Journal of Environmental Management 202 (2017) 217–224

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Electrochemical treatment of biologically pre-treated dairy wastewater using dimensionally stable anodes

Vlasia Markou [a], Maria-Christina Kontogianni [a], Zacharias Frontistis [a, *], Athanasia G. Tekerlekopoulou [b], Alexandros Katsaounis [a], Dimitris Vayenas [a, c]

[a] Department of Chemical Engineering, University of Patras, Caratheodory 1, GR-26504 Patras, Greece
[b] Department of Environmental & Natural Resources Management, University of Patras, Agrinio, Greece
[c] Institute of Chemical Engineering Sciences, Foundation for Research and Technology, PO Box 1414, GR-26504 Patras, Greece

ARTICLE INFO

Article history:
Received 8 May 2017
Received in revised form
21 June 2017
Accepted 17 July 2017

Keywords:
Dairy
Wastewater
Electrochemical
Dimensionally stable anodes

ABSTRACT

In this work, electrochemical oxidation of aerobically pre-treated dairy wastewaters using IrO_2-Pt coated dimensionally stable anodes was investigated. It was found that IrO_2/Ti electrode outperforming Pt/Ti and IrO_2-Pt/Ti at lower current densities, while Pt/Ti achieved better efficiency at higher current density. Among the different parameters which were studied, the current density was the most crucial for the efficiency of the process. A current density of 100 mA/cm^2 led to almost complete removal of 3700 mg/L COD after 360 min of treatment using IrO_2/Ti electrode and 0.2 M of sodium chloride while complete decolorization was achieved in less than 60 min. Electrolytes also found to significantly affect the process. More specific, the use of sodium chloride instead of sodium sulfate enhanced both COD and color removal due to the formation of active chlorine species. The effect of temperature was relative low; the process was favourable at elevated temperatures while increasing COD loading resulted in a decrease of COD and color removal.

1. Introduction

Since ancient times the consumption of dairy products constitutes an important part of human nutrition. In recent years, due to the intensification of the dairy industry the management of dairy effluents has become a major problem since dairy wastewaters can be a significant threat, mostly for the aquatic environment (Carvalho et al., 2013; Prazeres et al., 2012). Consequently, there is a significant need to improve the management and treatment of dairy effluents in order to reduce environmental problems and to ensure the economic viability of this essential agricultural industry. (Sarkar et al., 2006).

Several research groups have studied the biological treatment of dairy wastewater, either under aerobic condition (Bumbac et al., 2015; Tatoulis et al., 2015) or anaerobic conditions (Venetsaneas et al., 2009; Demirel et al., 2005) with the simultaneous production of hydrogen and methane. However, even though biological processes may lead to a significant reduction of the organic material, usually they fail to meet the limits settled by environmental legislations for the disposal of effluents into the environment. Therefore, the combination of biological treatment with other treatment processes such as constructed wetlands (Sultana et al., 2016) and intermittent sand filters (Healy et al., 2007) have been proposed in literature.

At the same time, a considerable research on agro-industrial wastewaters treatment using physical processes like membrane technology, mainly reverse osmosis and nanofiltration (Suárez and Riera, 2015; Vourch et al., 2008; László et al., 2007) or adsorption (Kushwaha et al., 2010) has been carried out. Nevertheless, the main drawback of the physical processes is the fact that they transfer the problem from one phase to another resulting in the necessity either of the further concentrated solution treatment (Perez et al., 2010), or the regeneration of the adsorption material (Ehrenmann et al., 2011).

Advanced Oxidation Processes (AOPs) is a family of technologies based on the in situ production of highly reactive radicals. Among various AOPs most studies related to dairy wastewaters have been conducted with Fenton, photo Fenton and electro Fenton like reactions (Davarnejad and Nikseresht, 2016; Loures et al., 2014; Prazeres et al., 2013; Vlyssides et al., 2013), photocatalysis (Lamas

* Corresponding author.
E-mail address: zfrontistis@chemeng.upatras.gr (Z. Frontistis).

http://dx.doi.org/10.1016/j.jenvman.2017.07.046
0301-4797/

Samanamud et al., 2012), ozonation (Varga and Szigeti, 2016), electro-coagulation and electro flocculation (Melchiors et al., 2016; Şengil and Özacar, 2006). More specific, Loures et al. (2014) studied the photo Fenton process for the treatment of dairy effluents with an initial COD (chemical oxygen demand) concentration of 9500 mg/L. They found that more than 90.7% COD and 78.8% BOD can be removed under optimal conditions (35 g H_2O_2, 3.6 g Fe^{2+}, pH 3.5 and UV light 28 W). Sivrioğlu and Yonar (2017) applied ozonation for the degradation of dairy wastewater with initial COD concentration of 6300 mg/L. Ozonation led to COD removal up to 70% after 240 min of treatment with ozone dose equal to 2 gr/h.

Şengil and Özacar (2006) treated dairy wastewaters by electrocoagulation using steel electrodes. COD efficiency reached the value of 98% while the optimum current density, pH and treatment time for COD equal to 18,300 mg/L were 0.6 mA/cm^2, 7 and 1 min, respectively. Melchiors et al. (2016) examined the efficiency of electroflocculation method for the treatment of dairy wastewater with initial COD of 8303 mg/L. A significant removal of organic matter was achieved (97.4%) using iron electrodes at final pH of 7.4. However, despite the high COD removal the main problem of electroflocculation and electrocoagulation processes remains firstly the ''sacrificial'' electrodes and their dilution into the wastewater streams (because of their oxidation) and secondly the generation of significant quantities of sludge during the process (Bensadok et al., 2011).

On the other hand, electrochemical oxidation (EO) doesn't suffer from these drawbacks and seems to be a promising alternative approach, mainly due to its high efficiency, and ease of use and control (Särkkä et al., 2015; Valero et al., 2014; Anglada et al., 2009). EO is divided into direct and indirect oxidation (depending on the anode and its participation of the oxidation process), while the oxidizing agents include among others hydroxyl radicals, hypochlorite and ozone. In recent years, the use of dimensionally stable anodes (DSA) like RuO_2/Ti, PbO_2/Ti and TiO_2–RuO_2–IrO_2/Ti has increased significantly against other types of electrodes, due to their high stability and activity (Subba Rao and Venkatarangaiah, 2014; Turro et al., 2012; Chatzisymeon et al., 2009; FaridaYunus et al., 2009).

Borbón et al. (2014) studied the oxidation of dairy wastewater using electrochemistry over an IrO_2-Ta_2O_5/Ti electrode. They used different electrochemical techniques like cyclic voltammetry, pulsed differential voltammetry and chronoamperometry and concluded that two different processes/pathways exist using the above DSA-type electrode: one indirect (via hydroxyl radicals) and one direct oxidation (with the active participation of the electrode) (Borbón et al., 2014). However, they suggested that further research is needed to study the variables that affect the efficiency of the system.

Considering that the kinetics of electrochemical oxidations of industrial effluents with high organic loading follows near zero-order rate with respect to the organic loading (Chatzisymeon et al., 2009) the approach to couple an electrochemical process and a biological treatment seems to be rather advantageous. Indeed, several researchers (Zhang et al., 2011; Feki et al., 2009) have demonstrated the potential of the combined biological and physicochemical processes to treat industrial effluents like landfill leachates. Lei and Maekawa (2007) studied the electrooxidation of anaerobic digestion effluents using Pt-IrO_2/Ti electrode. They found that ammonia could be completely removed at 5 h under 1A and 1% NaCl, while the TOC and turbidity removal reached 51.4% and 95.5%, respectively.

Under this perspective, in this study, the electrochemical oxidation of an aerobically pretreated dairy wastewater is investigated giving attention to issues that have not been dealt with before; these include working electrode material (different DSA electrodes), current density, electrolytes, pH, treatment time, temperature and initial COD loading. According to our knowledge, this is the first report on the combination of a biological and an electrochemical process for the treatment of dairy effluents.

2. Materials and methods

2.1. Dairy effluent

Second cheese whey from cottage cheese production was obtained from a Greek cheese factory (Papathanasiou A.B.E.E.). The dairy effluent was firstly treated aerobically using a pilot-scale packed-bed bioreactor. The bioreactor as well as the bioprocess have been described in previous study (Tatoulis et al., 2015). The COD and pH of the pilot plant effluent were in the range of 2500–15.000 mg/L and 6–7.5, respectively, depending on the operating conditions of the bioreactor.

2.2. Electrodes

The preparation method of the DSA-type electrodes has been explained extensively in previous studies (Kapałka et al., 2010; Papastefanakis et al., 2010; Chatzisymeon et al., 2009). Briefly, the IrO_2 or Pt working electrodes was prepared by thermal decomposition of 250 mM H_2IrCl_6 (Acros Organics, 40%) or H_2PtCl_6 metal precursors dissolved in isopropanol (Fluka, 99.5%) on a squared-shaped titanium support, taking into account that the deposition yield of Pt and IrO_2 is 60% and 100% respectively (Comninellis and Vercesi, 1991). The titanium substrate was sandblasted to ensure good adhesion of the deposit on its surface and chemically treated using oxalic acid solution (1M) to clean its surface from residual sands. The substrate was then dried in an oven at 70 °C and weighed. The precursor solution was spread on the titanium substrate forming a thin film layer on the electron surface. Afterwards, the sample was treated in an oven for 10 min to allow solvent evaporation. This step was followed by treatment in the furnace for the thermal decomposition of the precursor solution at 500 °C in air for 10 min. The same procedure was repeated several times and, after the last IrO_2 or Pt coating, the electrode remained at 500 °C for 1 h. The final metal loading in all cases was 1.2–1.3 mg/cm^2. For the Pt-IrO_2 binary electrode, (50/50 molar ratio), the above method was applied using solutions of the precursors in the appropriate ratio.

2.3. Scanning electron microscopy (SEM)

The morphology of the surface was explored with Scanning electron microscopy (SEM) using a FEI, FEG QUANTA 520 scanning electron microscope.

2.4. Electrochemical oxidation experiments

Experiments were conducted in a double wall glass reactor. The appropriate electrode (Pt/Ti, IrO_2/Ti or Pt-IrO_2/Ti) had working surface of 12.5 cm^2 and two zirconium bars served as cathodes. The distance between the anode and the cathodes was 1.5 cm while the electrodes were connected with a DC power supply (model QJ3005C). The volume of the solution inside the reactor was 150 mL and the biologically pretreated dairy wastewater stirred with a magnetic bar. The temperature remained constant using a water bath. All experiments were conducted with NaCl (>99%, Aldrich) as the electrolyte, while, in some cases, Na_2SO_4 (>99%, Aldrich) was also added. The majority of the experiments were performed in triplicate and the relative error was less than 5%.