Treatment of liquid effluents by electrochemical processes

Candidate: Ana Sofia dos Santos Fajardo (sofiafajardo@eq.uc.pt)

Supervisor: Rosa Maria Quinta-Ferreira

Co-supervisor: Rui Carlos Cardoso Martins

CIEPQPF – Chemical Process Engineering and Forest Products Research Centre, Department of Chemical Engineering, University of Coimbra, P3030 790 Coimbra, Portugal

ABSTRACT

Water quality and its exhaustion are topics of great importance in our daily life. The constant seeking for well-being and comfort is bringing the natural resources towards dangerous limits. Therefore, and as a result of social and political awareness, stricter legislation is being implemented regarding the wastewater discharge in natural water streams. The appearance of harmful organic pollutants recalcitrant to classical biological treatments stimulated the development of new depuration technologies operating at room conditions of pressure and temperature. Among them, the electrochemical processes have emerged as promising solutions with generally simple operations and inexpensive equipment. These techniques are versatile, robust and amenable to automation. In this regard, the aim of the present study consists in the use of electrocoagulation (ECG) and electrochemical oxidation (EO) processes to purify agro-industrial and dye wastewaters by reaching the operating conditions that lead to the best energy consumption/efficiency ratio.

The performance of the ECG process was evaluated by testing different sacrificial anode materials (Al, Cu, Fe, Pb and Zn) for the depuration of a simulated phenolic mixture containing six phenolic compounds typically found in olive mill wastewaters (OMW). The Zn material revealed to be an attractive option with the highest removal of total phenolic content (TPh) and chemical oxygen demand (COD), after 180 min of electrolysis. Subsequently several operating conditions were analysed and the optimal were pH_0 3.2, current density (*j*) of 25 mA cm^{-2}, distance between electrodes of 1.0 cm, 1.5 g L^{-1} of NaCl and stainless steel as cathode, promoting 84.2 % and 40.3 % for TPh and COD removal, respectively, with an energetic consumption of 40 kWh m^{-3}. Those parameters applied to a filtered real OMW without the NaCl addition led to 72.3 % of TPh and 20.9 % of COD abatements with a consumption of 34 kWh m^{-3}. Ecological impact was still detected by bio-luminescence analysis.

Aqueous solutions containing a Reactive Black 5 dye were treated by an ECG process using Al anodes in batch-stirred and recirculation flow reactor configurations. The best results for both systems were achieved at *j* of 16 mA cm^{-2}, pH_0 6 and an initial concentration of the dye of 100 mg L^{-1} (and 800 rpm for the batch-stirred reactor). In the batch-stirred, an actual textile effluent was also depurated using Al or Zn anode materials. Final satisfactory legal values of discharge were attained for both cases.

Regarding the EO process, it was applied to the treatment of a synthetic OMW in a batch-stirred reactor by testing the materials Ti/RuO_2 and the Ti/IrO_2 as anodes. After 180 min of reaction, each electrode allowed a total TPh abatement and 100 % or 84.8 % of COD removal for the ruthenium or iridium materials, respectively, with the following conditions, 10 g L^{-1} of NaCl, 119 mA cm^{-2} and initial pH 3.4. Although no morphological differences were observed between the fresh and used Ti/RuO_2 anode, the surface of Ti/IrO_2 evidenced some changes. The impact in neuronal activity of the untreated and treated phenolic effluents was evaluated through the formation of synaptic reactive oxygen species (ROS). The treated effluent caused a smaller depression and a larger potentiation upon its removal than the untreated one, probably due to the formation of end products obtained. The depuration of real undiluted OMWs (COD_0=6.5 and 23 gO_2 L^{-1}) with both active anodes revealed a high ability to remove phenolic content, achieving only COD removal around 17 %. Conversely, when a diluted OMW (COD_0=1.1 gO_2 L^{-1}) was tested with Ti/IrO_2 material, there was an increase of the COD abatement to 62.8 %. The results ensure the applicability of these approaches as pre-treatment processes.

In another study, electrochemical measurements (cyclic voltammetry and polarisation curves) and bulk electrolysis with one or two flow cells in series were employed to evaluate the performance of Ti/IrO_2-Ta_2O_5 and Nb/BDD anode materials in the elimination of Amaranth dye from aqueous solutions. Nb/BDD showed a major oxidation power to remove the dye. Similarly, the best colour (98.5–100 %) and COD removals (43.2–49.1 %) were attained by both materials individually at different *j* (30 or 60 mA cm^{-2}) and reaction times (60 or 360 min). The energy consumptions varied from 14.3 to 33.8 kWh m^{-3}. The combination Ti/IrO_2-Ta_2O_5+Nb/BDD at 30+30 mA cm^{-2} obtained the most interesting results, enhancing COD abatement to 75.1 %, after 60 min of treatment and consuming 25.4 kWh m^{-3}. This reveals that the efficiency of a serial configuration may be higher with less energy consumption than the sum of the individual cells. An analogous work was performed with Ti/Pt and Ti/Pt-SnSb materials in order to avoid dependence on the use of higher cost materials such as BDD. Polarisation curves demonstrated that Ti/Pt-SnSb has higher electroactivity to remove the dye when compared to Ti/Pt. Besides, after 360 min treatment, the experiment with the former anode at 30 mA cm^{-2} led to 97.5 % and 70.3 % of colour and COD removal, respectively, consuming 72 kWh m^{-3} of energy. The combination of the two active anodes in cells in series promoted a faster colour removal. Trials combining Ti/Pt-SnSb and Nb/BDD materials were also performed. Among them, the configuration Nb/BDD+Ti/Pt-SnSb at 30+30 mA cm^{-2} provided the best results after 180 min of reaction, with 100 % and 69.9 % of colour and COD removals, respectively, as well as 78 kWh m^{-3} of energy consumed. The most interesting strategy to purify a synthetic solution containing the Amaranth dye was endorsed by the Ti/IrO_2-Ta_2O_5+Nb/BDD at 30+30 mA cm^{-2} arrangement.

ECG and EO are versatile processes able to be quickly adjustable to different effluents, final target parameters and required thresholds.