis, 2 mm thick), $SnCl_2{\cdot}2H_2O$ ($\geq$99.99% trace metal basis), $TaCl_5$ ($\geq$99.99% trace metal basis), NaOH ($\geq$98% anhydrous), H_3PO_4 (85%), Na_2SO_4 ($\geq$99% anhydrous) were purchased from Sigma-Aldrich, USA. Commercial Ti/PbO_2 electrodes (5 cm × 10 cm × 2 mm) were supplied by Magneto, Netherlands.

A synthetic stock solution containing CBZ (20 mg L^{-1}) was prepared using Milli-Q water (18.2 MΩ.cm), stirred at 500 rpm for 24 h at room temperature [5]. Then, 0.1 M (14.2 mg L^{-1}) of Na_2SO_4 (better supporting electrolyte than NaCl regarding economical, effectiveness and environmental aspects) was added to increase conductivity of the solution. In this regard, the possible formation of organic chlorine by-products is also limiting the use of NaCl in electrochemical processes [5]. Finally, the synthetic stock solution was stored in the refrigerator at 4 °C for further use.

2.2. Preparation of Ti/Ta_2O_5-SnO_2 electrodes

Ti/Ta_2O_5-SnO_2 electrodes were prepared by thermal decomposition of precursor solutions on Ti substrates [25]. For the preparation of the electrodes, the methodology is detailed in a previous study conducted in our laboratory [26]. The optimized nominal composition of Ta (7.5 at.%) and Sn (92.5 at.%) were used to prepare precursor solutions by dissolving $SnCl_2{\cdot}2H_2O$ and $TaCl_5$ salts in absolute alcohol (pro analysis, Panreac), where total concentration of metal ions was kept constant (0.04 M). At first, Ti substrate plates (5 cm × 10 cm × 2 mm) were pre-treated by mechanical polishing and followed by degreasing in 10 wt.% NaOH for 10 min and etching in boiled 18 wt.% HCl (pro analysis, Fluka) for 30 min, and finally rinsed carefully using Milli-Q water. Secondly, the precursor solution was applied over only one side of the pre-treated Ti substrates by drop casting method. The precursor solution of 1 mL volume was dropped on to the Ti substrate, uniformly distributed using the tip of a Pasteur glass pipette, dried in oven at 80 °C for 5 min, and then annealed in muffle furnace at 550 °C for 5 min. The process was repeated until 8 layers of ultrathin film deposition of the precursor solution, which attributed highest electro-catalytic properties of the electrodes [26]. After the final layer, electrodes were additionally annealed at 550 °C for 10 h to enhance the formation of composite oxides of Ta and Sn on the electrode surface via thermal decomposition. The final composite oxides on Ti substrate gave the wide band gap *n*-type SnO_2 semi-conductor extrinsically doped with Ta_2O_5. After 10 h, electrodes were cooled down and kept in an ultrasonic bath for 5 min in order to remove the surface impurities and deformations, and then oven dried at 105 °C. Thus, the precursor material deposited only one side of Ti substrates had surface area of 50 cm^2 and the deposited material was equal to 1.10 mg cm^{-2} ± 5%.

2.3. Physicochemical and electrochemical characterization of the electrodes

Microstructure of the Ti/Ta_2O_5-SnO_2 electrodes was analyzed by using scanning electron microscope (SEM) (Hitachi, SU3500, Japan) using 5 kV of acceleration voltage. The chemical analysis of selected areas of the electrode surface was performed with energy-dispersive X-ray spectroscope (UltraDry™ Compact EDS Detector, Thermo Fisher, USA). The AFM images were taken by using atomic force microscope (AFM) (NX10, Park, Korea) using the non-contact mode.

The electrochemical characterization of the Ti/Ta_2O_5-SnO_2 electrode was performed by conducting cyclic voltammetry (CV) measurements using an Autolab (PGSTAT 12 Potentiostat/Galvanostat,