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Electrochemical treatment of dairy effluent using combined Al and Ti/Pt electrodes system

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ABSTRACT

This work deals with investigation of electrochemical technique for the treatment of milk liquid fractions. The removal of COD, phosphate and turbidity was investigated by varying the operating conditions. The batch experimental results revealed that the removal efficiencies of the overall turbidity, COD and phosphate concentration, depend on the nature of the electrodes material. The results indicated that turbidity is eliminated only by coagulation process and depends principally on aluminum concentration, whereas, soluble COD and phosphate might be eliminated by indirect oxidation. The greatest removal efficiency was obtained with the use of both cathode and anode made of aluminum (Al–Al system). With this latest system, optimal values of current density, initial pH, NaCl concentration and electrolysis time were 0.5 mA/cm^2, 6.6, 1.5 g/L and 2 min respectively. For these optimal parameter values, the removal efficiency of COD, phosphate and turbidity attained respectively 80%, 59% and 96%. Corresponding energy consumption was very low and equal 0.03 kWh/kg and 0.04 kWh/kg, for COD and phosphate removal respectively. Scanning electron microscopy (SEM), energy dispersion spectra (EDS) and fourier transform infrared spectroscopy (FT-IR), were used to characterize the resulting sludge.

1. Introduction

Oil-in-water (o/w) emulsions in foods are generally defined by their three components as follows: (i) the fat or oil that is inside the emulsion droplets, (ii) the interfacial matter between the lipidic phase and the aqueous phase representing part (iii) of the emulsion [1]. Each of these phases may be chemically complex. Milk consists also of three parts: (i) an oil-in-water emulsion in which the fat droplets are dispersed in the serum, (ii) a colloidal suspension of casein micelles, protein and lipoprotein particulates and the aqueous phase (iii) containing soluble proteins, mineral salts and vitamins [2].

The dairy industry, like most other agro-industries, generates large amounts of wastewaters produced in the form of o/w emulsions which are difficult to treat properly because of their complex behavior. Dairy waste effluents are concentrated in nature, and the main contributors of organic charge to these effluents are carbohydrates, proteins and fats originating from milk [3]. These liquid wastes are characterized by high levels of biological oxygen demand (BOD) and chemical oxygen demand (COD), together with the presence of nitrogen and phosphorus. Because of these polluting features, wastewaters issued from the dairy industry have to be treated before their discharge in the environment. Numerous processes can be used for the treatment of dairy wastewaters. They are based either on the recovery of valuable components, mainly proteins and lactose, or on the degradation of substances that can alter negatively the environmental quality of the water courses [4].

The leading techniques carried out to treat these types of oily wastewaters are conventional aerobic purification [5–7] and anaerobic processes [3,4,8]. However, others techniques have also been used, e.g. coagulation flocculation [9], nanofiltration (NF) [10], reverse osmosis (RO) [10,11] and use of membrane bioreactors [12]. Biological processes require big spaces and long time of treatment and generate great amount of sludge. The physico-chemical processes suffer the disadvantage that reagent costs are high and the soluble COD removal is low [4]. Besides, chemical treatments could induce a secondary pollution due to the fact that chemical additives may contaminate the treated water. Among physico-chemical methods, electrocoagulation technique is one of the processes which offer high removal efficiencies in compact reactors, with simple equipments for control and relatively moderate operating cost.

In milk, dispersed fat droplets are stabilized by the anionic and amphiphile casein proteins. Since dairy wastewater is considered as stable oil in water effluents, electrochemical processes such as electrocoagulation, electroflotation and electrooxydation could be alternative techniques for their treatment.

Electrocoagulation (EC) is an electrolysis process with reactive (or soluble) anode out of iron or aluminum. The action of the electrical

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current between the two electrodes allows the formation of metal ions (Al^{3+} or Fe^{2+}) by anode oxidation. The metallic ions combine with the hydroxyle ions produced by water electrolysis occurring at the cathode surface, to form metal hydroxides which favor the formation of flocs. The flocs formed can be recovered on the liquid surface by scrapping – when the bubbles of electrogenerated gas induce their flotation – or after setting depending on their density.

EC technique has been applied to treatment of water containing suspended solids [13]; fats, oils and greases [14–16]; color and dyes [17,18]; heavy metals [19]; landfill leachates [20] and phosphate [21].

The electrochemical reactions involving metal M (aluminum) as anode can be summarized as follows:At the anode:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-}. \quad (1)$$

The reaction occurring at the cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced through Eq. 2, whereas under acidic conditions Eq. 3 describes better hydrogen evolution at the cathode:

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \quad (2)$$

$$2H^{+}_{(aq)} + 2e \rightarrow H_{2(g)}. \quad (3)$$

The generated metal ions ($Al^{3+}_{(aq)}$) immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. The prevalence of the ionic or amorphous species is governed by operating conditions such as temperature, pH and the presence of other chemical species.

For practical applications, common electrolytes such as NaCl, Na_2SO_4 or KCl are most often added at low to moderate concentrations to obtain a sufficient electrical conductivity of the fluid to be treated, thereby increasing the efficiency of the process. When chlorides are present in the liquid waste, Cl_2 and OCl^- can be produced from anodic discharge of chloride ions according to Eqs. 4–6 [14,17]. Hypochlorous ion, OCl^-, is a strong oxidant, which could oxidize some of the organic molecules present in wastewater. Milk is a natural stable emulsion that originally contains chloride ions.

$$2Cl^{-} - 2e \rightarrow Cl_2 \quad (4)$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^{-} + H^{+} \quad (5)$$

$$HOCl \leftrightarrow OCl^{-} + H^{+}. \quad (6)$$

Electrocoagulation (EC) is a complicated process involving various chemical and physical phenomena. Previous researchers have developed a largely empirical approach to understand electrocoagulation [22,23]. The process performance is controlled by the lumped action of the electrochemical, physicochemical and hydrodynamic parameters.

In spite of the considerable success of electrocoagulation for the treatment of various types of wastewater, its application as a possible technique for the treatment of dairy wastewater is scarcely described in literature. However, electrocoagulation of dairy effluents has already been carried out by Sengyl and Ozacar [24] with steel electrodes and Tchamango et al. [25] with aluminum electrodes. But, to the best of our literature knowledge, effect of electrodes material on the electrocoagulation of dairy wastewater, has not yet been investigated. In the present study, electrochemical technique was used at bench scale to treat synthetic dairy effluents, obtained by dissolution of milk powder in distilled water and addition of sodium chloride. For this purpose, anodes and cathodes made of aluminum or platinized titanium (Ti/Pt), were used in different configurations. The feasibility and the main parameters influencing the performance of the process to remove COD, phosphates and turbidity, were evaluated.

2. Materials and methods

The electrochemical cell, consisting of a cylindrical vessel provided with two parallel plate electrodes, was used batch-wise in all experiments. Dimensions of aluminum electrodes were 30 mm × 150 mm × 2 mm, with an effective area of 12.10^{-4} m^2. Platinized titanium electrodes were 30 × 150 mm grids of expanded metal. The anode-to-cathode gap was maintained constant at 20 mm. Electrodes were connected to a DC power supply (ALTAI HEP-613; 0-30V; 0-2.5A) equipped with both ammeter and voltmeter, to measure the current passing through the circuit and the cell voltage, respectively. The experiments were carried out in the galvanostatic mode, i.e. at constant current. The effluent under treatment was homogenized by gentle magnetic stirring at 300 rpm. The agitation also allows the separation of gasses formed from the solution, thus avoiding the formation of foam which can affect the course of the batch process. To avoid electrode passivation and any contamination, after each experiment the electrochemical cell and the electrodes were cleaned with detergent and acetone, then rinsed with distilled water. All experiments were carried out at room temperature i.e. at 25 °C ± 2 °C), repeated twice and the experimental uncertainty could then be estimated to 3–5%.

Waste liquids were prepared from a commercial milk powder which was diluted in distilled water to form a very stable emulsion. The liquids were prepared on the basis of a real dairy wastewater, obtained from a dairy farming located east of Algiers and whose characteristics are reported in Table 1. A concentration of 4 g/L in milk powder, which was considered in all experiments, corresponded best to the actual dairy wastewater sample, in particular with very close COD values. The mean diameter droplet measured with a Malvern Mastersizer nano S was near 150 nm; the zeta potential of the emulsion determined using a Malvern Zetasizer 3000HS was found at 26 mV.

Electrochemical experiments in the batch process were followed by the measurement of COD, turbidity, phosphate, conductivity and pH. COD levels were determined using the standardized calorimetric technique with an excess of hexavalent chromium and subsequent measurement of the optical density. Turbidity was measured by a Hanna Instrument LP 2000 turbidimeter. The pH was measured using a Hanna pH-meter. Conductivity was measured by a Hanna instrument EC 214-EC 215. The analysis of phosphate was carried out using the standard yellow vanadomolybdophosphoric acid method by a double beam spectrophotometer Shimadzu UV-160 A. The dissolved aluminum concentration was determined by atomic absorption spectrometry (PYE UNICAM /SOLAAR 929), after nitric acidification and suitable dilution of samples taken in the electrolytic solutions.

All chemicals used in the experiments were of analytic grade. Aluminum electrodes were made alloy AU4G (2017-Al) which is widely used in mechanical construction and has a significant content of Cu (4%), with the presence of Fe (0.7%), Mg (0.7%), Mn (0.7%), Si (0.5%), Zn (0.25%) and Cr (0.1%).

The sludge formed during EC process was characterized by scanning electron microscopy (SEM) and X-ray microanalysis. The analysis was performed on a Phillips XL-30 microscope to determine the composition and configuration of the structure. SEM provides images of surface feature with a resolution of fractions of a micrometer; while energy disperse X-ray spectroscopy offers in situ

Table 1
Characteristics of real dairy wastewater and untreated sample, after addition of 1.5 g/L of NaCl.

Parameters	Real wastewater	Experimental sample
COD (mg d'O_2/L)	7280	7560
P-PO_4^{3-} (mg/L)	31	41
Turbidity (NTU)	1545	1348
pH	5.8	6.6
Conductivity (mS/cm)	3.9	3.1