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Elimination of whey proteins by electro-coagulation: investigation of some key operational parameters and modeling

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ABSTRACT

Whey proteins removal from water by electro-coagulation (EC), a non-specific electrochemical technology was investigated for the first time. Experiments were carried out in synthetic wastewater in batch mode using aluminum electrodes. The respective influences of initial pH (pH_i), initial whey proteins concentration, applied current and electrolyte concentration were investigated. Results showed that the best (100%) and fastest removal of whey proteins was observed at pH_i 4, current 4.5 A, and electrolyte concentration 6.25 g/L. The mechanism responsible for whey proteins elimination was found to be adsorption onto the flocs. Adsorption of whey proteins on flocs forming during EC at all tested currents (78.0 mg N/g solid, 61.57 mg N/g solid, and 53.18 mg N/g solid at current of 1.5 A, 3.0 A, and 4.5 A, respectively) was shown to be more efficient than adsorption of these whey proteins on preformed flocs (27.78 mg N/g solid) at the same initial concentration of 0.75 g/L. A model able to describe quantitatively protein removal was established. Experiments also showed that EC cost increased with increasing pH_i, current and electrolyte concentration. They demonstrate that EC is a promising technology for the elimination of whey proteins from dairy effluents.

Keywords: Whey proteins; Electro-coagulation; Wastewater treatment; Adsorption

1. Introduction

The increasing scarcity of clean water sets the need for appropriate management of available water resources. Regions suffering from a lack of water urgently need integrated environmental protection and resource conservation technologies in order to enable effective management of the available water resources [1]. As a solution for water scarcity, wastewater which has been altered by human activity, whether domestic, industrial or agricultural, must necessarily be treated, with the aim to preserve the resource, while promoting cost and energy savings.

The treatment of industrial wastewater is a difficult task as this exhibits large variations of flow rate and composition, high concentrations of organic matter and salts, and the presence of poorly biodegradable organic compounds or substances [2]. From these wastewaters, those from agro-industries are characterized by a high chemical oxygen demand (COD) due to their high organic content. The dairy industry which generates a huge quantity of wastewater is particularly concerned: approximately 0.2 L to 10 L of waste per liter of processed milk [3]. These wastewaters contain whey that is the liquid phase recovered from the curds formed during cheese production. This liquid represents 80–90% of the total volume of milk used in the cheese-mak-

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ing process. Whey can be processed and reused for animal feed or for human consumption [4]. Whey proteins which constitute about 10% of the total dry solids in whey and 15–20% of total milk proteins contribute to the increase of COD. These whey proteins are globular proteins with molar mass ranging from 14 to 1,000 kg/mol and are composed of 60% β-lactoglobulin (β-Lg), 22% α-lactalbumin (α-La), 9% immunoglobulins (Ig) and 5.5% bovine serum albumin (BSA) [5]. In small dairies producing cheese, whey reuse is not practicable and whey is, therefore, discharged as waste along with the rest of wastewater.

Actually, the disposal of whey produced during cheese production has always been a major problem because of its organic material content [6]. Dairy wastewaters are usually treated using biological methods, such as activated sludge process, aerated lagoons, aerobic bioreactor, trickling filters, sequencing batch reactor (SBR), up flow anaerobic sludge blanket (UASB) reactor, up flow anaerobic filters and biocoagulation. On the one hand, aerobic biological processes are highly energy intensive, whereas anaerobic treatment of dairy wastewater reflects a very poor nutrient removal, so that effluents treated by anaerobic biological processes need additional treatment [7]. In the last decades, it has been revealed that electro-coagulation (EC) is an attractive and appropriate method for the management of various kinds of wastewater due to various benefits, including environmental compatibility, versatility, energy efficiency, safety, selectivity, susceptibility to automation and cost efficiency [8]. Electro-coagulation which is a non-specific electrochemical technique has been proposed as a promising alternative to chemical coagulation for removing various pollutants from freshwaters and wastewaters. It is based upon the production of soluble metal cations and insoluble metal hydroxides in water using sacrificial metal anodes. These cations and hydroxides interact with pollutants through several mechanisms, including charge neutralization, adsorption, coprecipitation and enmeshment. Pollutants can also be removed from water by electro-flotation, caused by micrometer-sized hydrogen bubbles (15–23 μm diameter) which are produced on the cathode surface. This electro-flotation process can occur simultaneously with sedimentation, but solid particles can also be removed using filtration [9]. The reactions that take place at electrodes in EC are as follows. For aluminum electrodes, oxidation reaction takes place at the anode:

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

Reduction reaction takes place at the cathode:

$$3H_2O + 3e^- \rightarrow (3/2)H_2 + 3OH^- \quad (2)$$

Overall reaction during electrolysis can be summarized as [10]:

$$Al^{3+} \rightarrow Al(OH)_n^{(3-n)} \rightarrow Al_2(OH)_2^{4+} \rightarrow Al_3(OH)_4^{5+} \rightarrow Al_{13} \text{ complex} \rightarrow Al(OH)_3 \quad (3)$$

Electro-coagulation has successfully been used for the treatment of wastewaters, including dairy wastewater [11], alcohol distillery wastewater [12] and textile wastewater [13]. Meanwhile, EC process has been widely used to treat wastewater, including a high quantity of oil grease, COD and toxic substances, such as olive oil mill wastewater [14]. Moreover, even if electro-coagulation of dairy wastewater has been carried out by some researchers, only Guven et al. [15] and Un et al. [4] have studied electro-coagulation of cheese whey wastewater in the literature. However, concerning electro-coagulation of proteins, only Robić and Miranda [16] studied the recovery of bovine serum albumin and a phenolic compound, catechin, by EC. As far as the authors know, the literature describing the effect of electro-coagulation on whey proteins remains scarce.

In this study, the objective is, therefore, to investigate the elimination of whey proteins from water by electro-coagulation in the batch mode using aluminum electrodes as a function of current density. For this purpose, synthetic wastewater with various properties was prepared, so that the influence of initial whey proteins concentration, initial pH and electrolyte concentration could be studied on the efficiency of whey proteins removal. The results were used to better understand the mechanisms governing protein removal and to establish a model able to describe quantitatively the evolution of protein concentration *vs*. electrolysis time.

2. Materials and methods

2.1. Whey proteins solution preparation

The solution was prepared by dissolving whey protein isolate (PROMILK 852 FB1, 85% proteins in which nitrogen represents about 15.92%) with ultra-pure water by the help of a magnetic stirrer at a speed of 500 rpm for 2 h accompanied by gentle heating (40°C) to ensure a complete dissolution. Several initial concentrations were used (0.75 g/L, 1.5 g/L and 3.0 g/L). Initial pH (pH_i) was adjusted by a minute addition of 0.1 M HCl or KOH solution (pH_i 4, 7 or 9) in such a way that it did not modify significantly water conductivity (κ), knowing that the original pH of the solution is 6.7. Conductivity was modified by the addition of electrolyte (KCl) with various concentrations (1.25 g/L, 3.75 g/L and 6.25 g/L).

2.2. Experimental setup

In this study, electro-coagulation was applied to synthetic whey proteins solution. Electro-coagulation was carried out in a 4-L cylindrical tank, and agitation was performed by a Rushton turbine at a constant rate of 240 rpm. This rate was chosen since higher tested rotation speed up to 800 rpm consumes more energy and, at the same time, does not increase the efficiency of the process. EC was conducted in the galvanostatic mode using a 30 V-10 A power supply (ELC, France), while the cell voltage (U) was recorded to derive the electric power input. Current, which is the key parameter of EC, was also varied between 1.5 A and 4.5 A. The experimental setup is depicted in Fig. 1. Planar rectangular aluminum electrodes of identical dimensions (8.0 cm × 6.5 cm) were used as anode and cathode. Electrodes were rinsed with acetone and a 0.01 N HCl solution to remove organic and inorganic deposits, and then, weighed before

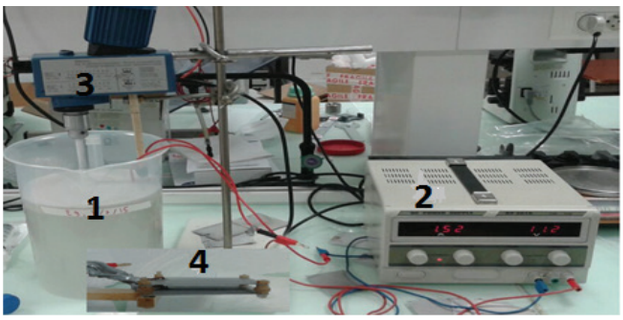


Fig. 1. Experimental setup (1: EC tank; 2: DC power supply; 3: Agitator; 4: Aluminum electrodes).

and after each use to calculate the faradaic yield. For all the runs, the inter-electrode gap was maintained at 1 cm. Electrolysis time (t) was 60 min. Experiments were carried out at room temperature and atmospheric pressure and each experiment was repeated twice for assessing reproducibility of data. During EC, samples were taken out at different time intervals and filtered by 0.45 µm filters (Macherey-Nagel GmbH, Germany); the filtrates were then used for subsequent chemical analysis.

2.3. Analyses

To test for the elimination of whey proteins, total nitrogen was measured in each liquid sample using a TNM-1 analyzer (Shimadzu, Japan).The pH and the conductivity of water were monitored over time using a Seven Easy pH meter (Mettler-Toledo, Switzerland) and a CDM210 conductimeter (Radiometer Analytical, France), respectively.

Flocs recovered by sedimentation/flotation were filtered, washed and dried at 120°C overnight before being weighed to quantify the mass of dry sludge. To test for the fate of the eliminated species, the solids were dissolved in HCl (0.1 M) to confirm the adsorption of whey proteins on the flocs during EC. The TNM-1 total nitrogen analyzer was used to estimate the amount of nitrogen in the dissolved solid phase. The solid phase was also characterized by nitrogen BET surface area analysis based on nitrogen adsorption at 77 K (Tristar II, Micromeritics Instr., USA).

2.4. Experimental strategy

The final objective is to develop a model based on a physical understanding of protein removal and robust against scale-up, which excludes for example design of experiments and response surface methodologies. The influence of wastewater properties on protein removal yield *vs*. electrolysis time will be investigated first: this study covers the initial pH to account for acid and neutral whey, respectively, and the effect of the initial concentration of whey proteins. Then, the operating parameter of electro-coagulation, current, will be investigated. Finally, the opportunity to enhance protein removal by changing water conductivity will be explored. These experimental results will be used to establish successively an economic analysis of the process, a better understanding of the mechanisms of protein removal and, lastly, a predictive model.

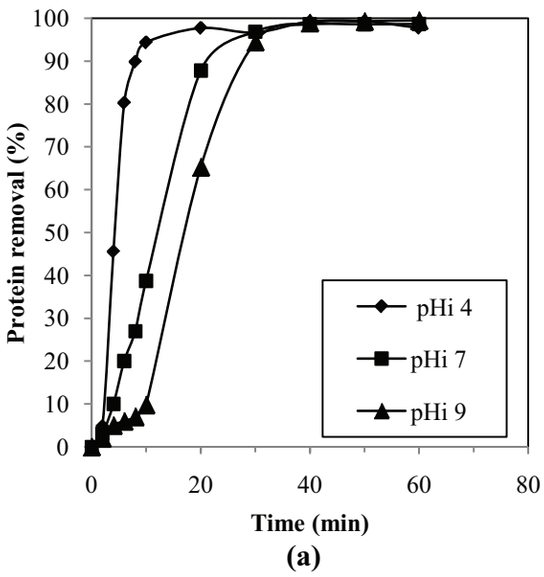
3. Results and discussion

3.1. Influence of initial pH

In chemical or electrochemical separation processes, pH is a key parameter and has a significant effect on the formation of hydroxide metal types and the mechanism of ion and pollutant removal [17]. The experimental data from the TNM-1 analyzer showed that, whatever the pH_i value, the protein removal yield reached about 99.5% after 40 min of treatment (Fig. 2(a)). However, the removal rate was the fastest at pH_i 4 where removal reached about 95% after only 10 min of treatment, which corresponded to 39% removal at pH_i 7 and only 10% removal at pH_i 9. This could be explained by the fact that usually, at pH 4–8, Al^{3+} and OH^- ions generated by electrodes react to form various monomeric and polymeric species that finally transform into insoluble amorphous $Al(OH)_3(s)$ through complex polymerization [18]. In this case, the highest rate of elimination at pH_i 4 would be explained by the adsorption of whey proteins on the solids during electro-coagulation. The removal that was enhanced at pH_i 4 is contradictory with almost all the literature data [11], and this can be explained by the fact that pH is increasing with time during EC (Fig. 2(b)). More precisely, and after 10 min of treatment, pH reached 6.1 when pH_i was 4 and the recovery was 95%; this is expected since solubility of $Al(OH)_3$ is minimum at pH 6–7 for very low Al^{3+} concentrations [14]. Conversely, pH reached 8.4 when pH_i was 7, which corresponded to 39% removal, since soluble anionic aluminum hydroxides start forming at this specific pH. Moreover, pH 4 is lower than the isoelectric point of the whey proteins. The isoelectric point of these proteins is 5.2 for β-Lg, from 4.2 to 4.5 for α-La, from 4.7 to 4.9 for BSA and between 5.5 and 6.8 for Ig [5]. This makes them less soluble when pH is close to 5 and, consequently, more easily captured by the solid flocs. On the other hand, at high pH, the concentration of the highly soluble monomeric anion $Al(OH)_4^-$ increases at the expense of $Al(OH)_{3(s)}$ [18]. Thus, floc formation is inhibited and, consequently, a lower efficiency of floc formation at higher pH_i values was proved experimentally, as only 1.1 g of solid was formed at pH_i 9 compared to about 1.5 g at pH_i 4 and 7. In addition, at pH higher than 8.5, all the aluminum hydroxides formed have lost their positive charge and; therefore, the adsorption of protein is reduced, since the gel and the proteins no longer have opposite charges under this condition [16]. Our results contradict, however; those of Robić and Miranda [16] who found that the maximal removal of BSA was at pH 8, but it must be reminded that BSA represents only a small fraction of whey proteins (~5.5%).

3.2. Influence of the initial concentration of whey proteins

A new set of experiments was dedicated to the study of the influence of the initial concentration of whey proteins on their removal efficiency. As shown in Fig. 3, after the end of treatment, about 100% of proteins were removed for both initial concentrations 0.75 g/L and 1.5 g/L; however, only 96% were removed when the initial concentration was 3.0 g/L. In addition, removal rate depended clearly on the initial concentration; this means that the evolution of the removal rate was faster with lower con-



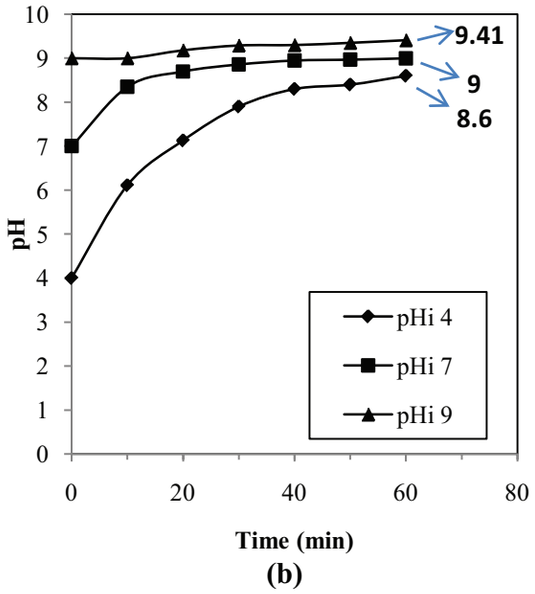


Fig. 2. Effect of initial pH (pH_i) on whey proteins removal (a) and on pH evolution (b) during electro-coagulation. Experimental conditions: Initial concentration of whey proteins 0.75 g/L, Current 1.5 A, KCl concentration 6.25 g/L, electrolysis time 60 min.

centrations, as it reached 85%, 55% and 50% for the initial concentrations 0.75 g/L, 1.5 g/L, and 3.0 g/L, respectively, after only 10 min of treatment, even though the quantity of proteins removed at time *t* increased with their initial concentration. So, as a rule of thumb, we can say that the removal efficiency of whey proteins decreases with an increase in the initial concentration of whey proteins for a constant current density. This results from the fact that the number of metal hydroxide flocs formed is insufficient to coagulate the greater number of protein molecules at

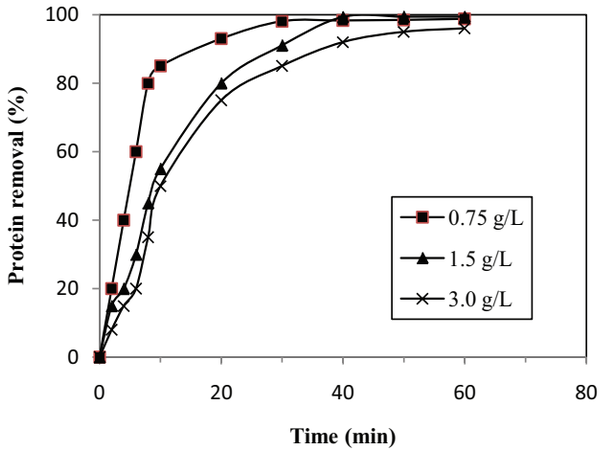


Fig. 3. Effect of initial concentration on whey proteins removal. Experimental conditions: current 1.5 A, KCl concentration 6.25 g/L, initial pH 6.7, electrolysis time 60 min.

higher initial concentration [10]. At the industrial scale, one must increase the surface of electrodes used, while keeping a constant current density to achieve the same removal efficiency as in our study.

3.3. Influence of current

In all the electrochemical processes, current density is the most important operating parameter for controlling the reaction rate inside the electrochemical reactor. It has been well shown that current can determine the production rate of coagulant, the production rate of bubbles, their size and distribution, and the rate of floc growth in electro-coagulation reaction with different electrodes [19]. This new set of experimental runs was dedicated to the study of the influence of the current (I) on whey proteins elimination using EC with Al electrodes. Three current values were tested (1.5 A, 3.0 A, and 4.5 A). In our results, complete elimination was obtained after 30 min of treatment with the three currents (Fig. 4(a)). However, the rate of removal was much faster with current 4.5 A where it was about 97% after 10 min of treatment, compared to only 30% and 72% with 1.5 A and 3.0 A, respectively, after the same time interval. This could be explained by the fact that at high current, the amount of aluminum oxidized increased, resulting in a greater quantity of precipitation [20].

To further investigate the relation between I and pH, and its influence on whey proteins elimination, pH change rate was investigated at different currents. It was found that the pH change rate depended strongly on the current applied to the EC unit. The highest current used led to the fastest rate of pH change during EC (Fig. 4(b)). It was also found that when current was 4.5 A, pH varied after 8 min of treatment between 7.0 and 8.2, which is the most suitable pH for floc formation. This results from the fact that during electro-coagulation, higher currents lead to a faster cathodic reduction and, thus, a faster production of OH^- anions. Moreover, the fastest elimination of whey proteins at the highest current is due to the highest dissolution rate

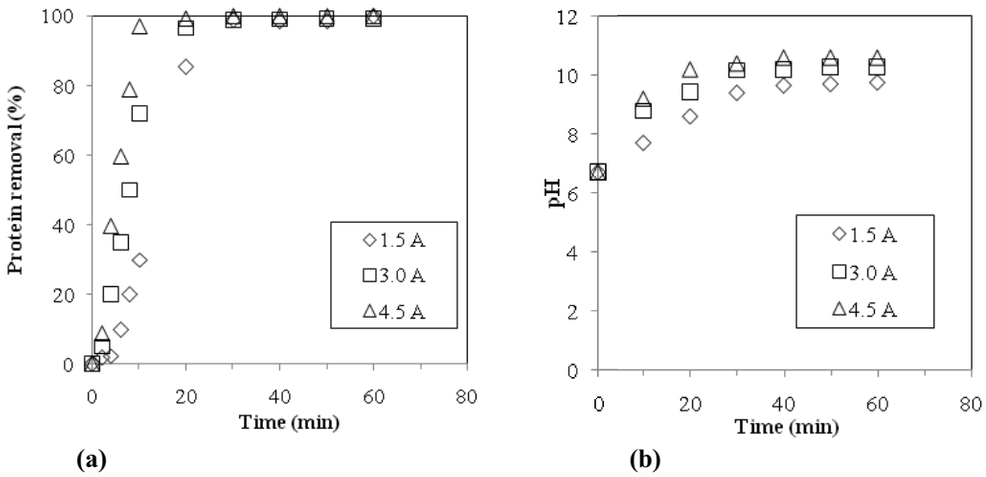


Fig. 4. Effect of current: (a) on whey proteins removal, and (b) on pH evolution during EC. Experimental conditions: initial whey proteins concentration 0.75 g/L, KCl concentration 6.25 g/L, pH_i 6.7, electrolysis time 60 min.

of the sacrificial aluminum anode, which in turn contributes to the release of more Al^{3+} cations and, consequently, faster floc formation over time.

3.4. Influence of electrolyte (KCl) concentration

The effect of supporting electrolyte (KCl) concentration (1.25 g/L, 3.75 g/L and 6.25 g/L) on the removal efficiency of whey proteins was investigated, so as to modify water conductivity. These concentrations correspond to conductivity values of 1.36 mS/cm, 3.79 mS/cm and 6.80 mS/cm, respectively. Our results show (Fig. 5) that KCl concentration did not have any significant effect on the final removal yield of proteins, as this was about 99.2% after 30 min for the three KCl concentrations used. However, the rate of elimination was much faster when KCl concentration was 6.25 g/L, as removal yield reached about 78.5% for KCl concentration of 6.25 g/L after 20 min of treatment, while this was only 66.3% and 39.9% for KCl concentrations of 3.75 g/L and 1.25 g/L, respectively. This could be explained by the higher amount of Cl^- anions which could enhance the dissolution of the aluminum anode by pitting corrosion [21]. Enhanced dissolution, in turn, leads to higher amounts of Al^{3+} ions that increase the production of $Al(OH)_3$, causing higher elimination of whey proteins. These results might also be explained by the fact that the increase of the conductivity of the solution induces a higher screening for the electrostatic interactions, which could improve protein capture by aluminum hydroxides. Another reason is that the increase of water conductivity reduces the ohmic drop (IR) which is described by Eq. (4):

$$IR = \frac{I \cdot d}{A \cdot \kappa} \quad (4)$$

where I is the current (A), d is the inter-electrode distance (m), A is the active anode surface (m^2), κ is the specific conductivity (S/m). At higher conductivity, the applied potential needed to maintain a constant current decreases. This

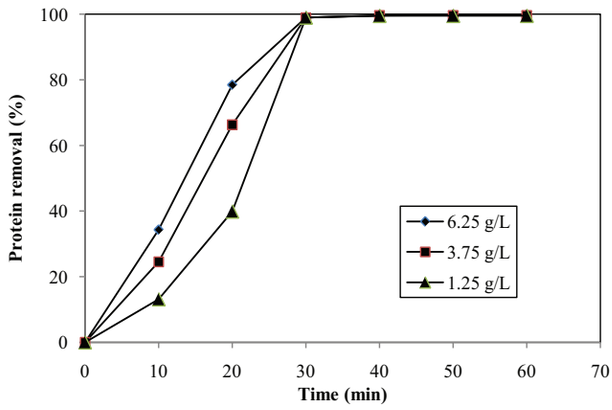


Fig. 5. Effect of electrolyte concentration on whey proteins removal. Experimental conditions: initial concentration of whey proteins 0.75 g/L, current 1.5 A, pH_i 6.7, electrolysis time 60 min.

means that the power requirements of EC also decrease. But in this work, it was also observed that the faradaic yield increased with water conductivity, which means that the rate of anodic oxidation also increased. As the faradaic yield becomes higher, the number of cations released at the anode also increases, and thus, removal efficiency increases.

3.5. EC cost analysis

One of the most important parameters that greatly influences the practical applicability of any technology of treatment is the cost of the applied process. The operating cost of EC ($/m^3$) was calculated as the sum of the costs of consumed material, electrical energy consumption and salt consumption. The price of electrical power used was considered 0.13 $/kWh, the price of the electrode material used was estimated as 1.5 $/kg Al, and the price of potassium chloride (KCl) was considered 0.30 $/kg. EEC is the

electrical energy consumption (kWh/m^3 water) after 60 min of whey proteins solution treatment. The electrical energy consumption was calculated in terms of kWh per m^3 of treated effluent using Eq. (5):

$$EEC(\text{kWh/m}^3) = \frac{U \cdot I \cdot t}{V} \quad (5)$$

where U is the cell voltage (V), I is the current (A), t is the electrolysis time (h) and V is the volume (L) of effluent to be treated. In parallel, EMC (kg/m^3) is the electrode material consumed at the same time t considered for EEC above. The amount of material dissolved from the anode is calculated by measuring electrode mass before and after electro-coagulation. Finally, SC is the salt consumption expressed in kg/m^3 and the EC cost was evaluated in terms of current, KCl concentration and pH_i, as follows:

$$\text{EC Cost}\ \left(\$/\text{m}^3\right) = 0.13 \cdot \text{EEC} + 1.5 \cdot \text{EMC} + 0.3 \cdot \text{SC} \quad (6)$$

First, it is clear from Fig. 6 that increasing KCl concentration always increases EC cost within the range studied. This increased from 1.11 \$/m^3 at KCl concentration of 1.25 g/L to 2.26 \$/m^3 at KCl concentration of 6.25 g/L. However, increasing KCl concentration decreased EEC cost due to conductivity increase, which decreased the total resistance (ohmic drop) of the solution; so, the needed voltage to maintain a given current decreased and, thus, electrical energy consumption decreased. However, this cost decrease was not enough to reduce the overall cost of the process, since at higher KCl concentration, SC increased from 0.375 \$/m^3 at KCl concentration of 1.25 g/L to 1.875 \$/m^3 at KCl concentration of 6.25 g/L. Moreover, faradaic yield increased from 105% at KCl concentration of 1.25 g/L to 120% at KCl concentration of 6.25 g/L, which also increased EMC from 0.198 \$/m^3 to 0.226 \$/m^3.

Then, Fig. 7 describes the influence of current on EC cost. A general observation that can be inferred is that higher current always leads to higher EC cost within the range investigated: increasing current from 1.5 A to 4.5 A increased EC cost from 2.31 \$/m^3 to 3.87 \$/m^3. In this figure, most of the costs at the three tested currents were due to SC, but this cost was identical for all the currents used. The difference in the total cost was due primarily to EEC. As current increased from 1.5 A to 3.0 A and 4.5 A, EEC contribution to EC cost increased, as it contributed to ~20% and ~33% from the total EC cost at current 3.0 A and 4.5 A, respectively, compared to ~8% at 1.5 A. Higher energy expenditure at higher current could be easily explained by Eq. (4), as this is linearly related to IR × I contribution. Another factor contributing to the difference in total cost of the process is EMC, as EMC increased from 0.23 \$/m^3 at current of 1.5 A to 0.69 \$/m^3 at current of 4.5 A.

Concerning the effect of pH_i on EC cost, we can say, as shown in Fig. 8, that cost was slightly higher at pH_i 9 than at pH_i 4 and pH_i 7; more precisely, at pH_i 9, EC cost was 3.05 \$/m^3 compared with 2.94 \$/m^3 at pH_i 4 and 2.99 \$/m^3 at pH_i 7. The difference in costs at different pH_i values was almost negligible and was due to more energy expenditure at pH_i 9, and higher EMC at higher pH_i values, as faradaic yield increased from 116% to 128% as pH_i increased from 4 to 9. Higher energy consumption at pH_i 9 could be explained by the fact that, at higher pH values, deposits on the anode surface lead to an increasing ohmic drop (because of the inert, little conducting layer formed) and to an increase in the electrical consumption [22]. Lower pH values are, thus, preferable both from efficiency and maintenance point of view.

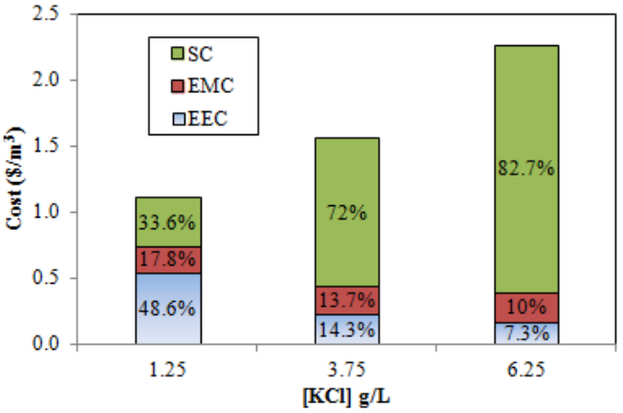


Fig. 6. Effect of electrolyte (KCl) concentration on EC cost. SC: salt consumption, EMC: electrode material consumption, EEC: electrical energy consumption. Experimental conditions: initial concentration of whey proteins 0.75 g/L, pH_i 6.7, current 1.5 A, electrolysis time 60 min.

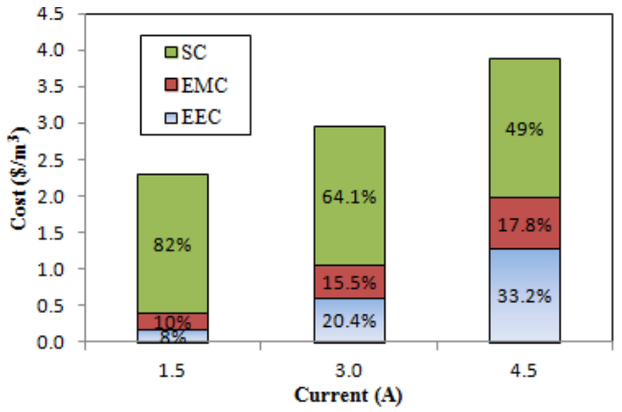


Fig. 7. Effect of current on EC cost. SC: salt consumption EMC: electrode material consumption, EEC: electrical energy consumption. Experimental conditions: initial concentration of whey proteins 0.75 g/L, pH_i 6.7, KCl concentration 6.25g/L, electrolysis time 60 min.

3.6. Analysis of the liquid and the solid phases

The analysis of liquid samples after 60 min electrolysis time, for I = 4.5 A and pH_i 4 using the TNM-1 analyzer, showed that almost 100% of whey proteins were removed from water. If there was no adsorption on the solid phase (flocs) or no gas release, that is to say only protein oxidation in the liquid phase, total nitrogen should have been constant over time in the liquid phase. However, experimental data (100% removal) highlight that proteins were

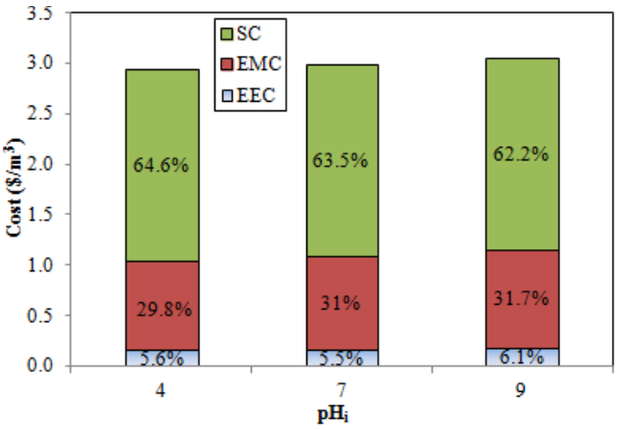


Fig. 8. Effect of pH_i on EC cost. SC: salt consumption, EMC: electrode material consumption, EEC: electrical energy consumption. Experimental conditions: initial concentration of whey proteins 0.75 g/L, current 1.5 A, KCl concentration 6.25 g/L, electrolysis time 60 min.

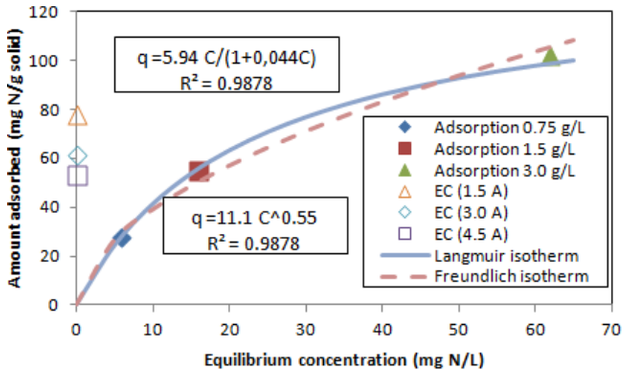


Fig. 9. Isotherms of whey proteins adsorption on preformed flocs at different initial concentrations without EC (filled symbols) and on flocs being formed during EC using a volume of water $V = 1$ L to standardize with adsorption experiments at different current (empty symbols). Conditions of floc formation: current 4.5 A, pH_i 6.7, KCl concentration 6.25 g/L, electrolysis time 60 min. Conditions of EC: initial concentration 0.75 g/L, pH_i 6.7, KCl concentration 6.25 g/L, electrolysis time 60 min.

preferentially adsorbed on the solid phase and that no CO_2 was produced. In fact, proteins with a low internal stability, the so-called "soft" proteins, such as bovine serum albumin (BSA), immunoglobulin (IgG) or α-lactalbumin generally tend to adsorb on all surfaces, irrespective of electrostatic interactions, owing to a gain in conformational entropy resulting from adsorption. Thus, the soft proteins do adsorb even on an electrostatically repelling surface [23], increasing adsorption on the solid at different operating conditions. This assumption is reinforced by Norde and Haynes [24] who studied the adsorption of α-lactalbumin on negatively charged polystyrene (PS) latex beads and on variably charged hematite. α-lactalbumin denatured on both PS, which has a hydrophobic surface, and on the hydrophilic surface of hematite. Here, we can say that the primary factor which determines the adsorption behavior of proteins to a sorbent is their structural stability. Whey proteins in which many soft proteins can be found exhibit therefore a weak internal stability, and are prone to adsorb on the surface of aluminum hydroxide. Moreover, the analysis of the dried flocs (solid phase) by nitrogen adsorption isotherm has shown that they exhibit a BET specific surface area that ranges between 30 and 50 m^2/g, which enhances the possibility of protein adsorption.

To investigate the fate of proteins during EC, the flocs were dissolved with 0.1 M HCl. The analysis done by TNM-1 analyzer ensured the presence of nitrogen entities in all tested conditions. The amount of these nitrogen entities is almost 98% of the initial nitrogen amount. To be sure that adsorption was responsible for whey proteins removal from the liquid, the same solid was produced by EC without the addition of proteins at current of 4.5 A, pH_i 6.7 and KCl concentration of 6.25 g/L. Four grams from the produced solid were added to whey proteins solutions of different concentrations (0.75 g/L, 1.5 g/Land 3.0 g/L). The solids were set in contact with the same initial concentrations of whey proteins used during EC for 24 h to reach equilibrium in order to test for adsorption. Analyzing the liquid phase using the TNM-1 analyzer showed an average of 95.2% decrease of the whey proteins initial concentration. This ensures definitely that during electro-coagulation, adsorption is the main mechanism responsible for the removal of whey proteins.

For comparison purposes, adsorption data are illustrated by Fig. 9. This compares the adsorption isotherms of whey proteins on preformed flocs and on flocs forming during EC. Results show that whey proteins are significantly adsorbed on preformed flocs at all tested initial concentrations. Equilibrium concentrations of 5.85 mg N/L, 15.98 mg N/L and 62 mg N/L were found at initial concentrations of 0.75 g/L, 1.5 g/L and 3.0 g/L, respectively. These equilibrium concentrations correspond to 95%, 93.2% and 86.8% removal efficiency at initial concentrations of 0.75 g/L, 1.5 g/L and 3.0 g/L, respectively. As formed flocs and whey proteins are not oppositely charged at pH 6.7, electrostatic attraction is not a possible mechanism for protein adsorption which is mainly driven by hydrophobic interactions. The effect of surface hydrophobicity on the adsorption of β-Lg (the main whey protein), was tested by Krisdhasima et al. [25]: they found that increasing hydrophobicity of silicon leads to increasing adsorbed amounts of β-Lg. Usually, an interaction with a hydrophobic surface is energetically more favored than with a hydrophilic surface because water molecules are released from the surface and from the protein, which leads to a large entropy gain.

The adsorption behavior of whey proteins on preformed flocs in our case seems to be best fitted by Langmuir adsorption model, as shown in Fig. 9. However, this model ignores the problem of reversibility, the fact that adsorption does not occur on fixed sites, that the spatial conformation of molecules usually changes upon adsorption and that lateral interaction may take place. This means that Langmuir assumptions are not necessarily correct for whey proteins, despite the good quantitative agreement in Fig. 9. Our experiments ensured the adsorption of whey proteins into

flocs, but the comparison of adsorption of whey proteins into already formed flocs to adsorption of these proteins on flocs being formed continuously during EC at the same initial concentration of 0.75 g/L displayed better adsorption during EC at all tested current values (Fig. 9). Experimental data showed that equilibrium concentration was always close to zero when the quantity of nitrogen adsorbed was 78.0 mg N/g solid, 61.57 mg N/g solid, and 53.18 mg N/g solid at current of 1.5 A, 3 A, and 4.5 A, respectively, compared with a maximum of 27.78 mg N/g solid for the quantity adsorbed on preformed flocs at the same initial protein concentration (0.75 g/L). This highlights that flocs formed during EC can contain far more proteins than preformed flocs, but also that protein removal is irreversible only during EC. This better adsorption performance with EC may be explained first by the enhanced mixing and mass transfer conditions near the anode: very small solid particles are formed in this region during EC, which leads to a very high inter-facial area, while hydrogen bubbles strongly contribute to the reduction of mass transfer limitation, which is known to be the main limiting step of protein adsorption due to the molecular weight of whey proteins. In addition, proteins adsorbed on very small flocs can be progressively imprisoned by the growth and the aggregation of solid particles during electrolysis; this makes adsorption irreversible and clearly differs from conventional adsorption in which inter facial area is constant. However, if current increases, more $Al(OH)_3$ is formed: so, the mass ratio of proteins to flocs decreases at constant protein concentration, leading to lower quantity of nitrogen adsorbed per gram of solid. As a result, higher adsorption at lower current during EC is due to the slower formation of flocs, so that a smaller amount of solid is more rapidly saturated by adsorbed proteins. Further work is still necessary to validate this analysis.

As a conclusion, our results demonstrate clearly that electro-coagulation is more efficient than conventional adsorption for the removal of whey proteins and that the *in situ* production of flocs is probably responsible for the enhanced effectiveness of EC.

3.7. Modeling of whey protein removal using EC

Contributions to process modeling based on EC are quite rare in the literature. Typical examples can be found on solid particles and chemical oxygen demand (COD) abatement [26] and fluoride anions removal [27]. EC is known as a process difficult to simulate because of the various mechanisms that contribute in parallel to pollution abatement, such as adsorption, coprecipitation, physical enmeshment and oxidoreduction in the bulk or on the electrodes. In this work, a simple model has been established from the mass balance on proteins using the following assumptions:

– Adsorption is the governing mechanism of protein removal;

– The mass of floc, *i.e.*, adsorbent, changes with time and is proportional to the mass of aluminum m released by electrodes, which can be deduced from Faraday's law using a constant faradaic yield over time $\phi_{Al} = 120\%$, the molar mass of Al (M_{Al}) and Faraday's constant (F):

$$m = M_{Al} \cdot \phi_{Al} \frac{I}{3F} t \tag{7}$$

Adsorption is thermodynamically driven, without mass transfer limitation, and can be described using Langmuir isotherm that relates the amount of proteins adsorbed (q, expressed in g proteins/g Al) to their concentration in the liquid phase (C, g proteins/L) using the mono-layer capacity q_m(g/g) and the affinity constant K (L/g Al):

$$q = q_m \frac{KC}{1+KC} \tag{8}$$

Consequently, the mass balance can be derived as follows:

$$V\frac{dC}{dt} = -q\frac{dm}{dt} - m\frac{dq}{dt} \tag{9}$$

Considering the derivatives of m and q as a function of time,

$$\frac{dm}{dt} = M_{Al} \cdot \phi_{Al} \frac{I}{3F} \; and \; \frac{dq}{dt} = q_m \frac{K}{(1+KC)^2}\frac{dC}{dt} \tag{10}$$

one finally gets the following ordinary differential equation that can be solved mathematically using a free (GNU Octave) or a commercial (Matlab®, The Math Works) equation solver:

$$\frac{dC}{dt} = -q_m \frac{dm}{dt}\frac{KC}{1+KC}\left[\frac{(1+KC)^2}{V\cdot(1+KC)^2 + mq_m \cdot K}\right] \tag{11}$$

K and q_m are the only adjustable parameters that can be deduced by fitting experimental data. This model differs from those described previously that neglect the transient concentration term dC/dt [25], or the dq/dt term [26].

The model was used, first, to investigate the influence of current. Using current loading, $I{\cdot}t$, as a unique variable able to describe data for current between 1.5 and 4.5 A at constant initial concentration and pH_i, the fair agreement between experimental and predicted data is presented in Fig. 10(a). An empirical model can also be adjusted on pH evolution as a function of current loading, which follows an exponential trend, *i.e.*, a first-order trend (Fig. 10(b)). Finally, Fig. 10 validates the assumptions of the model and highlights that protein removal can be easily predicted as a function of current and electrolysis time using Eq. (11). The comparison between the data from Fig. 9 and Fig. 10 is not straightforward, but using K = 15 L/g Al and q_m = 15 g proteins/g Al, one can estimate, for instance, that when 99% proteins are removed from water with an initial concentration of 0.75 g/L, q should be 1.5 g/g. Taking into account the 6.28 factor between nitrogen and proteins and the fact that Al content in flocs is between 25% and 33% w/w, one finally deduces that it corresponds to 60–80 mg N/g solid, which is in agreement with the experimental data extracted from Fig. 9.

Then, the effect of initial concentration was analyzed using the same model. Fitting the data was, however, more complex as far as the initial content of whey protein increases, as shown in Fig. 11. While the model fits perfectly the initial concentration 0.75 g/L for which it has been established with the same q_m and K values as in Fig. 10, it agrees reasonably with experimental data for 1.5 g/L and it deviates between 2,500 and 7,500 C when the initial content

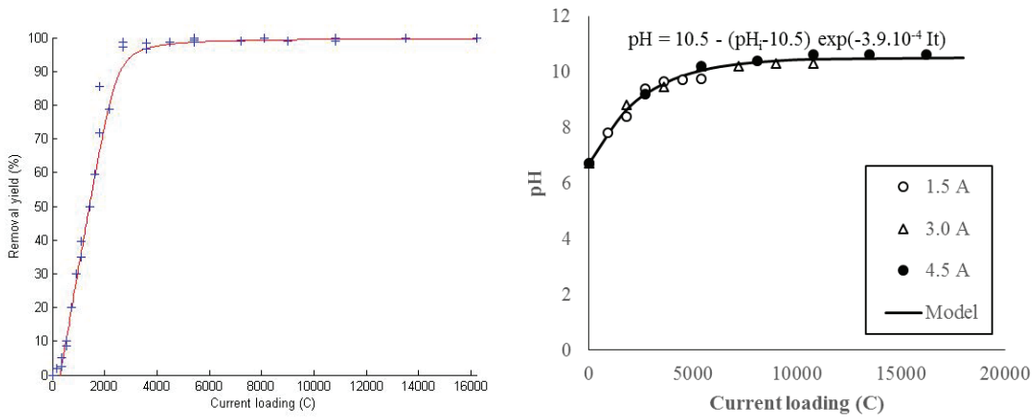


Fig. 10. Comparison of predicted (q_m = 15 g proteins/g Al and K = 15 L/g Al) and experimental data as a function of current loading: (a) protein removal yield; (b) pH. Experimental conditions: initial whey proteins concentration 0.75 g/L, KCl concentration 6.25 g/L, pH_i 6.7, electrolysis time 60 min.

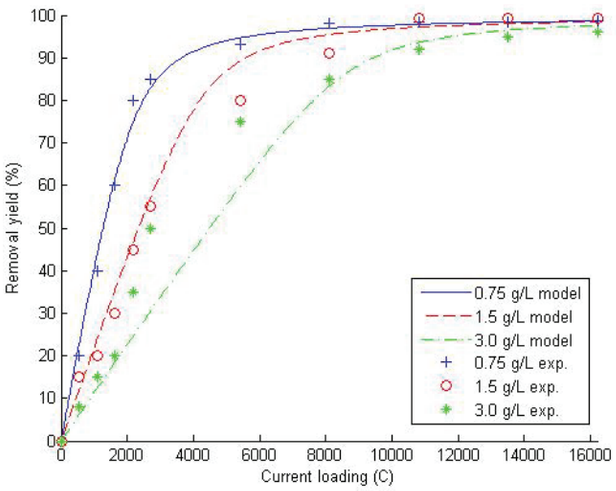


Fig. 11. Comparison of predicted (q_m = 15 g/g and K = 15 L/g) and experimental protein removal yield as a function of initial concentration. Experimental conditions: I = 4.5 A, KCl concentration 6.25 g/L, pH_i 6.7, electrolysis time 60 min.

is 3.0 g/L. But contrary to expectations, this deviation does not correspond to an overestimation of the removal rate due to a mass transfer limitation, but to an acceleration of protein removal. A parametric analysis of the model showed that only an increase of q_m from 15 to 20 g proteins/g Al can better fit the data when the initial protein concentration is 3 g/L, while the effect of K remains weak. This highlights an increase of the adsorption capacity of the flocs.

Several reasons can explain this trend, among which a self-aggregation mechanism of proteins in the liquid phase seems the most probable. This could be due to the electric field at high protein content when the initial protein concentration is high. The consequence would be to enhance protein removal, as this could lead to the adsorption of aggregates. This corresponds to an "apparent" multilayer adsorption that contradicts the assumption of Langmuir isotherm and cannot be predicted by the present model. In the literature, multilayer adsorption of whey proteins has already been reported [28], which reinforces this assumption, even though the detailed mechanism has not been studied in the presence of an electric field.

As a conclusion, the model described by Eqs. (7)–(11) can predict quantitatively protein removal for current between 1.5 A and 4.5 A, and for initial concentrations between 0.75 and 1.5 g/L, and to estimate the time needed for a complete removal at higher initial concentration up to 3 g/L. It requires only two adjustable parameters that must be readjusted only as a function of initial pH and conductivity. Even though it can still be improved to account for higher concentrations, the robustness of the parameters estimated at constant pH_i and conductivity when simulations are carried out as a function of current and initial concentration outperforms other models from the literature that usually require to adjust parameters for each new set of operating conditions. This model constitutes, therefore, a valuable tool for the design of EC process in the future.

4. Conclusion and perspectives

The treatment of water containing whey proteins by electro-coagulation using aluminum electrodes was studied in a batch reactor. Elimination of whey proteins has been investigated as a function of the following parameters: initial concentration, initial pH (pH_i), current and electrolyte concentration. Experimental results showed that the fastest removal of whey proteins occurred at pH_i 4, current 4.5 A, and electrolyte concentration of 6.25 g/L. Moreover, increasing the initial concentration of whey proteins decreased the rate of removal. Adsorption was found to be the main mechanism responsible for whey proteins elimination. Adsorption of whey proteins on flocs forming during EC at all tested currents (78.0 mg N/g solid, 61.57

mg N/g solid, and 53.18 mg N/g solid at current of 1.5 A, 3 A, and 4.5 A, respectively) was shown to be more efficient than adsorption of these whey proteins on preformed flocs (27.78 mg N/g solid) at the same initial concentration of 0.75 g/L. In addition, experimental data showed that a reduction of EC cost could be achieved by working at the lowest pH_i (4), where EC cost was 2.94 $/m^3, at the lowest current 1.5 A which resulted in EC cost of 2.31 $/m^3, and at the lowest KCl concentration (1.25 g/L), where EC cost was 1.11 $/m^3. An unexpected result is the high cost of salt consumption that must also be minimized using cheaper salts, such as NaCl (0.065 $/kg). Finally, a robust predictive model based on mass balance equations, Faraday's law and Langmuir isotherm was also established to describe protein removal using EC; this is not only able to fit experimental data, but it is also promising for other applications involving EC process.

Now, testing real dairy wastewater is the priority for further work so as to estimate the interaction between proteins and other matrix components on their removal. In addition, further work should be carried out to investigate whether adsorption may be reversible and if proteins refold to their native conformation after desorption.

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