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Christa Aoude

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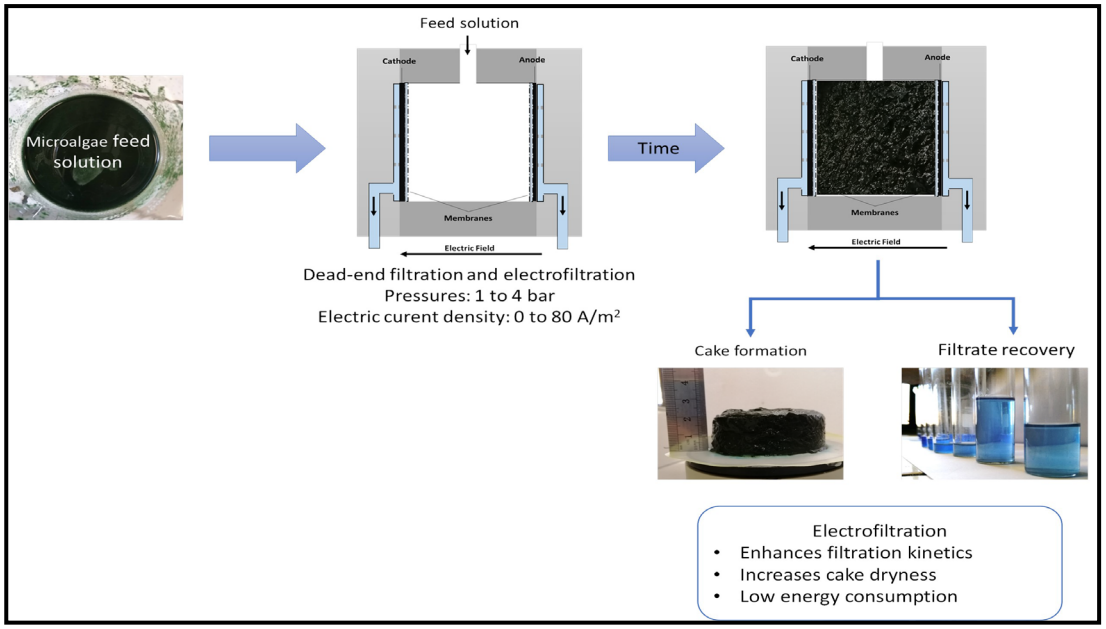
Thèse présentée en cotutelle pour l'obtention du grade de Docteur de l'UTC



Soutenue le 4 novembre 2022

Spécialité : Génie des Procédés Industriels : Transformations intégrées de la matière renouvelable (EA-4297)

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Concentration of the microalgae Arthrospira Platensis and Chlorella vulgaris by electrofiltration

Spécialité : Génie des Procédés Industriels

Par Christa AOUDE

Soutenue le 4 Novembre 2022

Devant la commission d'examen formée de:

Mme. Loubna Firdaous	Maitre de conférences (HDR), Institut Universitaire de Technologie (IUT) de Lille	Rapporteur
Mme. Maryline Vian	Professeur, Institut Universitaire de Technologie (IUT) d'Avignon	Rapporteur
M. Luhui Ding	Professeur, Université de Technologie de Compiègne, Compiègne, France	Examinateur
Mme. Jessica Desabres	Docteur, Société CHOQUENET France	Examinateur
M. Nabil Grimi	Professeur, Université de Technologie de Compiègne, Compiègne, France	Encadrant de these (Membre invité)
M. Henri El Zakhem	Professeur, University of Balamand, Balamand, Lebanon	Directeur de thèse
M. Eugène Vorobiev	Professeur, Université de Technologie de Compiègne, Compiègne, France	Directeur de thèse

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Abstract

Microalgae are microscopic organisms that present many beneficial properties and can be used in a wide range of industrial applications. One of the main issues encountered in microalgae biorefineries are the costs associated with the harvesting step, this is due to the energy intensive nature of the most commonly used processes for microalgae harvesting. Depending on the application, the microalgae can undergo further processing after the harvesting steps for the extraction of its intercellular compounds. *Chlorella vulgaris* and *Arthrospira platensis* are two types of microalgae that are commercially used in a wide range of applications. Given their industrial relevance, they are the microalgae strains that are studied in the context of this thesis.

The aim of this thesis is to optimize the use of dead-end filtration as a microalgae harvesting technique, this is achieved by studying the use of pressure driven dead-end filtration as well as electrically assisted dead-end filtration (hereby referred to as electrofiltration). In this context, the present work investigates the effects of the operating pressure, the electric current density, and the combination of the two on the filtration kinetics and the properties of the filter cake and filtrates. This work also assesses the possibility of using dead-end filtration as an in-situ extraction technique as well as the use of cake washing to recover biocompounds trapped in the pores of a microalgal cake. Three different cake washing configurations were assessed: pressure driven (pressure washing), electrically driven (electrowashing), and electrically enhanced pressure washing (pressure electrowashing).

Résumé

Les microalgues sont des organismes microscopiques qui présentent de nombreuses propriétés avantageuses et peuvent être utilisées dans différentes applications industrielles. L'un des problèmes principaux rencontrés dans les bioraffineries de microalgues est le coût associé à l'étape de récolte, cela est lié à la consommation énergétique élevée des processus les plus couramment utilisés pour la récolte des microalgues. En fonction de l'application, les microalgues peuvent subir un traitement supplémentaire après les étapes de récolte pour l'extraction de leurs composés intercellulaires. *Chlorella vulgaris* et *Arthrospira platensis* sont deux types de microalgues commercialisés et utilisés dans un large éventail d'industries. Compte tenu de leur pertinence industrielle, ce sont les souches de microalgues qui sont étudiées dans le cadre de cette thèse.

L'objectif de cette thèse est d'optimiser l'utilisation de la filtration frontale comme technique de récolte des microalgues, en étudiant l'utilisation de la filtration frontale sous pression ainsi que la filtration frontale sous pression avec l'application d'un champ électrique externe (appelée électrofiltration). Dans ce contexte, ce travail étudie les effets de la pression, de l'intensité du champ électrique, et de la combinaison des deux sur la cinétique de filtration et les propriétés du gâteau de filtration et des filtrats. Ce travail également évalue la possibilité d'utiliser la filtration frontale comme technique d'extraction « in-situ » ainsi que l'utilisation du lavage des gâteaux pour récupérer les biocomposés résiduels présents dans les pores d'un gâteau de microalgues. Trois configurations différentes de lavage du gâteau de filtration ont été évaluées : sous pression, sous un champ électrique (électrolavage), et sous pression assistée par un champ électrique (électrolavage sous pression).

List of publications

Journals

(1) Aoude, C., Grimi, N., El Zakhem, H., & Vorobiev, E. Dewatering of *Arthrospira platensis* microalgae suspension by electrofiltration (submitted May 5, 2022), Drying Technology.

(2) Aoude, C., Grimi, N., El Zakhem, H., & Vorobiev, E. Effect of electrofiltration on the extraction of biocompounds from *Arthrospira platensis* (undergoing submission)

(3) Aoude, C., Grimi, N., El Zakhem, H., & Vorobiev, E. *Electrowashing of microalgae Arthrospira Platensis filter cake*, (submitted July 12, 2022), Separation Science and Technology.

Conferences

(1) C. Aoude, N. Grimi, H. El Zakhem, E. Vorobiev. Novel dewatering method for microalgae: electrofiltration of *Chlorella vulgaris* and *Arthrospira platensis*, in Les Journées Jeunes Chercheurs Condorcet J2C2, Online, 2021.

(2) C. Aoude, N. Grimi, H. El Zakhem, E. Vorobiev. Improvement of *Arthrospira Platensis* dewatering by electrically assisted dead-end filtration, in: Algaeurope, Online, December 2021.

(3) C. Aoude, N. Grimi, H. El Zakhem, E. Vorobiev. Récolte et déshydratation de la microalgue *Chlorella vulgaris* par filtration frontale et électrofiltration, in the « 18ème congrès de la Société Française de Génie des Procédés (SFGP 2022) », November 2022, Toulouse.

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General Introduction

Microalgae have become a popular sustainable resource with a large range of applications in different industries, i.e. food, pharmaceuticals, cosmetics, water treatment, and biofuels, among many others [1–5]. This is due to microalgae's ability to accumulate a wide variety of biocompounds in an economically viable manner, making it an alternative source of industrial raw materials, i.e. proteins, lipids, carbohydrates, pigments, nutraceuticals, and antioxidants. Moreover, the production and processing of this alternative source of raw materials can be easily and sustainably scaled up within the context of a circular economy [6]. One of the main issues encountered in microalgal biorefineries are the costs associated with harvesting, concentrating, and drying the microalgal cells. Other problems encountered in these processing steps are related to the energy consumption of the process, its efficiency, and the effect of processing on the quality of the microalgae as well as its intracellular biocompounds [7–10].

Different factors must be taken into account when choosing and optimizing the most suitable harvesting, concentration, and/or drying technique in a biorefinery. For example, the shape and size of the microalgae that needs to be dewatered, the quantity of microalgae that needs to be harvested, and the industrial application the microalgae needs to be harvested for [9,11,12].

Some of the most commonly commercialized techniques are flotation, coagulation/flocculation, centrifugation, and filtration [8,12,13]. In some cases, a combination of different techniques is used in order to reach the desired concentration of microalgal cells while reducing the energy consumption of the dewatering process. Each harvesting technique presents its own advantages and disadvantages. Centrifugation is efficient at cell harvesting, but it is rather complex for large scale operations, and it is energy intensive. Coagulation and flocculation can be expensive depending on the chemicals that need to be used during harvesting as well as the need to separate those toxic chemicals from the concentrated microalgal cells. The use of filtration as a harvesting technique has been found to be efficient, reaching final concentrations of up to 27%, and consumes less energy than its counterparts. Despite the advantages of filtration, the technique still presents some limitations, such as membrane fouling which could subsequently lower the processing speed as well as its efficiency [11,14–17]. Many studies have developed methods to improve the performance of filtration techniques by developing methods (chemical or mechanical based) to reduce membrane fouling [18–22]. Two studies have assessed the use of electrofiltration for the dewatering of microalgae [23,24], and in both cases the filtration rates were improved compared to the same filtration process without the application of an electric field. Optimizing electrofiltration as a microalgae dewatering technique is promising, especially given the enhanced filtration kinetics and the increase in the cakes solid contents after the electrofiltration of various solutions, i.e. clay, as well as industrial, waste and drilling sludge [25–27].

After forming a filter cake, many valuable compounds and, in some cases, impurities may remain trapped in the cake. Based on the same concept of electrofiltration, electrowashing can be

applied to help remove the desired or undesired compounds from the filter cake [28–32]. To the best of our knowledge, there are no studies that have explored the potential of washing microalgal filter cakes, making cake washing a novel process when applied in biorefineries.

Therefore, the objective of this thesis is to explore the use of electrofiltration as a harvesting (dewatering) technique to reach high harvesting efficiencies for lower energy requirements than the conventionally used microalgal harvesting techniques. This thesis covers the following concepts: filtration, electrofiltration, and electrowashing techniques applied to two types of microalga (*A. platensis* and *C. vulgaris*). It is divided into 6 chapters, the findings have been presented in conferences and/or published or submitted for publication as journal articles.

Chapter 1 gives general information about the concepts applied in algal biorefineries, highlighting the importance of the harvesting and downstream processing techniques. Special attention is given to filtration, showing the potential benefits of using an electrically assisted technique. Specific examples are given for two strains of microalgae: *Chlorella vulgaris* and *Arthrospira platensis.*

Chapter 2 showcases the materials as well as the experimental and analytical methods used during this study.

Chapter 3 studies the use of simple and electrically assisted filtration to concentrate and extract bioactive compounds from a 5% solution of *Arthrospira platensis*. This chapter also studies the optimization of the processing parameters (electric field strength and pressure) as well as their effects on the overall filtration process. This chapter is composed of one article and some of the data has been presented in a conference.

Chapter 4 explores the effect of pretreating *A. platensis* (by ultrasonication) on the filtration kinetics with and without the application of an electric field. This chapter also studies the effect of freeze drying on the composition of the microalgal cake formed by filtration and electrofiltration. The filtrate and cake properties (dryness, structure, and compressibility) as well as their pigment and protein contents were assessed. This chapter is composed of 1 article.

Chapter 5 explores the use of different cake washing techniques (with and without an electric field) and their effect on the extraction of bioactive compounds trapped in a well formed *Arthrospira platensis* cake. This chapter is composed of 1 article that explores the use of 3 different washing configurations to wash an *A. platensis* filter cake formed by dead-end filtration.

Chapter 6 studies the use of simple and electrically assisted filtration to concentrate a 5% solution of *Chlorella vulgaris,* in order to compare the effectiveness of electrofiltration for microalgae with different properties. The processing parameters are optimized and the effect of pressure and electric field strength on the overall filtration process are assessed (similarly to Chapter 3). The process is further optimized by investigating the use of a recirculation unit on the anode side and studying the effect of the recirculation rate on the filtration's performance. This chapter covers findings that have been accepted for dissemination in an international conference

with the opportunity to publish the work as an article in the conference proceedings. Part of this chapter has already been presented in a second conference as well.

Finally, Chapter 7 summarizes the conclusions that were derived from each chapter and outlines suggestions for future work.

Chapter 1: Literature review

1.1 Microalgae composition and processing

1.1.1 Introduction

The potential of employing microalgae as a sustainable, renewable and economic source of added value products has led to a worldwide interest in its use in various industrial applications [33–35]. This is due to the cells' ability to accumulate different bioactive compounds. Many studies have been conducted and reviewed [36–40] to assess the prospect of integrating microalgae and its derived products in food, pharmaceutical, aquaculture, energy, and many other industries.

It is estimated that the number of algal species range from 30,000 to more than 1 million. Algae can be aquatic (submerged in water) or subaerial (exposed to atmosphere). Aquatic algae are found in fresh or salt waterbodies, whereas planktonic algae live in the lighted regions of a waterbody. Benthic algae live in shallow areas within sediments or in even deeper regions (200 m) when the waterbody has a high level of clarity [41]. In many cases, microalgae have been classified according to their color; however, other classification criteria exist such as the types of pigments in the specimen, the constituents of the cell wall, the nature of the cell's storage products, and morphological and cytological characters (flagella structure, mode of cell division, membranes around chloroplast, etc...) [42].

Microalgae can be generally classified as prokaryotic or eukaryotic. Cyanobacteria are prokaryotic algae that can be differentiated under two different classes (phylum) based on the type of chlorophyll present in the cell [42]:

- Cyanophyta: Mainly contain chlorophyll a, but the chlorophyll pigmentation is masked by the presence of phycoerythrin and phycocyanin, hence its nomenclature as a blue-green algae.
- Prochlorophyta: produce both chlorophyll-*a* and chlorophyll-*b*.

The algal cell wall serves various functions, but it mainly acts as a barrier that separates the intracellular contents from the outer environment while allowing the exchange of compounds through the membrane (selective osmotic barrier), this aids in protecting the cell from pathogens, predators, and desiccation. Four cell types are distinguished [43,44]:

- Simple cell membrane, referred to as Type 1: It is a lipid bilayer that is 7 to 8 nm thick and contains peripheral and integrated proteins. In some cases, a glycolipid and glycoprotein cap encase the cell membrane's outer surface.

- Cell membranes with additional extracellular material, referred to as Type 2: various structures are associated to this cell membrane type, such as the cell wall, scales, mucilage and sheaths, skeleton, lorica, and fustules.
- Cell membranes with additional intracellular materials in vesicles, referred to as Type 3: the plasma in the cell is underlined by vesicles. The latter may contain one or multiple thecal plates that are primarily made out of cellulose.
- Cell membranes with intra- and extra- cellular material, referred to as Type 4: This type of cell wall is mainly present in cryptophyes and euglenophytes.

Other functions of the cell wall include the excretion and secretion of compounds, cell signaling, species identification, and cell to cell interactions [44].

1.1.2 Chemical composition of microalgae

The chemical composition of microalgae depends on various factors, mainly the algal species and strain, as well as its culture conditions [45]. The composition of different algal species is summarized in Table 1.1.

Lipids are primarily composed of fatty acids, that are straight chained aliphatic hydrocarbons with a hydrophilic carboxyl group as its functional termination, its general formula is $CH_3–(CH_2)_n–COOH$ for n ranging from 12 to 20 [46]. Fatty acids and lipids are found in all plant cells, serving the function of membrane components, metabolites, storage products, and energy source. On average, lipid content is found to range from 1 to 40% of the cells dry weight, but it can reach 85% when cultured under certain conditions. Lipids are classified based on their polarity which is dependent on its lipophilic carbon chains (non-polar fatty acids) and the hydrophilic moieties (polar carboxylic groups, sugars, alcohols…). Free fatty acids and triglycerides are non-polar lipids, whereas glycerides are considered polar when at least one fatty acid has been replaced with a polar group, such as glycolipids and phospholipids. Algal lipids can be saturated or unsaturated, and mainly include glycerol, bases or sugars that are esterified to fatty acids with carbon numbers ranging from C_{12} to C_{22} [45]. Among all the fatty acids accumulated in algal cells, polyunsaturated fatty acids (PUFAs) are the most important ones from a commercial perspective, due to their health benefits. Some PUFAs are linolenic acid, β-linolenic acid, dihomo-linoleic acid, eicosapentaenoic acid, arachidonic acid, and γ-linolenic acid [5,33,47,48].

Algae are high in protein (50 to 70%) [35], which makes them a good additive in human and animal nutrition [35,45,49]. Amino acids are the main components of proteins; therefore the quality of the protein is related to its amino acid content, availability and proportion [49]. Some of the essential amino acids found in algae are Valine, Methionine, Isoleucine, Leucine, Phenylalanine, Lysine, and Tryptophan. Other amino acids include Aspartic acid, Serine, Glutamic acid, Glycine, Proline, Alanine, Tyrosine, Histidine, and Arginine [50].

Carbohydrates are saccharides with $(CH_2O)_n$ as their general formula, for $n \geq 3$. It is a monosaccharide for n ranging between 3 and 9, in this case it can be an aldehyde or a ketone. Two monosaccharides can condense to form a disaccharide; whereas, polysaccharides are formed by condensing more than two monosaccharides [46]. In algae, carbohydrates are in the form of cellulose, starch, sugars, and different kinds of polysaccharides [35,45].

Pigments found in microalgae are divided in three basic classes: chlorophylls, carotenoids, and phycobiliproteins [35,45]. Chlorophyll comprises 0.5 to 1.5% of algae's dry weight and can be present in the form of chlorophyll- *a, b, c, d,* and/or *e*; noting that chlorophyll-*a* is present in all algae classes, whereas the other forms of chlorophyll do not have the same presence [45]. These pigments are soluble in lipids and are characterized by their low polarity [35]. Carotenoids are orange, yellow or red lipophilic pigments that form 0.1 to 0.2% of algae's dry weight. They are distinguished in two major groups: oxygen-free hydrocarbon based pigments (carotenes) or their oxygenated derivatives (xanthophylls or oxycarotenoids) [45,51]. As a bioactive compound, carotenoids have a high level of importance in different industries (nutraceuticals, pharmaceuticals, cosmetics, animal feed, food and dietary supplements) due to their health promoting properties; such as, anti-cancer, anti-aging, anti-inflammatory, antioxidant, and natural colorant properties, among many other benefits reported in literature [33–36,47,51]. Phycobiliproteins are deep-colored proteinaceous pigments that are soluble in water. This class of pigment is mainly found in Cyanobacteria, Cryptophyta, and Rhodophyta [45]. Phycobiliproteins are used as fluorescent agents in microscopy [52] and as a natural food colorant [34,35]. It is also applied in health related sectors due to its neuro protective, anti-inflammatory, anti-cancer, anti-allergenic, antioxidant, and antiviral properties [35].

Vitamins are also present in relatively high amounts in microalgae when compared to other sources [35]. A few examples of vitamins that can be extracted from microalgae are vitamin A (β-carotene), vitamins B_1, B_2, B_6, B_{12}, C, and E [33,53,54].

Many bio-toxins are also produced by microalgae, mainly by cyanobacteria and dinoflagellates [55,56]; however these toxins can be used in biotechnological applications [55,57].

Table 1.1. Chemical composition of different species of microalgae

Microalgae	Protein (%)	Carbohydrate (%)	Lipid (%)	References
Anabaena cylindrica	43-56	25-30	4-7	[58,59]
Aphanizomenon flosaquae	62	23	3	[58]
Arthrospira maxima	60-71	13-16	6-7	[59]
Arthrospira platensis	55-70	15-25	4-7	[60]
Botryococcus braunii	4	20	86	[58]
Chlamydomonas rheinhardii	48	17	21	[58,59]
Chlorella pyrenoidosa	57	26	2	[58,59]
Chlorella sorokiniana	21-53	5-25	20-36	[58]
Chlorella vulgaris	51-58	12-17	14-22	[58,59]
Dunaliella salina	57	32	6	[58,59]
Dunaliella bioculata	49	4	8	[58]
Euglena gracilis	39-61	14-18	14-22	[58,59]
Prymnesium parvum	28-45	25-33	22-38	[58,59]
Porphyridium cruentum	28-39	40-57	9-14	[58]
Scenedesmus obliquus	50-56	10-17	12-14	[58,59]
Scenedesmus quadricauda	47	-	1.9	[58]
Scenedesmus dimorphus	8-18	21-52	16-40	[58,59]
Spirulina maxima	60-71	13-16	6-7	[58,59]
Spirogyra sp.	6-20	33-64	11-21	[58,59]
Spirulina platensis	46-63	8-14	4-9	[58]
Synechococcus sp.	63	15	11	[58,59]
Tetraselmis maculata	52	15	3	[58]

Arthrospira platensis (*A. platensis*) and *Chlorella vulgaris* (*C. vulgaris*) are two species that have been commercialized in various applications, making them industrially relevant to improve the upstream and downstream processing steps related to these two species. For this reason, *A. platensis* and *C. vulgaris* are the two algal species used in this thesis.

A. platensis is a type of planktonic cyanobacteria that is filamentous and is composed of individual cells. On average, it has a diameter ranging between 3 to 12 μm with a length of a few millimeters. It is commonly known to have a helical shape, but depending on its culture conditions it can become a loose spiral or a straight filament [61]. *A. platensis*, commercially referred to as spirulina, has been incorporated in a large range of products. This has been achieved by using the entire microalgal cell or extracts from the cell itself. The most commonly used compound derived from *A. platensis* is the phycobiliprotein, phycocyanin, that has gained popularity as a natural blue pigment. It has been used in the production of cosmetics [62–65], medicinal products [66] and food, such as ice-cream [67], pasta [2,68,69], cookies [70,71], sourdough crostini [72], breadsticks [73], snacks [74,75], kefir [76], yogurt and dairy products [77–82], meat substitute [83–86], and smoothies [87] among many other foods [88,89].

Chlorella is a unicellular microalga that grows in various water habitats. This green cell has a spherical shape with a size that ranges from 2 to 10 μm in diameter. *Chlorella* is scientifically classified in the domain of eukaryote and its algal species is recognized as *Chlorella vulgaris* [90]. This algal species is known for the rigidity of its cell wall [91,92], whose structure varies from one strain to another and is dependent on the algae's growth conditions [43]. In general, a rigid microfibril based structure is embedded in a continuous matrix to form the alga's inner cell wall. This layer contains a glycan-resembling chitin as a primary amino sugar coupled with high amounts of cellulose [43,91]. Mature cells of *Chlorella* are characterized by a two layered cell wall: a trilaminar sporopollenin based sheath, hence it is mainly composed of a material that is resistant to acetolysis. The secondary layer is composed of mannose and a polysaccharide that is similar to chitin [93]. However, the extracellular cell wall of *C. vulgaris* is a polysaccharide structure that lacks a trilaminar matrix [91]. *C. vulgaris* is commercially valuable, due to its potential as a source of added value components (proteins, lipids, vitamins, minerals, carbohydrates) that can be used in different applications: pharmaceuticals, cosmetics, aquaculture, biofuels, animal feed and dyes [90,94]. Its main use as a health food has rendered this species as the most important one in the micro-algal industry [42].

1.1.3 Processing

In order to commercially produce these intracellular metabolites, four major steps must be carried out at a large or industrial scale: the first step is the proper cultivation of an appropriate microalgal biomass; the second step consists in the recovery or harvesting of the cultivated biomass from a dilute broth; the third step consists in processing the biomass for metabolite extraction; and the fourth step is the purification of the obtained crude extract [95]. These 4 processing steps are presented in Figure 1.1 and are thoroughly explained in Sections 1.1.3.1 to 1.1.3.4.

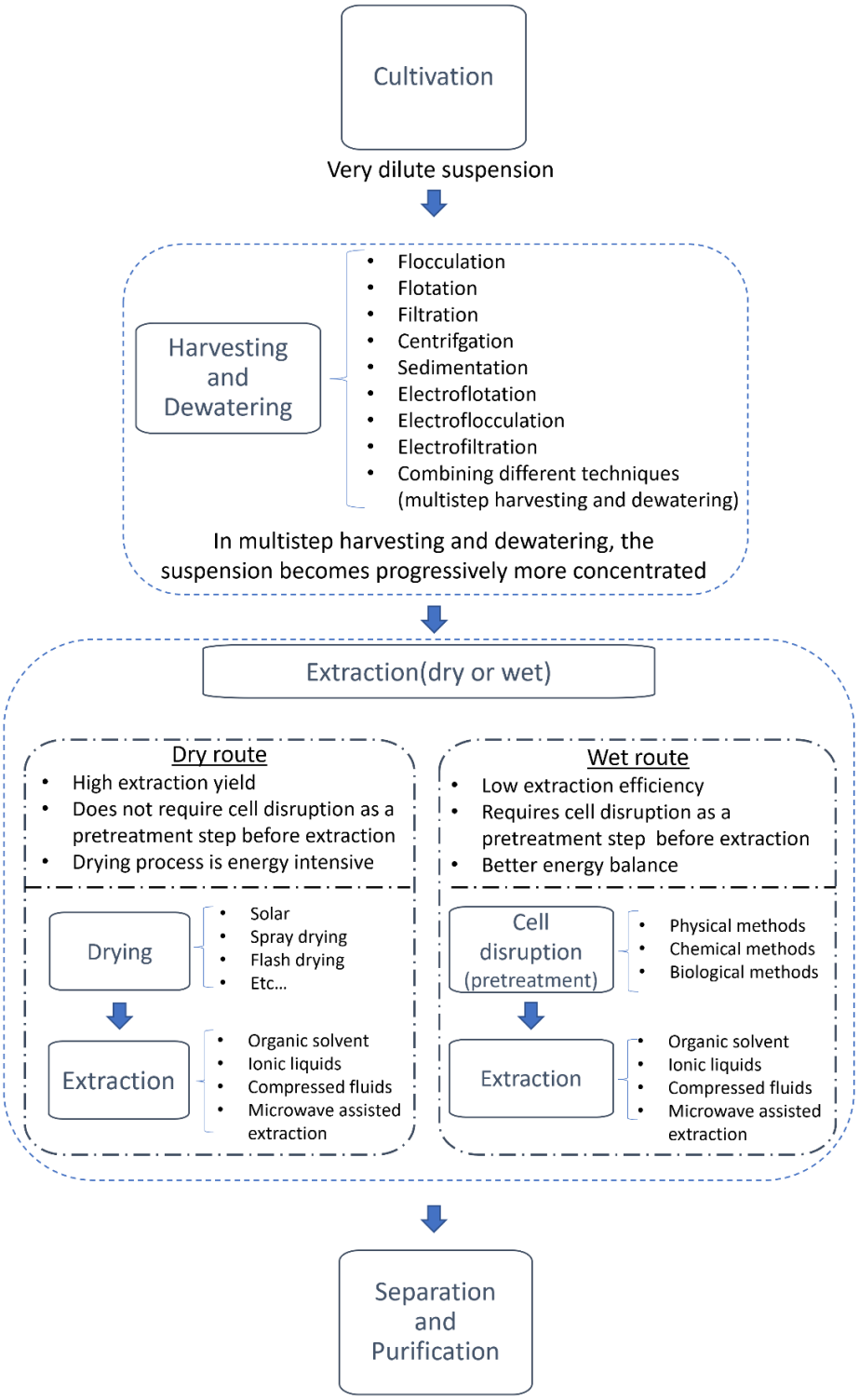

Figure 1.1. Schematic representation of the processing steps used in microalgal biorefineries

1.1.3.1 Cultivation

The chemical composition of microalgae is highly dependent on its strain, as well as the culture conditions used for each batch. This includes, but is not limited to, the temperature, light conditions, salinity and mineral content in the culture medium, pH, supply of carbon dioxide, mixing, and nutrient concentration [45,96–98]. Many studies relating the effects of the cultivation conditions of different microalgae on their composition have been cited in literature, mainly comparing the accumulation of certain bioactive compounds in the cells [99,100]. A large number of studies have also worked on optimizing the culture conditions of *A. platensis* and *C. vulgaris*, with the aim of increasing the microalgae's ability to accumulate and produce specific biocompounds of interest (lipids, proteins, pigments…) [100–111]. Since the cultivation step is not within the scope of this study, this section briefly describes the basic concepts related to microalgae cultivation.

The environmental factors that affect algae cultivation are light and temperature. The light intensity and its distribution in the culture system directly affect the cell's ability to produce light harvesting pigments and secondary carotenoids. In low light intensities, the production of primary carotenoids, chlorophyll (a, b, and c), and phycobiliproteins increases. Whereas, in higher light intensities, the production of intracellular compounds that are involved in photosynthesis decreases (photo-inhibition) [96,112], and secondary carotenoids that have the function of photoprotective agents increase. The latter includes, but is not limited to β-carotene, zeaxanthin, and astaxanthin. Temperature is considered as one of the most important environmental factors affecting the composition of algae, more specifically lipid content and composition in cell membranes [96]. The temperature at which the algae are collected is considered the optimal temperature at which the culture should be maintained [112]. A decrease in temperature leads to an increase in the number of unsaturated fatty acids present in the cell membrane, in turn this enhances the fluidity and stability of the cell membrane. Temperature can be changed (lowered or elevated in comparison to the optimal level) in order to promote cell growth (increased volumes) and increase their biochemical content [96].

While carbon sources play an important role in photosynthesis [97,113] and microalgae biomass growth consist of 40 to 50% carbon [97] other nutritional factors influence cellular composition such as nitrogen, phosphorous, and iron availability [52,96].

Algal cells generally have a nitrogen composition of 7 to 10% of dry cell weight, which is an essential component in functional and structural proteins in algal cells. When growing under nitrogen-limited conditions, algae tend to accumulate secondary carotenoids, lipids and/or carbohydrates, while exhibiting a decrease in chlorophyll content and the degradation of certain proteins [96].

Based on the microalgae's type of metabolism, they can grow photoautotrophically, heterotrophically, mixotrophically, or photoheterotrophically. Each metabolism has its own characteristics [58,97,99]:

- Phototrophic metabolism: algae use light as their only source of energy by converting it into chemical energy through photosynthesis of carbon sourced from carbon dioxide or other inorganic sources.
- Heterotrophic metabolism: the sources of energy and carbon are both organic for this type of metabolism, and both of them are based on organic carbon that can be sourced from bacteria under dark conditions. Hence the organic carbon is also used as energy instead of light.
- Mixotrophic metabolism: microalgae with this type of metabolism can live under heterotrophic or phototrophic conditions.
- Photoheterotrophic metabolism: the energy source is light, whereas the carbon source is organic. Hence, this type of metabolism requires the presence of light and organic carbon (sugar) in the culture medium.

Moreover, according to Barsanti and Gualtieri [112], various culture mediums are available and different culture methods (modes of culture) can be carried out, such as batch cultures, continuous, semi-continuous, open ponds, closed ponds, and photobioreactors. Immobilized cultures have also been developed, such as entrapment and absorption methods [114].

1.1.3.2 Harvesting

After cultivation, the biomass is recovered from the growth medium (harvested) then dewatered prior to metabolite extraction. Economically, the use of microalgae in commercial applications is not sustainable due to the high costs that are associated with the harvesting process [8,10]. The contribution of the harvesting and dewatering steps in microalgae processing has been reported as 3 to 15% of the algal biomass production costs, given that methods with low energy consumption were carried out after the open or closed system cultivation of biomass [16]. Microalgae harvesting can be divided into two steps, the first one is a concentration step which increases the cell concentration from 0.5 or 1% dry weight to approximately 3% dry weight, whereas the second step is the dewatering step that is capable of increasing the cell concentration to up to 25% dry weight or even higher depending on the technique used [115].

To move towards a more general commercialization of microalgae industries, the production costs related to microalgae production need to be minimized, this mainly includes targeting the harvesting step. According to Pahl *et al.*, the recovery of microalgae can be done using a single stage or multistage process [9]. In some cases, the harvesting and dewatering processes are combined in a single step, or the harvesting can be followed by one or two dewatering processes [16]. The choice of the type of process highly depends on the desired concentration and/or quality of the product, as well as, the microalgal species. The latter affects the harvesting process due the following properties [9]:

- Size
- Shape
- Charge
- Specific weight

Different harvesting techniques are available such as, centrifugation, flocculation, gravity sedimentation, flotation, filtration, and electrophoresis techniques [18,116–125], and in many cases a combination of techniques can be used [8,10,99]. Table 1.2 summarizes the characteristics of different harvesting techniques.

Table 1.2. Different harvesting techniques used in microalgal biorefineries

Technique	Mechanism	Advantages	Disadvantages	References
Centrifugation	Centrifugal force	• Quick • Efficient • Suitable for small microalgae	• High shear forces can damage the microalgal cells • High capital and operational costs • High energy consumption • Expensive for large scale harvesting • Time consuming • Harvesting efficiency depends on microalgae shape and size	[8,17,115]
Coagulation/ Flocculation	Formation of larger cell aggregates followed by sedimentation	• Quick • Suitable for large scale • Suitable for a wide variety of microalgal species • Less energy intensive than other techniques • In some cases, auto and bioflocculation may take place, making the process even cheaper	• Need to separate the coagulant/flocculant from the harvested microalgae, which presents some difficulties • Limitations in recycling the culture medium • Possibility of contaminating the microalgal cells • Chemicals (flocculants and coagulants) may be expensive • Process is pH dependent	[8,10,17]
Gravity sedimentation	Gravity	• Simple • Inexpensive	• Time consuming • Low separation efficiency • Low final concentration (0.5-3%)	[8,17]

Table 1.2. continued

Flotation	Air bubbles become attached to the microalgal cells and increase their buoyancy, helping the microalgae float to the surface of the culture medium. The microalgae are then collected by skimming the surface of the flotation tank.	• Quick • Suitable for large scale • Low cost • Low space requirements • Suitable for lighter microalgae that do not sediment easily	• Requires the use of surfactants • Process needs to be tailored for different types of microalgae (algae specific) • High capital and operational costs	[17,126]
Cross-flow microfiltration	Pressure gradient	• No chemicals needed • Can recycle the culture medium and water • Consumes less energy than other techniques (pressure and gravity filtration) • Cost effective • Low shear stress (does not damage microalgal cells) • Can reach high concentrations of microalgae (efficient separation) • New methods are being developed to reduce membrane fouling	• Slow • Requires pressure or vacuum • Vacuum filtration is energy intensive • Membrane fouling and clogging (requires replacement which could increase costs) • Challenging to use for small microalgae • Low recovery per pass typically 1 to 5%, but can reach 20% • Requires retentate recirculation for higher recovery which leads to higher operational costs	[8,10,17,127,128]
Dead-end filtration	Pressure gradient	• Particle- free filtrate (100% recovery) • Chemical free • Low shear stress (does not damage microalgal cells) • New methods are being developed to reduce membrane fouling	• Reduced filtrate flux • Requires membrane cleaning or replacement (leading to a discontinuous operation)	[8,10,17,128]
Electrically assisted techniques (electro-flocculation, flotation, or sedimentation)	Negatively charged microalgal cells migrate towards the negatively charged electrode (electrophoresis) For electro-flotation: gas bubbles are	• Efficient (Increases recovery yield) • Suitable for different microalgal species • Suitable for large scale operations	• Requires electrodes • Can cause chemical changes due to electrolysis reactions • High operating and maintenance costs • Metal contamination	[8,17,126,129]

Table 1.2. continued

	produced by water electrolysis			
Electrofiltration	Electrophoresis and electroosmosis combined with pressure gradient	• Improved filtration kinetics • Quick • High recovery yield • Can be adapted for different microalgal species • Equipment can be used for biocompounds separation and recovery (fractionation) • Low energy consumption • Has been industrialized in different industrial sectors	• Research gaps (technique still needs to be optimized) • Requires electrodes • Can cause chemical changes due to electrolysis reactions • High operating and maintenance costs • Metal contamination	[23,24,26,130,131]

Many publications have provided a detailed review on different methods used for microalgae harvesting, while explaining the mechanisms of each technique, their advantages, and their limitations [11,12,15,90,115,132,133]. For example, Nitsos *et al.* reviewed techniques such as sedimentation, coagulation-flocculation, flotation, centrifugation, and membrane filtration, while providing an abundant number of examples detailing the processes' efficiencies and energy consumptions for different microalgal species [115]. The following paragraphs will provide more details about some of the harvesting techniques mentioned in Table 1.2.

During flocculation, negatively charged microalgal cells that are dispersed in a liquid medium form lager cell aggregates that sediment more easily. The aggregation is induced by charge neutralization, where the negatively charged microalgal cells interact with positively charged molecules in the medium (flocculants) [120,134]. The larger size of the aggregates increases the settling rate and helps speed up the harvesting process [120]. Flocculation can be induced by the addition of polymers, biological flocculants, chemical flocculants, or metal salts that are a source of cations such as Fe^{3+}, Al^{3+}, or Zn^{2+} [121,134–136]. In some cases, auto-flocculation or bioflocculation can occur, and it is usually induced by algae-algae interactions, pH changes in the medium, the use of metal ions, or interactions between the microalgal cells and the bioactive compounds they secrete [137,138]. Even though flocculation has a relatively high harvesting efficiency, it is not the most suitable option when taking into account the time it requires, the cost of the flocculant, and the additional costs related to separating the flocculants from the algal cells after harvesting [120]. Flocculation can further be enhanced by combining it with other techniques. For example, one study enhanced the flocculation of *Chlorella vulgaris* with chitosan by electrolysis, which helped enhance chitosan flocculation [136]. Some of the advantages of flocculation are that this technique is quick, simple, relatively low cost with the large variety of flocculants that are available. The limitations related to using flocculation for microalgae

harvesting are the need to remove the flocculants after harvesting as well as some issues encountered when it comes to recycling the microalgal culture media. On average flocculation can help reach a dry solid concentration of 3 to 8% [17].

Harvesting microalgae by centrifugation is a mechanical separation technique where the solids are separated from the liquids, based on the size of the solid particles and the density of the liquid, under the influence of centrifugal forces. Centrifugation is used as an additional dewatering technique after a primary harvesting step (such as flocculation) to maintain a cost effective separation process [13]. Some of the types of centrifuges that are used for microalgae harvesting and thickening are basket centrifuges, spiral plate, imperforated and hydro cyclones, decanters, and disk stack centrifuges. The last two are the ones that are most commonly used [13,17]. Some of the advantages of centrifugation are its suitability for small microalgal cells, its high efficiency, and it does not require the use of chemicals. The limitations related to using centrifugation for microalgae harvesting are the high capital and operational costs that are required for the use of this technique, the potential of damaging the microalgal cells due to high shear forces, and that centrifugation is expensive for microalgal harvesting on a large scale. On average centrifugation can help reach a dry solid concentration of 10 to 22% [17].

Filtration, as a microalgae harvesting technique separates microalgae cells from the liquid solution they are dispersed in. The process is usually operated in dead-end mode under the influence of pressure or vacuum [17]. Membrane or cross-flow filtration is classified into different categories based on the size of the membrane's pores, the most commonly used categories for microalgae harvesting are reverse osmosis, microfiltration, and in some cases, ultrafiltration [139–142]. Other techniques and their combination have also been explored, for example, forward osmosis of *C. vulgaris* has been shown to increase the concentration of the algal cells by 1.5 to 4 folds depending on the operating conditions [143–146]. Another study assessed the use of a dual stage ultrafiltration system and a hybrid ultrafiltration-reverse osmosis system to dewater *Tetraselmis sp*, both systems were able to concentrate the feed solution by 37.3 folds, but the hybrid ultrafiltration-reverse osmosis system consumed (0.36 kWh/m^3 water removed) 24% less energy than the dual ultrafiltration system (0.47 kWh/m^3 water removed) [147]. Some of the benefits of using filtration for microalgae harvesting are that the technique is cost effective, consumes less energy compared to other techniques, does not require the use of chemicals, potential for recycling the water obtained after separation [17]. Despite all of these advantages, filtration for microalgae harvesting presents some drawbacks, such as membrane fouling, additional operating costs and time required to clean and/or replace the membranes, and it is not suitable for small microalgal cells (more difficult to filter) [13,17,148,149]. Filtration can help achieve a final cell concentration in the range of 2 to 27% (dry weight) [17], making it suitable as a primary and/or secondary harvesting step. Many studies have focused on optimizing different filtration techniques for microalgae harvesting [131,150–152], as well as exploring the use of multistep hybrid systems that combine the use of other harvesting techniques with filtration [153,154]. However more research is needed to further optimize the use of filtration as a harvesting

technique (especially given its potential to recycle and recover compounds from the recovered liquid phase).

Table 1.3 summarizes the efficiency and energy consumption of different harvesting techniques applied to various microalgal species.

Table 1.3. Different harvesting and concentration techniques for microalgal cells

Technique	Microalgal species	Concentration (g dry weight/L)		Recovery efficiency (%)	Energy consumption	Reference
		Feed solution	Final product			
Centrifugation	*Ankistrodesmus falcatus*	2.88	-	93.41	65.34 kWh/kg recovered algae	[153]
Flocculation (Chitosan)	*Scenedesmus obliquus*	-	-	76.98	-	[153]
Flocculation (Alum)	*Scenedesmus obliquus*	-	-	91.35	-	[153]
Electrochemical flocculation	*Chlorella vulgaris*	0.74 - 1.5	-	90	1.36 kWh/kg recovered algae	[155]
Flotation	*Chlorella vulgaris*	-	-	89.23	-	[156]
Electrochemical harvesting	*Ankistrodesmus falcatus*	2.88	-	69.71 - 91.71	0.84 - 3.62 kWh/kg recovered algae	[153]
	Scenedesmus obliquus	2.76	-	67.73	-	[153]
		2.4	-	54.2 - 83	2.13 - 9.5 kWh/kg recovered algae	[157]
Gravity settling	*Chlorella vulgaris*	2	8	55	-	[124]
	Scenedesmus dimorphus	2	7.2	70 - 80	-	[124]
Forward osmosis	*Tetraselmis* sp	0.43	0.53	-	0.13 kWh/m^3 water removed	[147]
Filtration (Cross-flow)	*Arthospira platensis*	0.45	2.5	-	-	[158]
	Tetraselmis sp	0.43	15.7	-	0.23 kWh/m^3 water removed	[147]
Stirred dead-end filtration	*Chlorella vulgaris*	0.14 - 0.34	-	-	-	[139]
Electrofiltration (Cross-flow)	*Chlorella sp.*	1.2 - 1.4	7 - 9	-	2.94 - 3.4 kWh/m^3 water removed	[24]
Pressurized electro-osmotic dewatering	*Microcystis aeruginosa*	0.35	-	-	-	[23]

Electrochemical harvesting was found to be an effective technique to recover microalgae, reaching a recovery yield of 83% with an energy consumption of 3.84 kWh/kg recovered algae when harvesting *Scenedesmus obliquus* at an electric current intensity of 1.5 A and a pH of 9 with the addition of 6 g/L NaCl in the medium [157]. Increasing the conductivity by increasing the electrolyte concentration or increasing the pH (making it more alkaline) has been found to increase harvesting efficiencies while decreasing the power consumption [16,157].

Fasaei *et al.* assessed the energy consumption of different harvesting techniques (from 0.1 to 5 kWh/kg microalgae recovered), the study also reported that the use of pressure filtration as a harvesting technique, followed by the use of centrifugation for dewatering led to the lowest energy consumption and processing costs when compared with 28 different combinations of techniques [16]. Other promising operations were found to be pressure filtration followed by spiral plate technology; and flocculation followed by membrane filtration then centrifugation or spiral plate technology. The low energy consumption of the flocculation technique leads to a decrease in operating costs; however, this reduction in costs is comparatively cancelled out by the flocculate costs and the low recovery yield of biomass [16]. Another study assessed the use of harvesting techniques based on the quantity and quality of biomass, the required processing time, cost, specificity towards a species, and toxicity. Based on these criteria, the three most preferred techniques were found to be coagulation and flocculation, centrifugation, and filtration. These techniques can also be used in combination, such as flocculation followed by filtration or centrifugation; or flocculation combined with sedimentation [8]. However, despite the potential of using filtration as a cost effective alternative to dewatering techniques, membrane fouling remains a potential issue [20,21,125,149,159]. Assisted mechanical techniques have also been used, these include dewatering by thermal mechanical techniques, acoustic mechanical techniques, magnetic mechanical techniques, electrical mechanical techniques, and electro-acoustic mechanical techniques [129].

Based on the data presented in Tables 1.2 and 1.3, filtration and electrofiltration are promising methods for microalgae harvesting and thickening. These methods consume less energy than the other methods that have been discussed in this section and lead to high microalgal cell recovery yields. Moreover, electrofiltration has not been properly explored as a microalgal harvesting and thickening technique, to the best of our knowledge, one study explored the use of cross-flow electrofiltration [160] of *Chlorella vulgaris*, whereas another study explored the electrofiltration and pressurized electro-osmotic dewatering of *Microcystis aeruginosa* [23]. This shows the need to tackle different research gaps related to the use of electrofiltration for microalgae harvesting and dewatering, some of the proposed work includes but is not limited to: (1) studying the use of other electrofiltration apparatuses, (2) studying the suitability of electrofiltration for dewatering different microalgal species, (3) studying the effect of the physical and chemical properties of the microalgal cells and the microalgal feed solution on the filtration process, (4) studying the effect of electrofiltration on the microalgal cells and the formed microalgal cake, (5) comparing the

difference in filtration performance between electrofiltration and conventional filtration without the application of an electric field.

Given that *A. platensis* and *C. vulgaris* are the two types of microalgae studied in this thesis, Table 1.4 illustrates some examples of filtration techniques used to harvest these two species of microalgae.

Table 1.4. Filtration techniques applied for the harvesting of *A. platensis* and *C. vulgaris*

Filtration technique	Filtration area (m^2)	Membrane pore size	Membrane material	Microalgae harvested (size - cell concentration)	Reference
Cross-flow	0.01	• 0.1 µm • 0.2 µm • 0.4 µm • 0.8 µm • 1.5 µm	PVDF	*A. platensis* (n.d. - 0.45 g/L)	[158]
Submerged membrane panel (tilted)	0.01	• 0.42 µm • 0.04 µm	• PVDF (microfiltration) • PSF (Ultrafiltration)	*Spirulina sp* (40 µm - 1.2g/L)	[161]
Submerged membrane reactor (disc)	0.0417	• 10-40 nm • 20-80 nm	PVDF	*Arthrospira maxima* (n.d. - 6 g/L and 40 g/L)	[162]
Dead-end microfiltration (vacuum)	0.005026	0.45 µm	• PVDF • Cellulose ester	*Chlorella* (4.42 µm - 15 to 240 mg/L)	[20]
Cross-flow	14	• 0.45 µm • 0.2 µm	PVA coated: • PVDF • PET	*Chlorella* (3 µm - 1.2 to 1.4 g/L)	[160]
Cross-flow (electrically assisted)	14	n.d.	Electromembrane (carbon cloth treated with PVDF and PEO dissolved in NMP	*Chlorella* (3 µm - 1.2 to 1.4 g/L)	[24]
Stirred ultrafiltration	0.00278	0.91	PFTE	*Chlorella* (2 to 3 µm - n.d.)	[154]

Abbreviations: Polyvinylidene difluoride (PVDF), hydrophilic polyvinyl alcohol polymer (PVA), polyethylene terephthalate (PET), Polytetrafluoroethylene (PFTE), polyethyleneoxide (PEO), N-methyl-2-pyrrolidone (NMP). n.d: not determined

Harvesting *A. platensis* by membrane filtration was capable of concentrating the cells by 5 to 10 folds, but the exopolymers extracted from the cells contributed to membrane fouling

[158,163,164]. The helical strain of *A. platensis* was found to be easily harvested by filtration, whereas the straight strain was harvested better by centrifugation [164]. Harvesting *C. vulgaris* by membrane filtration has also been studied [18,22,165,166]. One paper reported that the properties of the culture medium as well as the amount of exopolymeric materials in the broth influenced the extent of membrane fouling during *C. vulgaris* harvesting [139].

Given the ability of electrofiltration to improve filtration kinetics and increase the concentration of dry mass in the formed cake [131,167], exploring the use of electrofiltration for the harvesting and thickening of *A. platensis* and *C. vulgaris* could help alleviate some of the limitations of using membrane filtration as a microalgal harvesting technique.

1.1.3.3 Extraction (Metabolite Recovery)

This processing step generally consists in the pretreatment and disruption of the harvested biomass. Extraction can be carried out on wet or dry biomass (Figure 1.1). When wet biomass is used, the cells must undergo a pretreatment technique to disrupt and permeabilize the microalgae's membrane [168]. This helps increase the extraction yield and efficiency. When the dry extraction route is followed, solvents are used to extract the biocompounds of interest from the dried biomass, and it has been observed that the action of the solvent on the dry cells leads to their disruption [169]. In some cases, the dried microalgae can also undergo a non-essential cell disruption technique to help release the biocompounds of interest that are trapped in the microalgal cells and subsequently increase the extraction yield [170]. The choice of using the dry or wet route for biocompound extraction heavily depends on the properties of the extracts. The dry extraction route is most commonly used for the extraction of hydrophobic biocompounds (i.e. lipids) despite the higher processing costs associated with the microalgae dewatering and drying steps [169,171,172], the dry route has also been used for the extraction of proteins and pigments [141,173–176]. Cell disruption is not the main objective studied in this thesis, for this reason, the different disruption techniques that are available have been briefly described, for a more detailed review of different dry and wet processing routes, the following references have been cited [115,171,177–182].

When filtration is used as a dewatering technique, the pores in the formed cake could contain biocompounds of interest. The latter can be removed from the cake's pores by cake washing, which can be carried out before further processing the microalgae cells for the extraction of compounds of interests. Cake washing is discussed in Section 1.3.

1.1.3.3.1 Dry route

In order to extend the shelf like of harvested microalgae, the microalgal cells can be dried. The dried cells can then undergo further processing steps to recover bioactive compounds of interest trapped within the cells. The dry route is associated with higher operating costs when compared to the wet route (processing without going through a drying step), this is due to the high energy

consumption of the drying process. Different drying techniques are summarized in Table 1.5. Before selecting a processing technique different parameters should be considered, especially product safety and the processing costs [183]. It is also important to ensure that the selected drying technique does not have a negative impact on the quality of the biocompounds that are intended to be recovered.

Table 1.5. Summary of different drying techniques

Technique	Advantages	Disadvantages	References
Rotary drying	Two functions: sterilizing and disruption	High energy cost to run dryer	[14,17,170]
Spray drying	• Rapid and efficient drying method • Appropriate for production of algae for human consumption • Suitable for large scale processing	• Degradation in product quality due to high-pressure atomization • High operating cost • Low digestibility of dried algae	[170,184]
Solar drying	The most feasible drying means in remote vicinities lacking energy supply	• Weather dependent • Issues with overheating and unreliable operation • Not suitable for algal products intended for human consumption	[9,14,170]
Cross-flow air drying	Relatively cheap and fast drying (cheaper than drum drying and quicker than sun drying)	High energy cost	[7,13,170]
Vacuum-shelf drying	Efficient and fast drying	High capital and running costs	[170]
Flash drying	Rapid removal of moisture	Cost of drying and the final product quality greatly influenced by hot gas source	[14,170]
Incinerator drying	Burning or scorching heat sensitive algal biomass can be prevented	Complicated and high capital cost	[170]

Moreover, the energy requirements and subsequently the processing costs are highly dependent on the operating conditions used for drying; hence the values of the energy consumption for some of the drying techniques in Table 1.6 serve as an example and are not to be generalized.

Table 1.6. Examples of different drying techniques applied to various species of microalgae

Drying technique	Microalgae	Drying conditions	Results	Ref.
Solar drying	*Chlorella sp.*	Thin layer of microalgae (5 mm thick) dried from 9 am to 5 pm, in: • Direct sunlight (average temperature around 30 ˚C) • A natural convection direct solar dryer, the maximal temperature reached was 60 ˚C (with a minimum of 30 ˚C) Air humidity was between 8.3 to 19.6%	Drying time required for complete removal of moisture: • 390 min (direct sunlight) • 330 min (solar dryer) Both methods exhibited a decreasing drying rate over time.	[184]
	Scenedesmus obliquus	Direct natural sunlight and ambient conditions (temperature between 18 and 27 °C) for 2 to 3 days.	Energy consumption of 0.056 kWh/kg lipid extracted	[185]
Freeze drying	*Scenedesmus obliquus*	Biofreezer for 24 hours at −84 °C and a power of 0.9 kW	Energy consumption of 21.81 kWh/kg lipid extracted (takes into account the freezing, vacuuming, and sublimation steps)	[185]
Convective air dryer	*Chlorella vulgaris*	Thin layer of microalgae (3 mm) with an initial moisture content of 66.4% Airflow rate 50 L/min Air temperatures: 40, 60, 80, 100, 120, and 140˚C	Equilibrium moisture for each temperature was respectively 16.9 ± 2.0, 9.9 ± 0.8, 5.1 ± 1.4, 3.0 ± 1.1, 2.2 ± 0.9, and 1.3 ± 0.3%, this was reached after a drying time of 555 ± 10, 420 ± 6, 360 ± 13, 207 ± 15, 124 ± 13, and 82 ± 6 min respectively.	[186]
	Arthrospira platensis	Moisture content between 3 to 9 kg water/kg dry matter (after filtration as a primary dewatering step) Air velocity: 1.9 to 3.8 m/s Temperature: 40–60 °C	Data not available	[187]
	Chlorella sp.	Hot air oven drying was tested for a layer of microalgae with a thickness of 5 mm for a	Drying times at 50, 60, and 70 °C were respectively 350, 250, and 190 min.	[184]

Table 1.6. continued

		temperature of 50, 60, and 70 °C with an air velocity of 1.5 m/s.	The drying rate increased with temperature. The drying rate at each temperature decreased with time. Energy consumption for 50 and 70 °C were respectively 55.1 and 51.7 kWh/kg water removed	
	Scenedesmus obliquus	Air oven for 12 h at 60 °C and a power of 0.5 kW	Energy consumption of 6.33 kWh/kg lipid extracted	[185]
Convective drying (Microwave)	*Chlorella vulgaris*	Power:100, 300, and 600 W	Energy consumption of respectively 0.192, 0.244, and 0.286 kWh/kg water removed to achieve a final moisture content of 10%	[188]
	Chlorella sp.	Thin layer of microalgae with a thickness of 5 mm. Power: 450, 600, and 700 W Frequency: 2450 MHz	Drying times (for completely dry microalgae) were respectively 160, 130 and 90 min for a power of 450, 600, and 700 W. Microwave drying was found to be quicker than hot air drying and solar drying. Energy consumption for 400 and 700 W were respectively 34.9 and 26.2 kWh/kg water removed (less energy intensive than hot air drying)	[184]

Different drying techniques have been used to dry various strains of microalgae. Overall, the energy requirements of the drying process were related to both the operating conditions such as the temperature, power, pressure, and initial moisture content of the microalgal paste, as well as the type of microalgae that was being dried.

In some cases, before the extraction of biocompounds from the dried cells, another non mandatory pre-treatment step could be carried out to reduce the particle size of the dried algae (i.e. bead milling), this could help further increase the extraction yield by increasing the surface of contact between the cell debris and the extraction solvent [182].

Bead milling is a mechanical disruption technique that uses kinetic energy to drive small beads to collide with algae cells and each other at high velocities [170,178,179,189]. The beads can be made out of steel, glass, plastic or ceramic [178]. Several parameters affect the efficiency of this disruption technique, such as the geometry of the chamber and agitator, the agitator speed, the concentration of biomass, suspension flow rate, bead type and diameter, and bead filling ratio

[190]. In many cases, using bead milling has been found to be highly inefficient in terms of its energy consumption, since a large portion of the energy is used for bead displacement, whereas another portion is lost by mechanical dissipation [191].

After cell drying and potentially bead milling, the dried biomass is submerged in a solvent to extract the desired biocompounds [170,192]. In general, there are two processes that can be employed during solvent extraction: the first one consists in using moderate amounts of solvent that dissolve into the cell membrane and increase compound permeation, whereas the second process is based on dissolving dry biomass components in a suitable solvent (determined based on the nature of the desired bioactive compound) [193]. The solvents used are non-polar (not soluble in water) such as toluene and benzene [193], for lipid extraction in industrial processes acetone, hexane, chloroform, and cyclohexane may also be used [170]. Another extraction technique involves the use of ionic liquids, which are slats with low melting temperatures composed of a small anion (organic or inorganic) and a large cation (organic). Ionic liquids are known for their ability to be modified according to the type of compound that needs to be extracted, this is achieved by modifying the combination of anions and cations. Moreover, ionic liquids are generally safe to use and do not damage biocompounds, making it an attractive technique for the extraction of biocompounds from microalgae [194,195]. Subcritical and supercritical solvents have also been used to extract biocompounds from dried biomass [171].

Overall, the optimization of the processing parameters depends on the strain of algae being disrupted.

1.1.3.3.2 Wet route

The microalgal cells undergo a cell disruption technique to help release the biocompounds trapped within the cell walls. Cell disruption is an essential step that is required to obtain adequate extraction yields. The type of cell wall disruption technique is highly dependent on the structure of the microalgae cell, this is also important to optimize the recovery of value-added intracellular compounds [91,170]. The cost effectiveness of the process is another important parameter to consider, especially in industrial applications. The cost is highly dependent on the dry cell weight of the algae suspension to be treated, the energy consumption (per kg of dry weight), consumables used for disruption, disruption time for acceptable yields, product quality, and many other expenses. More specifically the strain of algae used influences the cost of disruption, based on the cell wall rigidity, growth stage, and size of the cell [178].

Disruption techniques can generally be classified as chemical, mechanical, enzymatic, and other physical methods [91,92,170,171,178,189,192]. The main physical methods are pulsed electric fields (PEF), high voltage electric discharge (HVED), ultrasonication, and microwave assisted extraction [92,171,196,197]. Freeze thawing has also been considered an attractive treatment method for the extraction of temperature sensitive compounds from wet biomass [198–201].

According to Zhang *et al.* [171], some techniques can be grouped under the following classification:

- Chemical: organic solvents (suitable for wet and dry extraction), ionic liquids, and using surfactants as an additive in a solvent.
- Mechanical: hydraulic pressing, bead milling (mainly used for dry extraction), high pressure homogenization, high shear mixer, and other methods based on hydrodynamic cavitation or shear forces.
- Physical methods: microwaves, ultrasounds, high voltage electrical discharges, and pulsed electric fields.

HVED has been used in a wide range of applications and it is based on chemical reactions accompanied by physical processes [92]. Many studies have been conducted on the use of HVED for the extraction of valuable bioactive compounds from different sources, such as fruits, vegetables and microalgae [92,202–206]. HVEF is an electrostatic field treatment (non-pulsed) that has the potential to be used for the inactivation of enzymes and microorganisms in liquid foods [92]. HVEF has been used to control the size of ice crystals formed in foods during freezing processes [207] and as a thawing technique [208–210]. It has been found that HVEF can lead to the modification of the structural properties of vegetable and animal tissues [92,211–213]. Alkaline treatment is a chemical treatment method, where the cell membrane is solubilized through saponification with a base. The latter is dissolved in alcohol or water, with a ratio dependent on the composition of biomass. The base used can be potassium or sodium hydroxide, whereas the alcohol can be methanol, ethanol, or isopropanol. The small molecules produced by the alkali treatment are then extracted by using a low polarity solvent [193]. This method has been found to be effective as a pre-treatment step for fermentation and for the extraction of intracellular components such as pigments and lipids [178]. Similarly, acid treatment can be carried out, in this case the base is replaced with an acid, such as sulfuric acid. However, this method can lead to pigment degradation [178].

During ultrasonication (US), different mechanisms are responsible for the disruption of the treated cells, the main two are acoustic streaming and cavitation, other mechanisms that have been reported are microbubble formation, shear forces, high pressure in the liquid, and in some cases temperature changes. The temperature can be monitored and controlled during US treatment to avoid the possible deterioration of the quality of the extracts [214,215]. US can also be used in the dry route for biocompound extraction, commonly referred to as ultrasound assisted extraction [171]. This method is versatile given the ability to control the operating temperature during processing and modify the solvents used to further increase the extraction yield. The treatment time, frequency, and power can also be selected to optimize the extraction yield as explained in a review by *Liu et al.* that also compared the performance of various parameters on the disruption of different types of microalgae [215].

Enzymatic hydrolysis leads to cell wall degradation and perforation by enzymes; the choice of enzyme is highly dependent on the cell wall structure that is desired to be disrupted [193]. The enzymes ensure the biological specificity of the cell disruption while potentially having a high selectivity, mild operating conditions, high yield of conversion, and low energy consumption, among other benefits, based on the selected enzyme [178]. This method can be used as a pre-treatment step for cell lysis or protoplast preparation [193].

Decompression, which is a laboratory scale pressure based technique used for biocompound extraction, disrupts cells by suddenly increasing their intracellular pressure. This is achieved by dissolving a pressurized gas in the cell suspension, followed by a rapid release of the pressure which creates microbubbles inside the cells [193]. For example, an explosive decompression device has been used as a novel way to disrupt algal cells [216]. Another form of disruption by decompression is the controlled instantaneous decompression technique, also known as "Détente Instantanée Contrôlée (DIC)" in French. This technique has been used for the extraction of compounds of interest with the added benefit of serving as a drying technique [217–220]. A more primitive form of DIC is the Explosion puffing drying technique [221]. To the best of our knowledge, no studies have reported using DIC for the disruption of algal cells, making it a novel application worth exploring.

Osmotic shock disruption occurs by lysis based on the cells' turgor pressure, but it requires the use of a pretreatment method for fungal, bacterial, and plant cells [193]. This technique is based on the reduction of movement of water across the cell membrane which is induced by a high concentration of solute, such as a salt or substrate, in the suspension medium. This forces the cell to rupture and release its intracellular components [170,189].

During high pressure homogenization (HPH) cells are disrupted by a velocity gradient that is created when the microalgae concentrate (suspension) is pumped through the narrow homogenizer valve (80-200 µm that is under high pressure (138 to 400 MPa) to create a high velocity when the suspension transitions into a lower pressure chamber [178,193]. In this context, the radial flow of the suspended cells accompanied by the pressure drop leads to the disruption of the cells by shear stress from hydrodynamic cavitation and high pressure impact [192]. Another technique, the French press, operates based on the same principle as high pressure homogenization, but on a smaller scale [193].

Table 1.7 lists the advantages and disadvantages of some of the wet and dry processing routes (mainly cell disruption and extraction techniques) that can be used for the recovery of biocompounds from microalgal cells. The advantages and disadvantages of different drying techniques were discussed in Section 1.1.3.3.1. and thus were not added to Table 1.7.

Table 1.7. Advantages and disadvantages of different disruption and extraction techniques

Technique	Use	Suitable for wet or dry route	Mechanism	Advantage	Disadvantage	Reference
Bead milling	Disruption	Dry	Shear generated by bead collision (compaction or solid shearing)	Easy for large scale application; high disruption efficiency; rapid method; high biomass loading; can be applied on slurries; reproducible; temperature control (overheating can be avoided by cooling)	High energy required at large scale; disruption degree depends on bead size; heat generation; fine cell debris formation; increased cost (from energy consumption and downstream processing)	[170,178,179,189, 191,222]
Ultrasonication	Cell wall and membrane disruption	Wet or dry (resuspended in liquid)	Acoustic streaming and cavitation	Short extraction time; can be used for any species (universal); can combine with other processes to reduce solvent consumption and energy demand	Overheating (requires cooling); high energy consumption; can cause production of reactive hydroxyl radicals	[170,178,179,222]
Enzymatic treatment	Cell wall degradation, protein solubilization and extraction	Wet	Biological	Specific and highly selective; used with other techniques to increase extraction yields; low energy consumption	Expensive; long extraction time; can cause product inhibition	[170,179]
Pulsed electric field	Cell membrane disruption	Wet	Electroporat-ion	Energetically efficient; relatively quick; allows selective extraction; can be used as a pre-treatment method	May cause lethal damage to cells; decomposition of some compounds; temperature increase; efficiency depends on operating conditions (medium, solvent, temperature);	[92,170, 178,179, 189,223]

Table 1.7. continued

					high capital cost	
Osmotic shock	Disruption	Wet	Osmotic gradient	Does not require using dried algae; simple technique	Costly for large scale applications	[170,189]
High pressure homogenizat-ion	Disruption	Wet	Shear stress	Scalable; reproducible; free of contaminating substances or solvents	Low concentration dry cell weight; increased separation cost (cell debris)	[192,222]
High shear homogenizat-ion	Disruption/pre-treatment	Wet	Shear force and hydrodynamic cavitation	Can use high concentrations of dry cells; short processing time; advantageous as pretreatment for lipid extraction from *Nannochloropsis* sp. and protein extraction from *Chlorella* sp.	Aggressive technique; difficulty scaling up; not suitable for bio-refining due to complex cell extracts	[222]
Organic solvent extraction	Extraction	Wet or dry	Solvent-solute solubility	-	-	-
Supercritical fluid (CO_2)	Extraction	Dry	Solvent-solute solubility	No harmful solvent residue present in extracts (no product contamination); selective extraction; environmentally friendly; reduces risk of metabolite degradation	Requires co-solvent for protein and carbohydrate extraction; CO_2 should be recovered and recycled; expensive (high pressure equipment and operation costs)	[46,92,180,224]

Other techniques include the use of surfactants, impingement, milking, and autolysis [225]. In the impingement technique, cells are disrupted by a high velocity gradient inducing a stress onto the cell wall [193]. The microorganism milking process refers to the extraction of bioactive compounds without destroying the cells, this can be repeated in cycles which could enhance low productivity of intracellular components in some micro-algal cultures [193,226]. Autolysis occurs after the death of the cells: it is a self-degradation process carried out by the enzymes in the dead cell. In many cases, PEF is used to enhance the yield of extracts produced by autolysis [227,228] and it has been applied to microalgae [223]. Moreover, membrane permeability can be increased

by using a molecule that enhances pore formation; these molecules can be antibiotic additives or drugs, such as natamycine or nisin [193].

1.1.3.3.3 Examples

Different studies have investigated the extraction of biocompounds from *A. platensis and C. vulgaris* as shown in Table 1.8. For the extraction of phycocyanin from *A. platensis*, the use of dry biomass is favored over fresh microalgae [176,229–232]. Solvent extraction has been applied for the recovery of carbohydrates, proteins, and lipids, among many other bioactive compounds [195,233–238]. However, one of the drawbacks of using this technique is the need to perforate or destroy the microalgal cell wall by pretreating it with techniques such as pulsed electric fields [204,232,239,240], high pressure homogenization [241,242], bead milling, extrusion, and microwaves to name a few [243]. Performing the extraction without permeabilizing the microalgal cell walls has been linked to lower extraction yields.

Table 1.8. Extraction techniques used in literature

Microalgae (initial state)	Processing technique	Remarks	Ref.
A. platensis (dry)	Solvent extraction	Extraction of phycocyanin using a phosphate buffer within 3 hours at room temperature (pH = 7.5). After extraction the pH is immediately adjusted to 6 - 6.5	[173]
A. platensis (dry)	Ultrasonication (probe)	Protein extraction assisted by manothermosonication at 20 kHz increased the extraction yield by 229% compared to extraction without ultrasonication, reaching a concentration of 28.42 ± 1.15 g protein/100 g dry weight	[174]
A. platensis (dry)	Bead milling followed by centrifugation	The cells were disrupted by temperature controlled bead milling. Solid debris and liquid phase were separated by centrifugation. The supernatant was filtered to purify the extracts	[141]
A. platensis (dry)	Ultrasound (2.5 min at 50% amplitude) assisted enzymatic extraction (0.6% enzyme concentration, 16 h incubation, 1:6 solid to liquid ratio)	C-phycocyanin yield of 98.24 mg/g dry biomass (82.55%), with a purity of 1.09	[176]
A. platensis (wet)	No pretreatment. Only water extraction (3 h at 25 °C, and agitation at 160 rpm)	C-phycocyanin extracted: 0.2 mg/g dry biomass, water soluble protein extracted: 12.3 mg/g dry biomass	[242]
	High pressure homogenization (3 passes at 150 MPa) followed by water extraction	Energy consumption: 110.5 ± 5.9 kWh/kg dry weight extract	
	PEF (pulse width: 5 µs, electric field strength: 20 kW/cm and total specific energy input: 100 kJ/kg followed by water extraction	C-phycocyanin extracted: 26 mg/g dry biomass with a purity of 0.97, water soluble protein extracted: 174 mg/g dry biomass Energy consumption: 52.9 ± 6.1 kWh/kg dry weight extract	

Table 1.8. continued

	High shear homogenization (HSH) for 1 min at 20,000 rpm followed by water extraction	Energy consumption: 79.6 ± 10.5 kWh/kg dry weight extract	
	PEF and HSH followed by water extraction	C-phycocyanin extracted: 53 mg/g dry biomass, water soluble protein extracted: 460 mg/g dry biomass Energy consumption: 51.2 ± 1.3 kWh/kg dry weight extract	
C. vulgaris (frozen then thawed)	High pressure cell disruption and / or chemical treatment	Cells were disrupted at 2.7 kbar at a pH of 12 Using the cell disruption technique twice with a pH of 12, led to a higher yield (98%) of protein extraction when compared to a pH of 7 (71%)	[50]
C. vulgaris (wet, frozen then thawed)	2 stage ethanol extraction (1:5 solvent to biomass ratio), for 30 min at room temperature (22–25 °C) from fresh and freeze-thawed microalgae	The freeze-thawed cells respectively released 1.8 folds and 12.3 folds more lutein and total chlorophyll than the fresh cells	[244]

Many studies [244–246] have also investigated the sequential extraction of multiple intracellular components, from *C. vulgaris* and *A. platensis*, as a method to reduce processing costs by increasing the amount of co-products that are being extracted. Based on a thorough review of literature, ultrasonication has been found to be an adequate technique for the extraction of water soluble proteins and pigments from *A. platensis* using dry, fresh, or freeze-thawed biomass [174,214,247–249]. PEF is also a suitable technique for the extraction of these compounds since it can reach high extraction yields depending on the processing parameters, as well as high purity levels. However PEF is generally limited to processing wet biomass [173,232,242,249].

1.1.3.4 Separation and purification

Different techniques have been adopted for the fractionation and purification of microalgal extracts, these include but are not limited to, crossflow ultrafiltration, and high performance liquid chromatography (HPLC) among others. This section briefly reviews some of the purification techniques that can be used in microalgal biorefineries and provides some examples of the techniques used to purify extracts from *A. platensis* and *C. vulgaris*.

HPLC is a relatively new technique, but it is also expensive which makes it less suitable for large scale applications [168]. Distillation is time consuming and requires the use of heat, which could potentially damage or alter the composition of the bioactive compounds that need to be recovered, making it unsuitable for the separation of temperature sensitive compounds. Ionic liquids have also been considered for the recovery of biomolecules extracted from microalgal cells, especially given its ability to selectively recover biocompounds [194,195,250]. However, the use of ionic liquids presents many limitations: toxicity, they need to be recycled, requires the use of multiple steps, and the process needs to be tailored for each type of biomolecule that needs to be separated [194]. Cross flow ultrafiltration is a selective process that can be commercialized at a

relatively low cost, it can also yield high purity products without the need to go through additional processing steps [251,252].

A multi-step approach has been used to purify phycocyanin extracted from *A. platensis.* The first step consisted in the partial purification of the extract by microfiltration and ultrafiltration, this mainly served as a phycocyanin recovery step after extraction. To further purify the phycocyanin recovered by microfiltration and ultrafiltration, different types of chromatography were explored: activated charcoal column, gel filtration chromatography, and ion-exchange chromatography [253]. Another study used a membrane diafiltration process to fractionate the water soluble phycobiliproteins extracted from *A. platensis*. This was achieved by testing different membrane pore sizes for the filtration of the crude extract (50 kDa, 150 kDa, 300 kDa, or 0.2 µm). The 0.2 µm membrane was found to efficiently separate allophycocyanin from C-phycocyanin with a global recovery over 89%, and no chlorophyl was present in the filtrate streams [141].

For the concentration of protein extracted from *C. vulgaris*, a preliminary centrifugation step was used to separate the cell debris of the disrupted cells from the liquid phase containing the extracts. The extracts in the supernatant were then fractionated and concentrated by two stage cross-flow ultrafiltration, where 300 kDa and 3kDa molecular weight cut off hollow fiber module membranes were respectively used in the first and second filtration stages [254].

Electrofiltration has been studied as a purification method that combines the principles of membrane filtration and electrophoresis. Different studies have reported the use of electrofiltration for the purification of various biocompounds [130,167,255,256]. Given the versatility of electrofiltration and the possibility of using it as a harvesting technique as well as a purification technique, Section 1.2 discusses the different aspects involved in electrofiltration processes while highlighting the use of dead-end filtration and exploring its suitability for microalgal biorefineries.

1.2 Electrofiltration for microalgae harvesting

This section describes the different electrokinetic phenomena that take place during electrofiltration, explains the basic principles and steps that occur during dead-end electrofiltration as well as the factors that affect the process. Different industrial applications of electrofiltration and its potential to be used with microalgae are also detailed in this section.

1.2.1 Electrokinetic phenomena

In order to gain a better understanding of the effect of an electric field on particles in suspension, it is important to understand the electrokinetic properties of these particles.

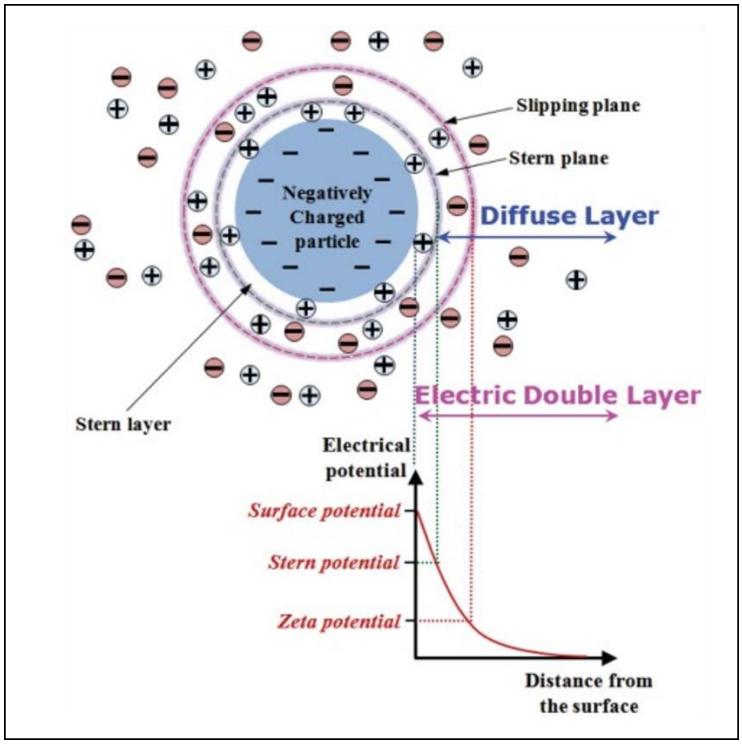

Figure 1.2. Schematic representation of the electrical double layer of a particle, from [257]

Fine particles suspended in aqueous media have a surface charge and are surrounded by ions with an opposite charge (dissolved in the aqueous medium), this forms an electric double layer [26,129]. Different models have been developed to describe the behavior of this electric double layer [258–260]. Figure 1.2 shows a schematic representation of a particle's electrical double layer.

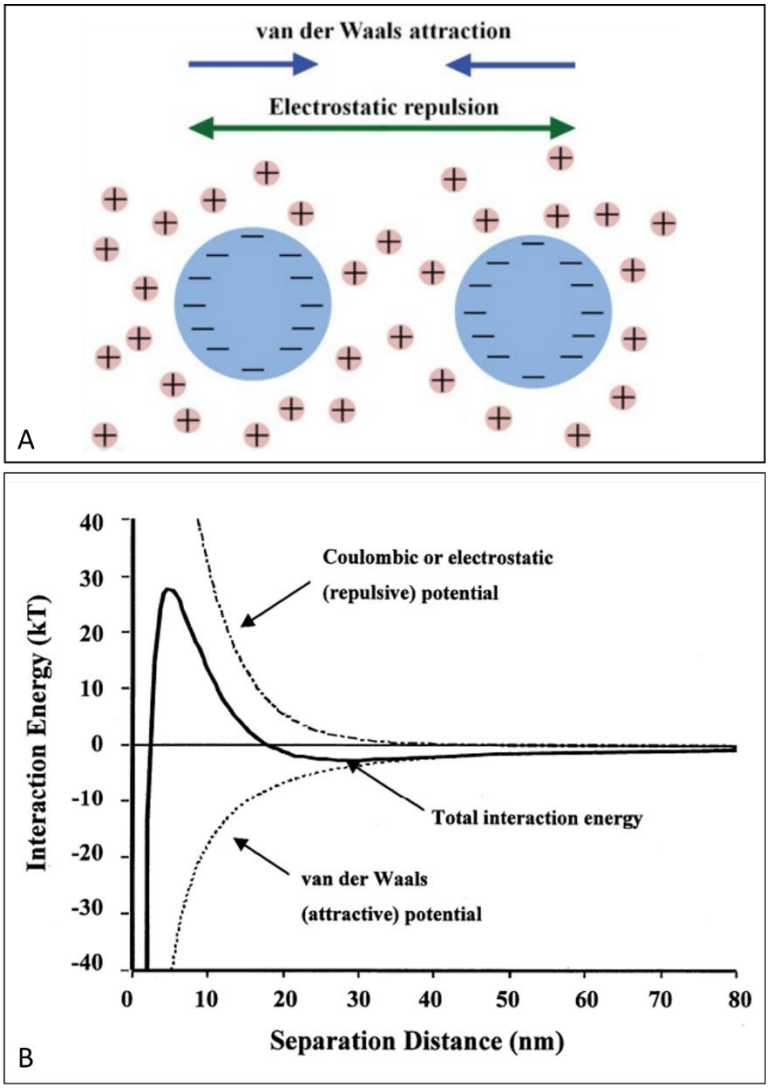

Figure 1.3. Schematic representation of (A) the potential energy of the interaction between two particles, from [257] and (B) interaction energy in function of the distance profiles of DLVO interactions, from [261]

It is also important to take into account particle-particle interactions. These interactions have been described by the DLVO theory [262,263], which relates the stability of particles (colloids) in suspension to the total potential energy between two adjacent particles. When two particles are close enough, their electrical double layers can become overlapped, creating a repulsive electrostatic force (Figure 1.3). The repulsive electrostatic force opposes the attractive van der Waals forces. Between two particles, the net interaction energy is the sum of the electrostatic and van der Waals forces [264]. DLVO theory has been used to describe the behavior of different biological cells such as microalgae and bacteria [264–267].

Due to the particles' surface charge, different electrokinetic phenomena play an important role during electrofiltration [26,129,268]:

- Electrophoresis: under the influence of an electric field, charged particles move in a relatively stationary liquid phase. The particles move towards the oppositely charged electrode. Electrophoresis depends on the zeta potential of the particles in suspension, which in turn, depends on the pH of the medium.
- Electroosmosis: movement of the ionized liquid around relatively immobile charged particles, due to the application of an electric field. This is induced by the electromigration of the ions in the particles' electrical double layer under the influence of the applied electric field
- Sedimentation potential (dorn effect): due to the movement of particles (by gravity sedimentation) their electric potential is modified.
- Streaming potential: due to hydraulic pressure, liquid flows around the particles which alters their electric potential as a result of the deformation of the particles' electrical double layer.
- Electromigration: movement of ions in a fluid under the influence of an applied electric field. The ions move towards the oppositely charged electrode.

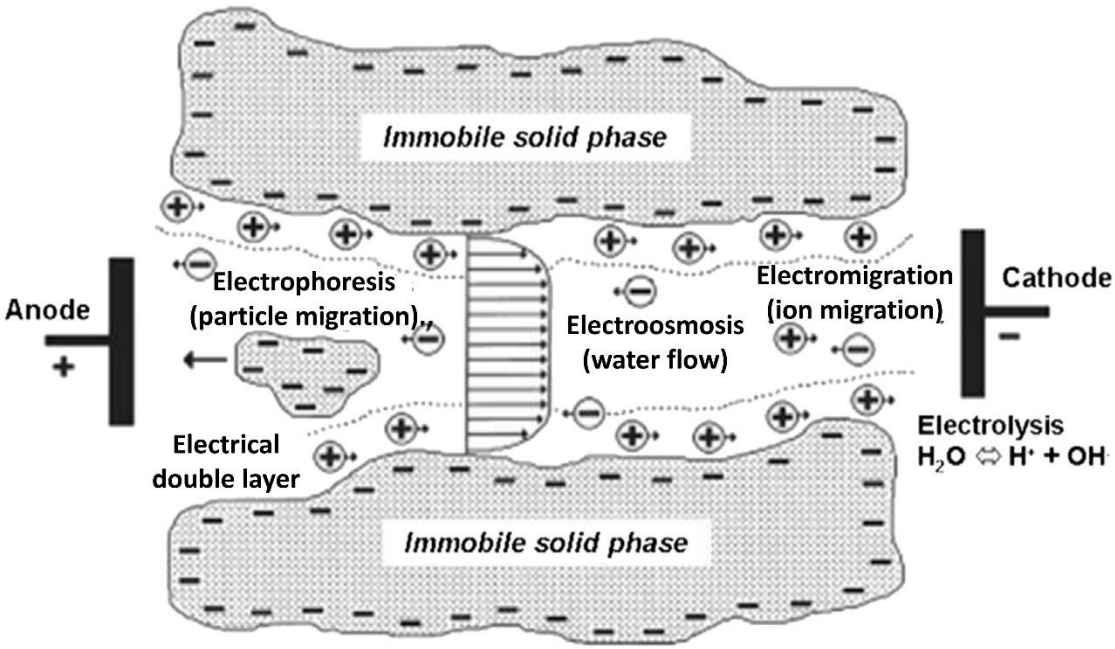

Figure 1.4. Schematic representation of the electrokinetic phenomena during electrofiltration. Adapted from [269]

In the context of electrofiltration, the filtration kinetics are improved due to the simultaneous action of the electrophoretic and electroosmotic forces. Under the influence of an applied electric field, the particles in the filtration cell are pushed away from the membrane carrying the same surface charge as them, whereas the liquid (filtrate) is driven out of the electrofiltration cell in the opposite direction of the movement of the particles, as illustrated in Figure 1.4. The slow buildup

of the filtration cake (for negatively charged particles), based on the steps involved in filter cake consolidation driven by the electrokinetic phenomena induced by an electric field, is shown in Figure 1.6. A.

Other processes have been designed based on the electrokinetic phenomena that take place in a suspension or semi-solid material placed between two electrodes. For example, electroosmotic dewatering can be applied to semi-solid materials to increase their dewatering rate and accelerate their consolidation. Unlike electrofiltration that relies on electrophoresis, electroosmotic dewatering relies on electroosmosis [26].

1.2.2 Dead-end electrofiltration

Dead-end electrofiltration is an electrically assisted filtration technique that consists in applying a direct current (DC) electric field to the electrodes situated on the sides of the filtration chamber as a method to enhance the mechanical separation of water from a sample. In the electrofiltration cell (Figure 1.5), the applied DC electric field is parallel to the direction of the flow of filtrate, this leads to an electrophoretic flux of charged particles in suspension towards the electrode with an opposite charge.

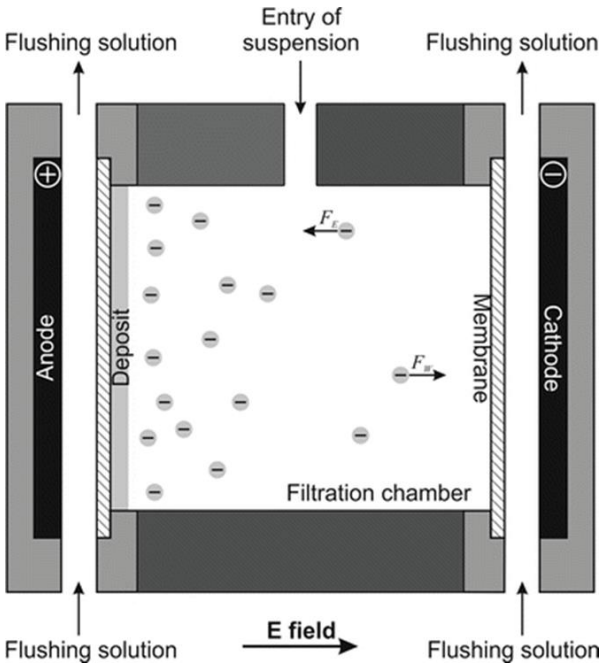

Figure 1.5. Schematic representation of the electrofiltration chamber with electrode flushing [270]

It has been observed that suspensions containing particles that are negatively charged exhibited filter cake growth at the side of the anode, whereas a thin layer of particles are deposited on the membrane at the side of the cathode. The layer deposited at the cathode side has a negligible effect on the flow of filtrate through the membrane, in other words, the flux is not negatively affected.

Hence, a higher flow rate of filtrate is observed at the outlet of the cathode side and not the anode side. Compared to mechanical pressure, electroosmotic flow is capable of removing more water from the filter cake and a higher compression of the latter is observed as well [26].

Many studies have investigated the use of dead-end filtration processes assisted by the application of an electric field, it has also been used in a variety of industrial applications: drilling sludge, wastewater and sewage sludge treatment, and food processing, among many other applications [24,131,271–274]. DC electric fields have also been applied to soil for electro-remediation [275]. However, regardless of the application, the same principles and theories are applied. Some of the undesired phenomena that are observed during electrofiltration are ohmic heating, electrode corrosion, increased acidity of filtrate on the anode side, increased alkalinity of the filtrate on the cathode side. Consequently, a number of studies have aimed to solve the problems that are related to electrodewatering [166,256,276–280].

Cake consolidation by electrofiltration occurs based on four main steps that are reportedly different for the anode and cathode side, whereas without an electric field, two main steps are identified; the first one is the cake formation step and the second one is the cake consolidation step [27].

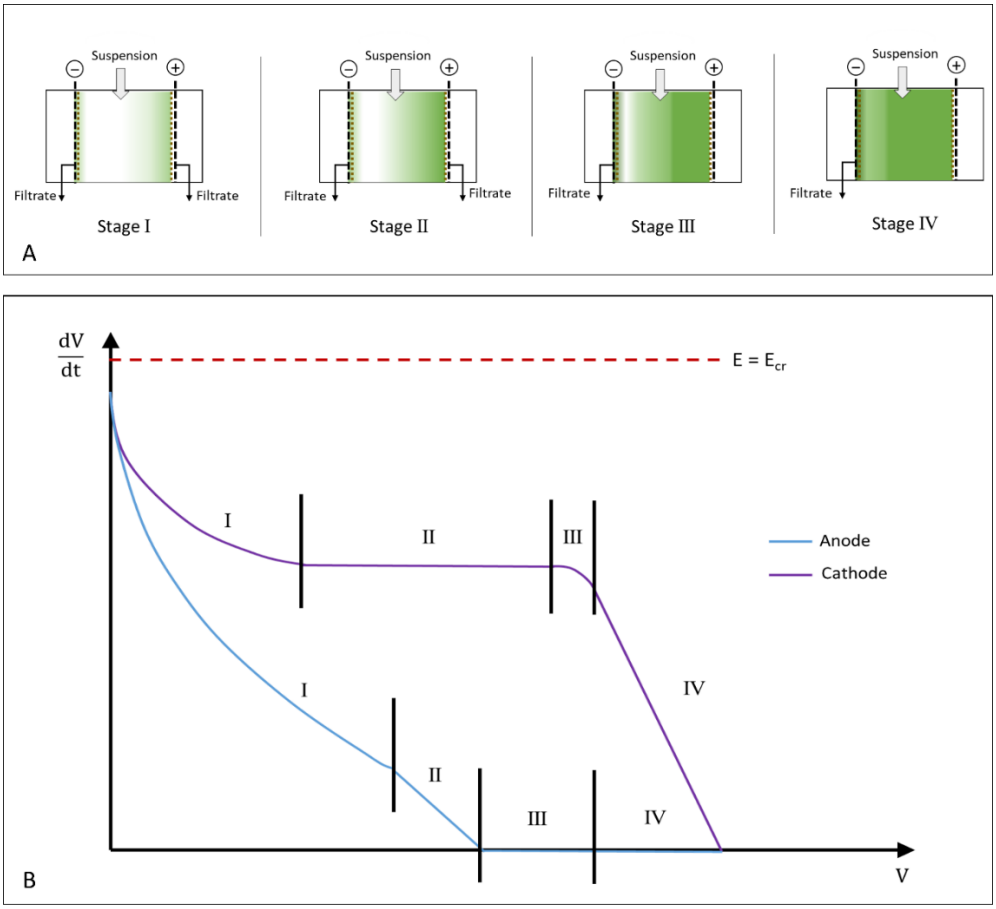

Figure 1.6. The different stages during dead-end electrofiltration. A: Schematic representation of electrofiltration in a filter press, B: Filtration rate in function of the filtrate volume. Adapted from [27]

For an electrofiltration process conducted using a filter press the following mechanism (Figure 1.6) has been reported on the anode and cathode side [27]:

On the cathode side:

- Stage I, cake formation. In order to stimulate the cake to form on the anode side, the intensity of the electric field should be lower than a critical value. The cake gradually becomes thicker, but at a slow pace on the cathode side, due to the electrophoretic forces involved. Thus the filtration rate at the cathode side gradually becomes slower with time. If the intensity of the electric field is larger than or equal to the critical value, all the negatively charged particles in suspension will migrate towards the anode, thus allowing the liquid to flow out of the cathode side at a constant rate.
- Stage II, constant flow rate. The filter cake has stopped growing on the cathode side and reached a constant thickness. The liquid that flows out of the filtration cell on the cathode side does so by going through the pores in the cake. For this reason, the flow rate of filtrate is also constant. In this stage, the filtration process is in a state of equilibrium.

- Stage III, intermediate step. The filtration chamber is almost completely filled by the filter cake and the cake thickness on the anode side increases even more. This renders the electrical resistance of the entire filter cake non negligeable, making it capable of decreasing the mobility of the particles in suspension in the filtration cell and subsequently decreases the intensity of the electric field. As a consequence, the filter cake on the cathode side starts to become even thicker and the flow rate of fluid through the cake decreases.
- Stage IV, hydraulic consolidation. The available filtration area decreases and the hydraulic consolidation of the filter cake becomes evident by the rapid exponential decrease of the filtration rate on the cathode side.

On the anode side:

- Stage I, cake formation with flow of filtrate.
- Stage II, intermediate step. It is characterized by cake growth and a rapid decrease in the filtrate flow rate at the anode side. This step takes place when the electroosmotic force is large enough to quickly decrease the filtration rate through the thick layer of cake buildup on the anode side.
- Stage III, cake buildup without the flow of filtrate. During this step, the cake keeps getting thicker on the anode side due to the migration of particles by electrophoresis, whereas the liquid no longer flows towards the anode. In other words the flow rate of filtrate from the anode side is zero.
- Stage IV, hydraulic consolidation. The flow rate of liquid from the anode side is still zero, the filtration area decreases during this step and the cake becomes consolidated.

More importantly, dead-end electrofiltration has been proven to enhance filtration kinetics, increase filter cake dryness, and reduce the onset of fouling during the filtration process compared to filtration without the assistance of an electric field [278,281–286]. This makes electrofiltration an attractive technique to explore in algal biorefineries.

1.2.3 Electrochemical reactions

During electrofiltration, the metal forming the anode undergoes an oxidation reaction, whereas the metal forming the cathode undergoes a reduction reaction. The oxidation-reduction reactions help maintain the charge equilibrium in the electrofiltration cell [287]. Thus, the reactions that take place are the following [287,288]:

Reactions on the anode are represented by R1 and R2, where M represents the metal used to form the anode. The standard potential of the electrode at a temperature of 298 K is 1.23 V, this value needs to be exceeded in order to have R2 take place without any kinetic restrictions. For this reason it is important to choose a metal based on the desired application, in other words, if the electrodes are being used in the context of electrocoagulation selecting an oxidizable metal is desired to ensure that R1 is favored over R2. During electrofiltration, R1 should not be favored

because the metallic ions that are produced could contaminate the filtrate as well as the retained solids, this could subsequently lead to the deterioration of the quality of these two components. In this case, the use of non-oxidizable metals is needed to favor R2 over R1. Examples of oxidizable metals are aluminum and iron, whereas non oxidizable materials that could be used to form the anode are precious metals such as silver, platinum, gold, as well as the alloys of precious metals with carbon, conductive ceramics, or metal oxides.

$$M \rightarrow M^{n+} + ne^- \quad (R1)$$
$$6H_2O \rightarrow O_2\,(g) + 4H_3O^+ + 4e^- \quad (R2)$$

The reactions on the cathode side are represented by R3, R4, and R5.

$$M^{n+} + ne^- \rightarrow M \quad (R3)$$
$$2H_2O + 2e^- \rightarrow H_2\,(g) + 2OH^- \quad (R4)$$
$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2(g) \quad (R5)$$

Water electrolysis (R4) takes place on the cathode side and is usually the main reaction that is more favorable over the reduction reaction on the cathode. The only case when the reduction reaction (R3) is favored over electrolysis on the cathode is when the cathode is made of one of these metals: Pb, Cu, Ag, Hg, Pt, or Au and that high concentrations of their metal ions are present in the filtration medium, which is unlikely to occur. R5 only takes place if a high concentration of H_3O^+ is present in the medium, this is also highly improbable [287].

During electrofiltration, an electrochemically triggered oxidation process also takes place, this leads to the production of free hydroxyl radicals (OH•). When Cl^- and SO_4^{2-} ions are present in the medium, a series of reactions (reactions R6 to R11) can take place, leading to the formation of Cl_2 and $S_2O_8^{2-}$, which are known as highly reactive oxidants. Other by-products can be formed when SO_4^{2-} and Cl^- react with OH•, as seen in reactions R12 and R13 [289].

$$H_2O \rightarrow OH\bullet + H^+ + e^- \quad (R6)$$
$$2OH\bullet \rightarrow H_2O_2 \quad (R7)$$
$$Cl^- \rightarrow Cl\bullet + e^- \quad (R8)$$
$$2Cl\bullet \rightarrow Cl_2 \quad (R9)$$
$$SO_4^{2-} \rightarrow SO_4\bullet^- + e^- \quad (R10)$$
$$2SO_4\bullet^- \rightarrow S_2O_8^{2-} \quad (R11)$$
$$SO_4^{2-} + OH\bullet \rightarrow SO_4\bullet^- + OH^- \quad (R12)$$
$$Cl^- + OH\bullet \rightarrow ClOH\bullet^- \quad (R13)$$

Due to the formation of chlorine at the electrodes, it is favorable to avoid using solutions containing chlorides, when possible, especially for electrode flushing [167].

The electrochemical reactions that take place have been associated with pH changes in the filtrate streams, the corrosion of the electrodes in case they are composed of metals that are susceptible to reduction or oxidation, and an increase in the concentration of ionic species in the filtrate streams [280,283,284,286,290]. Figure 1.7 shows the evolution of the pH profile of a filter cake after electrofiltration, the 70% of the cake closest to the anode side exhibits an acidic pH and the 30% of the cake closest to the cathode side shows a pH that progressively increases from acidic to alkaline the closer it gets to the cathode.

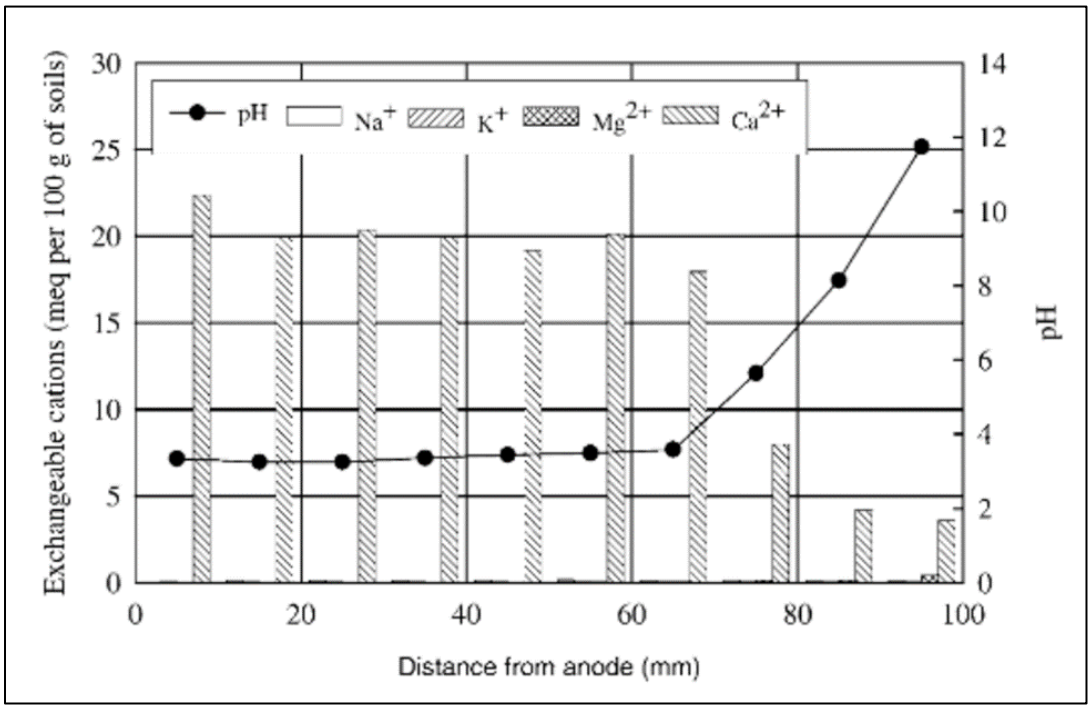

Figure 1.7. Evolution of the pH and cation concentration in a filter cake in function of the distance of the section from the anode. Adapted from [291]

Some techniques, such as electrode flushing, have been developed to regulate the pH, cool the electrodes and remove the electrolysis products, which subsequently prolongs the electrodes' lifetime [25,278,292]. In some cases the formation of a white layer on the cathode's surface has been observed [293].

1.2.4 Factors affecting the electrofiltration process

Many factors may influence the effectiveness of the separation process induced by an external electric field. A large number of these factors have been listed in literature [26]:

- The permittivity of the components in the solution or the type of suspension: the main parameter in this case is the permittivity of both the liquid and solid particles. The permittivity is a constant of proportionality relating the electric displacement in a material to the electric field it is exposed to. To ensure a good separation of the solids from the liquid, the permittivity

of the solid particles must be either much higher or lower than that of the liquid, in other words the gradient in the values of the permittivity must be large.

- The zeta potential of the particles (which is pH sensitive).
- The particle size distribution: larger particles are easier to separate because they lead to a higher dielectrophoretic force, however with small particles the fluid drag forces could be larger than the dielectrophoretic force, making dielectrophoretic separation an inefficient process.
- Solution conductivity (or salinity): electric fields with higher frequencies are required during the dielectrophoretic separation of solutions with high salinity. In general, nonconductive liquids are preferred to limit the use of stronger electric field strengths.
- Feed flow rate or velocity: this affects the fluid's drag forces, for this reason lower velocities are preferred over higher ones.
- Solution viscosity: lower viscosities (in the order of 10^{-3} Pa) are favored over relatively higher ones. More viscous fluids can potentially lead to the release of particles from the electrodes or the dielectric surface due to the fluid's drag force.
- Type of electric current: alternating (AC) or direct (DC).
- Electric field density, which is the electric field strength applied perpendicularly to the cross sectional area of the filtration chamber.
- Intensity of the electric field: it must be increased with the increase in the permittivity of the liquid phase in the solution to be separated.
- Temperature: this parameter affects many other parameters that must be controlled during the electrically induced separation process. An increase in temperature (caused by ohmic heating) leads to a decrease in fluid viscosity and density as well as an increase in the permittivity differential between the liquid and solid phases in solution.

These parameters can be modified in order to optimize the electrofiltration process. Many studies have already investigated the effect of the electric field strength (density and intensity), the conductivity, pH, the solution's zeta potential, as well as the combination of different factors [23–25,278,280,286,290,292,294].

Hofmann *et al.* suggested some general guidelines that should be taken into account during the electrofiltration of biomaterials [167]:

- Microfiltration membranes are more suitable than ultrafiltration membranes for electrofiltration, this is attributed to the microfiltration membranes' bigger porosity and better mechanical stability.
- It is more favorable to separate biopolymer dispersions with a lower specific conductance (smaller than 8 to 10 mS/cm) by electrofiltration. The costs of electrofiltration can be reduced by reducing the slat content of the biopolymer solution.
- Higher electric field strengths can be used with solutions that have lower conductivities, which in turn helps increase the electrofiltration kinetics. The conductivity of the biological solution can be decreased by electrode flushing and electrode cooling.

- It is important to take into account the potential of degrading sensitive molecules (enzymes) during electrofiltration, to the best of our knowledge, this has not been observed in existing literature so far.

Gözke and Posten [295] reviewed the use of electrofiltration to purify different biomaterials, i.e. poly(3-hydroxybutyrate), hyaluronic acid, chitosan, and xanthan. The review highlighted the effect of different parameters on the electrofiltration process, as well as electrofiltration's ability to overcome the challenges observed with conventional filtration techniques. Electrofiltration was able to increase the filtration rate as well as the concentration factor of the filtration process following an increasing trend with an increase in the applied voltage (Table 1.9). The study also reported that the purification of hyaluronic acid was more challenging due to the material's low zeta potential, high filter cake resistance, and high compressibility [295].

Table 1.9. Concentration factor of different biopolymers after filtration and electrofiltration [295].

Biopolymer		Chitosan from crabs	Chitosan from fungus	Hyaluronic acid from *Streptococcus equi*
Zeta potential (mV)		+ 65 (pH 3)		−22 (pH 6)
Concentration factor (after 3h of filtration at 4 bar and different applied voltages)	0 V/mm	16	28	5
	2 V/mm	30	50	15
	4 V/mm	39	84	18

When studying the use of electrofiltration for the dewatering of microalgae [23,296], the effect of the electric field strength and the conductivity of the feed solution was assessed by studying their effect on the filtration kinetics. However, more studies should be conducted to assess the suitability of the technique for different microalgal species and adapt the processing parameters accordingly. Section 1.2.6 discusses the potential of using electrofiltration for the concentration of microalgae suspensions.

1.2.5 Industrial applications

Electrofiltration has been used as a separation technique for the removal of certain compounds of interest [130,255,274,297,298]. It has also been used as a dewatering technique for mud, soil, industrial sludge, and sewage sludge [278,283–285,294]. Different types of suspensions treated by electrofiltration are presented in Table 1.10. For example, another electrically assisted filtration configuration consists the use of crossflow filtration assisted by dielectrophoresis, where an alternative current is used to improve the filtration kinetics and has the ability to decrease

membrane fouling [299–301]. However, the electrode is coated with low-dielectric materials to prevent short circuiting and electrochemical reactions, this coating must be thin enough to prevent the need of high voltages during filtration [26]. The use of an alternative current is not suitable for dead-end electrofiltration processes due to the constant variation of the electric field in opposite directions, this would subsequently eliminate the phenomena of electrophoresis and electroosmosis in the filtration cell.

Table 1.10. Different applications for dead-end electrofiltration. Adapted from [26]

Suspension	Equipment used	Process parameters	Efficiency (compared to pressure filtration without electric field)	Energy consumption
Kaolin clay	Dorr-Oliver Electrofilter (Lab scale)	Pressure: 6.9×10^3 Pa Electric current density: 25 to 100 A/m^2	Increase in flow rate by 7 to 36.5 folds	-
Kaolin clay (pH = 9, zeta potential: 8mV, particle size: 13.7 µm)	Vertical filter cell (Lab scale)	Pressure: 1.2×10^5 Pa Electric current density: 50 to 100 A/m^2	Increase in flow rate by 1.2 to 2.2 folds	32 – 51 kWh/m^3 water removed
Anatase suspension (TiO_2) 1% dry solids, size 0.3 µm	- (Lab scale)	Pressure: 1.7×10^5 Pa Electric current density: 6 A/m^2	53% increase in filtrate volume after 1000s	1.87 kWh/m^3 water removed
Pre-sedimentation basin water	Sand filter (Pilot scale)	Rate: 0.84 mm/s Voltage: 8 to 12 V	Factor of cells collected increased by a factor of approximately 1.2 to 1.26	0.1 – 0.27 kWh/m^3 water removed
Raw bentonitic drilling sludge (pH = 9.3, 23.4 % dry solids, particle size: 3 µm)	Vertical filter cell (Lab scale)	Pressure: 5×10^5 Pa Electric current density: 80 A/m^2	5 fold increase in filtrate flow rate Reached 64% dry solids	95 kWh/m^3 water removed
Xanthan	Filter press with electrode flushing (Lab scale)	Pressure: 4×10^5 Pa Electric field: 4 kV/m	23 fold increase in filtration kinetics	44.4 kWh/m^3 water removed
Poly(3-Hydroxybutyrate)	Filter press with electrode flushing (Lab scale)	Pressure: 4×10^5 Pa Electric field: 2 – 4 kV/m	Increase in filtration kinetics by 2.1 to 3.8 folds	-
Chitosan	Filter press with electrode flushing (Lab scale)	Pressure: 4×10^5 Pa Electric field: 2 – 4 kV/m	Increase in filtration kinetics by 1.9 to 3.1 folds	-
Hyaluronic acid	-	-	Increase in filtration kinetics by 2.7 to 3.6 folds	-

When compared to thermal evaporation, electrofiltration presents the added benefit of being able to control the temperature during processing, this is usually achieved by using a temperature controlled (cooled) flushing solution on the electrodes [167].

Different lab, pilot, and industrial scale electrofiltration equipment have been developed and used for the separation of various suspensions. For example, Desabres *et al.* [278] used a lab scale electrofiltration apparatus (Figure 1.8 A), with and without electrode flushing (Figure 1.8 B and C) for the dewatering of a kaolin suspension. The effect of using anode flushing was assessed and was found to improve the anode's lifetime through a better control of the physiochemical conditions in the filter chamber [278]. Figures 1.8, 1.9, and 1.10 present some of the electrofiltration equipment featured in Table 1.10.

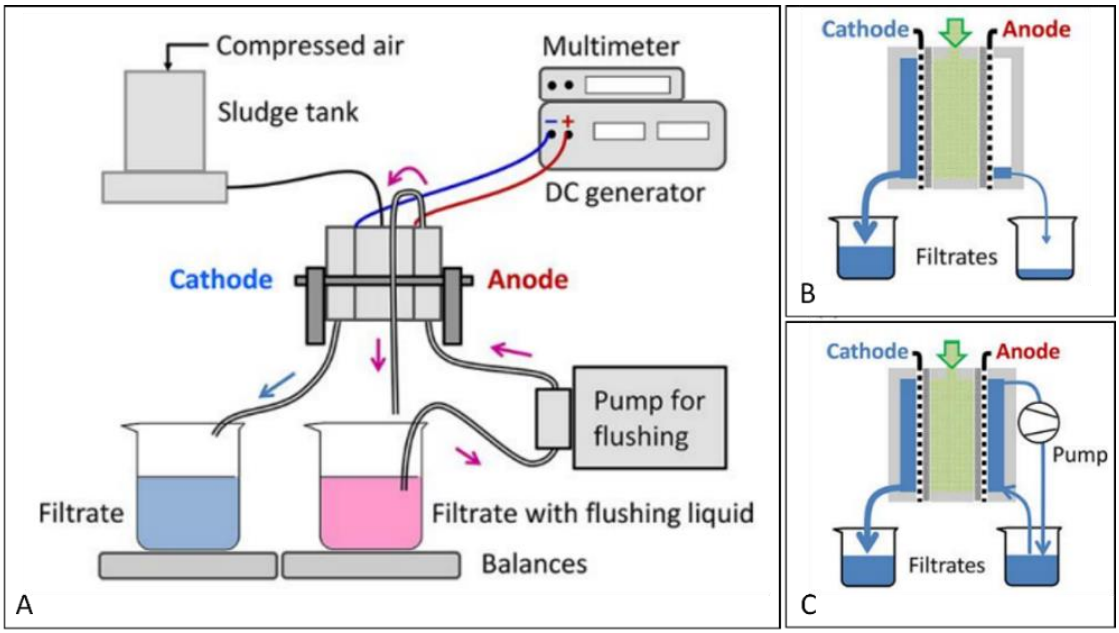

Figure 1.8. Schematic representation of (A) electrofiltration equipment, (B) filtration chamber without anode flushing, and (C) filtration chamber with anode flushing. Adapted from [278]

For example, Käpler and Posten [130], Hofmann and Posten [256], and Gözde *et al* [302] have used a lab scale dead-end electrofiltration apparatus with electrode flushing, similarly to the equipment illustrated in Figure 1.9.

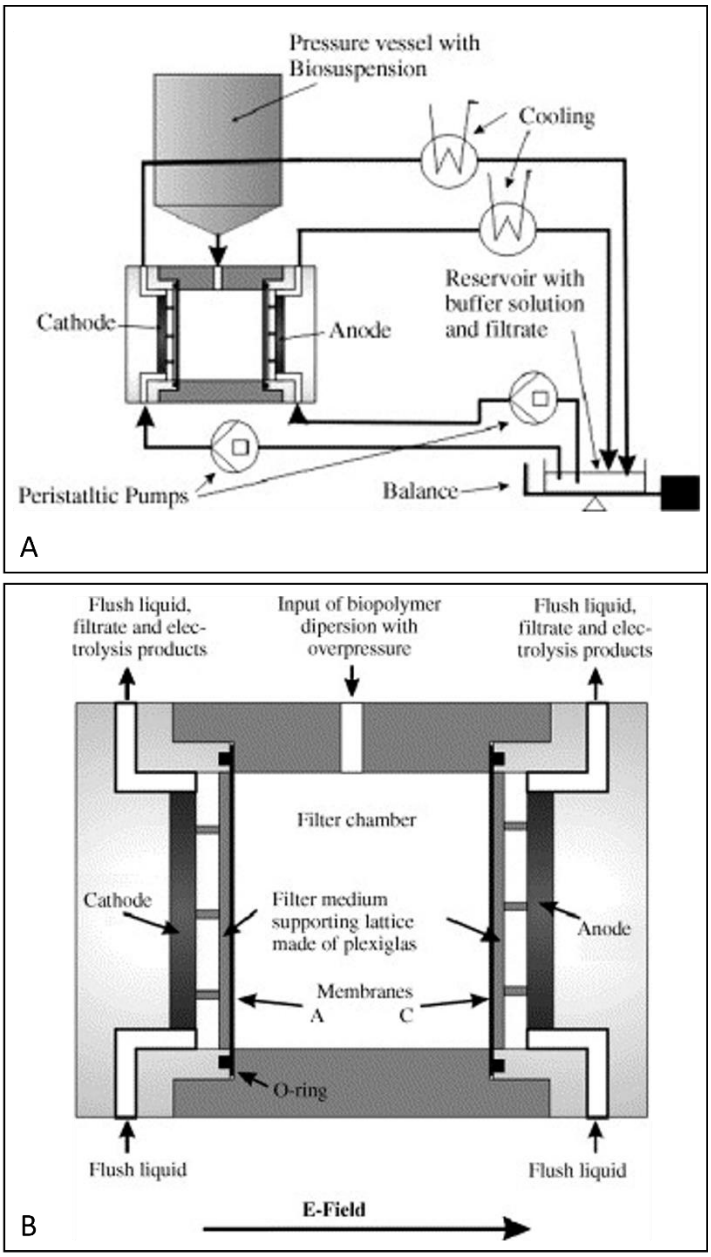

Figure 1.9. Schematic representation of a lab scale (A) filtration rig and (B) filter chamber. Adapted from [130]

Schlegel *et al.* [303] reported that the use of electrofiltration for the recovery of a polyhdroxyalkonate produced by the bacterium *Ralstonia eutropha* was able to reduce the number of processing steps required when compared with conventional techniques for the recovery of polyhdroxyalkonate from bacteria all while reducing the processing costs and increasing the recovery yield. The study also compared electrofiltration with pressure driven filtration (in the absence of an electric field) and found both the concentration factor and the filtrate flux increased with an increase in the electric field strength [303].

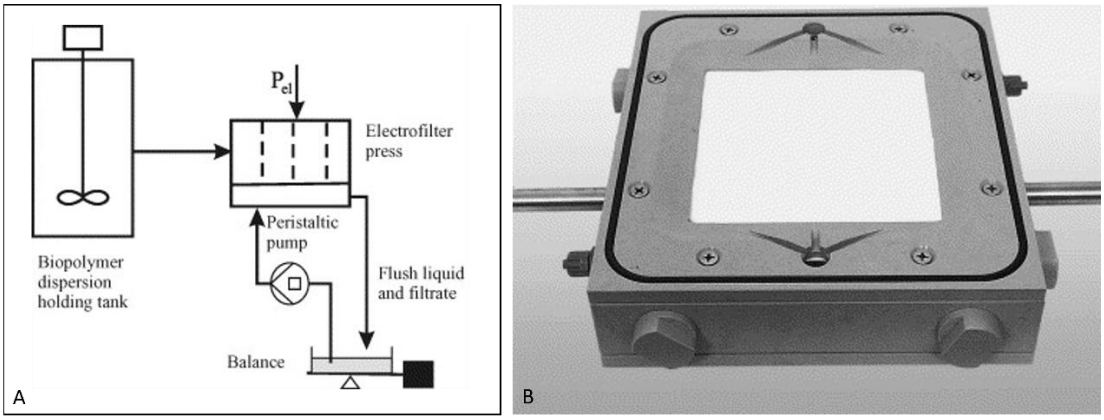

Figure 1.10. Schematic representation of pilot scale: electrofilter press (A) and electrofilter plate (B). Adapted from [304]

Hofmann *et al*. found that using an electrofilter plate (Figure 1.10) for the dewatering of an xanthan polysaccharide was able to increase the solution's concentration by 44 folds (from 5 g/L to 220 g/L) when operating at a pressure of 8 bar with an applied DC electric current of 50 V, it also reduced the processing time by 90% when compared to a filter press with conventional plates [304].

The pilot scale electrofilter press (Figure 1.11) can be used for dead-end electrofiltration as well as electroosmotic dewatering, without the installation of electrodes and the application of an electric field, the conventional filter press can be used for dead-end filtration [167,305]. The electrofilter press can be configured to have one or two outlets for the drainage of filtrate from the filter chamber. The two sided system is used more often since it has a larger filter area which subsequently increases the amount of filtrate that can be removed by mechanical pressure [282]. Other benefits of the two sided system are that (1) it allows the evacuation of the gases formed near the anode and cathode which subsequently helps avoid the formation of an insulating gas layer between the cake and electrodes [282], (2) it makes electrofiltration possible even if the surface charge of the particles changed [26], and (3) it doesn't inhibit the flow of filtrate out of the filter chamber if pole reversal was implemented (switching the direction of the applied electric field).

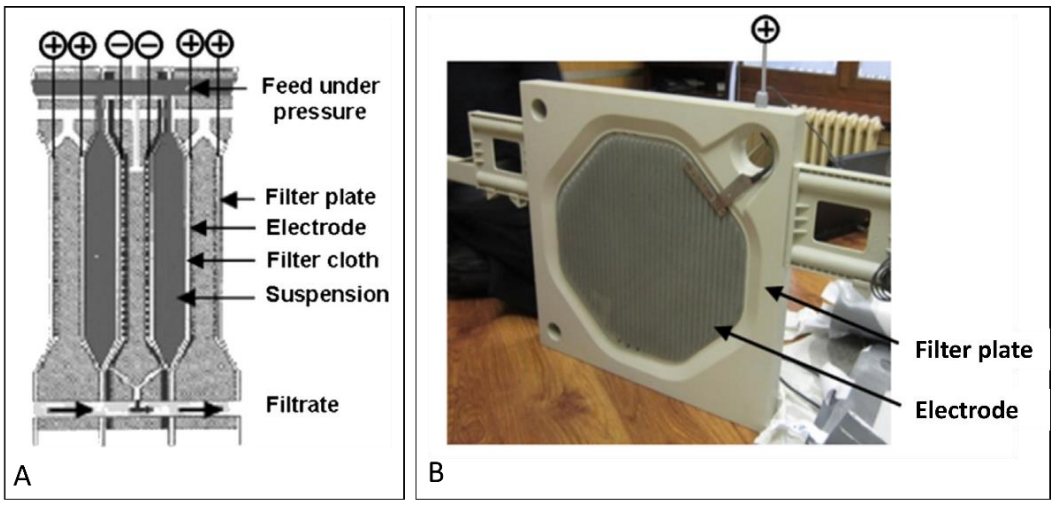

Figure 1.11. (A) Schematic representation of two subsequent electrofilter press chambers and (B) a picture of an electrofilter plate. Adapted from [26]

Other industrial, pilot, and lab scale equipment that are used for electrically assisted filtration processes have been reviewed in detail by Citeau *et al.* [26], this includes equipment such as, the Dorr-Oliver filter, a belt filter press, a pressure drum filter, and a depth bed filter, which can all be used for dead-end filtration. The review explains how the equipment works and specifies details about the materials used.

To sum up this section, as mentioned earlier, the use of dead-end electrofiltration (direct current) has been proven to increase the filtration rate as well as the final dry solid contents in the cake (Table 1.10). Electrofiltration also consumes relatively less energy than other harvesting techniques (see Table 1.10 and Table 1.3). However, a proper study comparing different separation techniques applied to the same suspension must be conducted in order to accurately compare the energy consumption of electrofiltration with other techniques. More specifically, studies must be conducted on a wider variety of suspensions, such as microalgae, to get a better understanding of the effectiveness of electrofiltration for microalgae dewatering.

1.2.6 Perspective for microalgae

Few studies have been conducted to investigate the efficiency of electrically assisted filtration of microalgal slurries. As discussed in Section 1.1.3.2, two studies investigated the use of an electric field to enhance the dewatering of microalgae by: cross-flow electrofiltration for *Chlorella* [24] and electroosmotic dewatering for *Microcystis aeruginosa* [23]. These studies show the need to fill more research gaps related to the use of electrofiltration for microalgae harvesting. Figure 1.12 shows the equipment used for the electrodewatering of microalgae in two different studies.

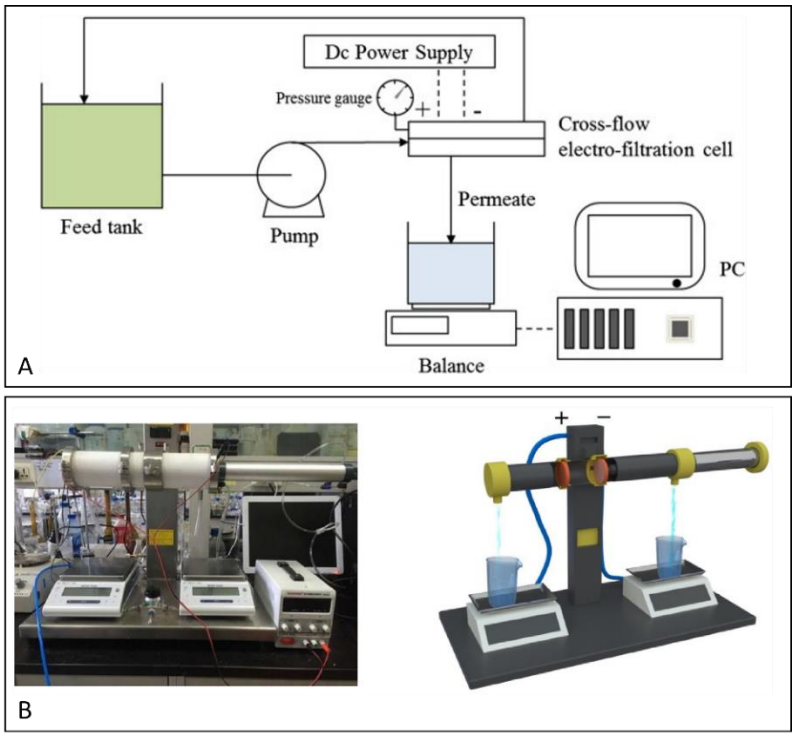

Figure 1.12. Electrodewatering equipment used in literature. (A) Cross-flow electrofiltration, from [24] and (B) Pressurized electroosmotic dewatering, from [23]

Kim *et al* [24] assessed the performance of continuous cross flow electrofiltration by using an electrically conductive membrane. Electrofiltration was able to increase the filtration efficiency by 150% for an electric current of 5 mA/cm^2 which is equivalent to an energy consumption of 1.09 kWh/m^3 water removed. A higher efficiency (203%) was achieved when the electric current was doubled, however this led to an increase of the energy consumption by 0.87 kWh/m^3. The study also assessed using the electric field in a discontinuous (periodic) manner to decrease its energy consumption: a current of 50 mA/cm^2 was applied for 30 s when the filtration flux was recorded below 50 L/m^2/h [24].

Cao *et al* [23] explored the use of electroosmotic dewatering for the concentration of a *Microcystis aeruginosa* suspension with a solid concentration of 0.35 g/L, a pH value of 9.26 and a zeta potential of –18.3 mV. A PVDF membrane with a pore size of 0.45 µm and non corrosive electrodes made out of titanium coated with metal oxide, also known as a dimensionally stable (DSA) electrodes were used. The study found that electrodewatering kinetics were improved with the increase in voltage and the ionic strength of the microalgal suspension. Biocompounds were also dissolved into the filtrate streams, the concentration of the extracted biocompounds in the filtrate from the anode and cathode sides increased with the increase in voltage and ionic strength [23]. This indicates that electrodewatering can be used as a dewatering technique with the added (potential) benefit of extracting biocompounds trapped within the microalgal cells, more research needs to be conducted in order to understand the mechanisms and assess the effects of biocompound extraction during electrically assisted dewatering of microalgae. In some cases, the

extraction of biocompounds during electrodewatering could be considered as a drawback, depending on the intended use of the formed microalgal cake.

This shows the scant amount of research that has been conducted on the use of electrofiltration for microalgae harvesting and dewatering, especially when compared to the amount of research that has been conducted on the optimization and scaling up of electrofiltration techniques for the dewatering of sludges, soil, clay, among other materials as discussed in Section 1.2.5.

1.3 Filter cake washing and electrowashing

Cake washing can be used as an additional processing technique, after filtration, to remove excess mother liquor that is trapped within the pores of the filter cake or to clean the solid potion of the cake before disposing of it. Industries could be interested in removing the trapped mother liquor because it contains valuable compounds that should be recovered for commercial purposes, or that the trapped liquor is considered as an impurity or contaminant if the solids are the product of commercial interest [306]. There are two main cake washing mechanisms: dilution and displacement. In cake washing based on the dilution mechanism, the cake is mixed to form a suspension with the washing solution, the agitation ensures that the solid/liquid interphase is high enough to yield an acceptable mass transfer rate. Whereas in the displacement method, the cake retains its structure and, thanks to a pressure gradient, a clean washing solution is pushed through the pores of the cake, replacing the previous liquid trapped in the pores (mother liquor) with fresh liquid from the washing solution. The main disadvantage that has been reported with the displacement method is the difficult distribution of the wash solution in vertical filtration surfaces. Whereas some of its advantages are [306]:

- The high washing efficiency.
- Lower quantity of washing solution is needed.
- Does not require new equipment, it can be directly applied to the filter cake in the filtration chamber. Subsequently, it requires less processing time due to the lower latency time between processes.
- Can be used with different types of filters.

Other problems that can be encountered, which may reduce the effectiveness of the washing technique, are cake cracking and the formation of large holes or voids in the filter cake. Cracking is more likely to occur with fine solids. The main issue with the formation of holes or voids in the filter cake, is that the washing solution will take the easier path (the voids) instead of going through the cake pores [306]. This reduces the residence time of the washing solution in the cake and the solution may not be able to properly diffuse into all of the cake's pores. Hence, a portion of the original mother liquor would remain trapped in the filter cake which leads to: (1) a loss of product if the mother liquor contains valuable compounds of interest and subsequently a loss of

profitability, or (2) an impure product if the aim is to rid the cake of the mother liquor in the pores and recuperate the solid phase as a final product.

For example, when washing cakes formed of fine particles, a longer residence time is needed, the cake is more likely to form cracks, and the cake is less permeable. The cake thickness also plays an important role in the washing performance: washing thicker cakes is more efficient than thinner cakes, however the thicker cakes would require more time to form [306].

In general, the driving force that governs the path of the washing solution through the cake is the same one that is used during the filtration process to form the cake, but diffusional phenomena also take place. The pores need to be open to flow to allow the washing solution to go through them [32]. Another factor that affects the cake washing procedure are the interactions within the system among the solid particles in the cake, the mother liquor trapped in the cake pores, and the washing solution being introduced into the pores [307].

Thus, cake washing after filtration can render biorefinery operations more efficient by using an integrated processing system. The use of integrated biorefinery systems presents the benefit of having a more economically viable production line, which in turn can help reduce the cost of the final products obtained by the extraction of co-products [5,7,27,28–30]. One of the challenges this could present is the selection of the order of the product extraction sequence, to maintain good extraction yields while maintaining the stability and functionality of the co-products being extracted. As mentioned earlier, the incorporation of an electric field has been investigated in filtration processes and cake washing. Hence the use of electrically assisted processes in an integrated biorefinery process could be beneficial, especially due to the enhanced process kinetics and the simultaneous release of electrochemicals. During chemical acid base treatments for biocompound extraction, the main mechanism of cell disintegration occurs due to the presence of ionic species that interact with the cell membranes to denature its structure. For example, one study investigated the effect of pH on *A. platensis* cells and it was found that the OH^- and H^+ ions can effectively permeabilize the cells by sequentially reacting and disintegrating the complex cell walls [313]. The release of OH^- and H^+ has been reported in electrically assisted filtration experiments as a product of water electrolysis [26,278,280,286,298,314].

Electrically enhanced cake washing has been investigated for the removal of solutes and liquor trapped within fine filter cakes. Tarleton *et al.* reported the effects of using a direct current while maintaining a constant voltage ranging from 0 to 30 V, during a vertical washing process by displacement [315]. The apparatus does not eliminate the effect of gravitational forces; however, those could be neglected when compared to the hydrodynamic and electromotive forces, especially given the small thickness of the cake, which was reported as 10 mm. The study found that the application of an electric field was able to enhance the washing process. When the porosity of the cake progressively decreased, the process's ability to improve the de-liquoring kinetics became less effective. Even though many parameters still require further investigation to gain a better understanding of the process and the variables that affect it the most, the application of

electrowashing was found to be promising, especially given its relatively low energy consumption [315]. Since the main driving force used during cake washing is the same one that drives the flow of fluid during the filtration process, it is supposed that the application of an electric field can also enhance the washing kinetics based on the findings in electrically assisted filtration studies, where, as reported earlier, the application of an electric field enhanced the filtration kinetics [26,129,278,280,286,314].

1.4 Conclusion and research objectives

Many techniques have been developed for the extraction of various bioactive compounds from different microalgal species, and there is a wide range of industries that use microalgal extracts in their products, such as pharmaceuticals, cosmetics, and animal feed, to name a few. As previously mentioned, numerous studies have investigated the use of different techniques in upstream and downstream processes in microalgae biorefineries. However, some of the research gaps that still need to be targeted are the optimization of the applied processes in terms of their costs and efficiencies, especially in the microalgae harvesting and dewatering steps. Less energy intensive techniques can be investigated for the dewatering (concentration) of harvested microalgae since the cost of dewatering and the high energy consumption have been reported as some of the main limitations in various studies. The use of filtration as a dewatering technique can reduce the energy consumption in microalgae harvesting and dewatering processes, however filtration techniques presented many limitations, such as membrane fouling, flux decline over time which makes the process slower, and the need to replace and clean the membranes. Another issue is the need to optimize pressure driven dead-end filtration for the concentration of algal solutions in order to efficiently separate algal extracts (lipids, proteins, carbohydrates, and pigments) from cell debris and other undesired materials. The main objectives of this research topic are:

- Studying the effect of the properties of the microalgal solution on the filtration kinetics and yield. This is achieved by studying the dead-end filtration of two types of microalgae (*A. platensis* and *C. vulgaris*) with different physical and chemical properties. This can help assess the suitability of using filtration and electrofiltration for the concentration of microalgal solutions, noting that *C. vulgaris* is far more difficult to filter than *A. platensis* given the smaller size of the former's cells.
- Studying the effect of the pressure and filtration time on the filtration kinetics, cake properties and filtrate properties, for both conventional dead-end filtration and electrofiltration.
- For electrofiltration, the optimal electric field strength and its combination with different pressures are assessed. The filtration kinetics and cake and filtrate properties are also assessed.
- Optimizing the operating conditions of electrofiltration based on the properties of the microalgal suspension that is being processed.

- Exploring the use of filtration and electrofiltration as a biocompounds separation technique after extraction of biocompounds from *A. platensis* by ultrasonication. Studying the effect of the process on the concentration of biocompounds extracted in the filtrate as well as the concentration of biocompounds retained in the cake.
- Cake washing with and without an electric field are also studied in this work as a way to extract any bioactive compounds that are trapped in the cake and help dewater the cake even more after conventional filtration.

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Chapter 2: Materials and Methods

This chapter presents the different types of microalgal suspensions that were studied. The characterization techniques (raw material and products), experimental setup, and procedure are also discussed in this chapter. Figure 2.1 schematically represents schematically the experiments conducted in our work.

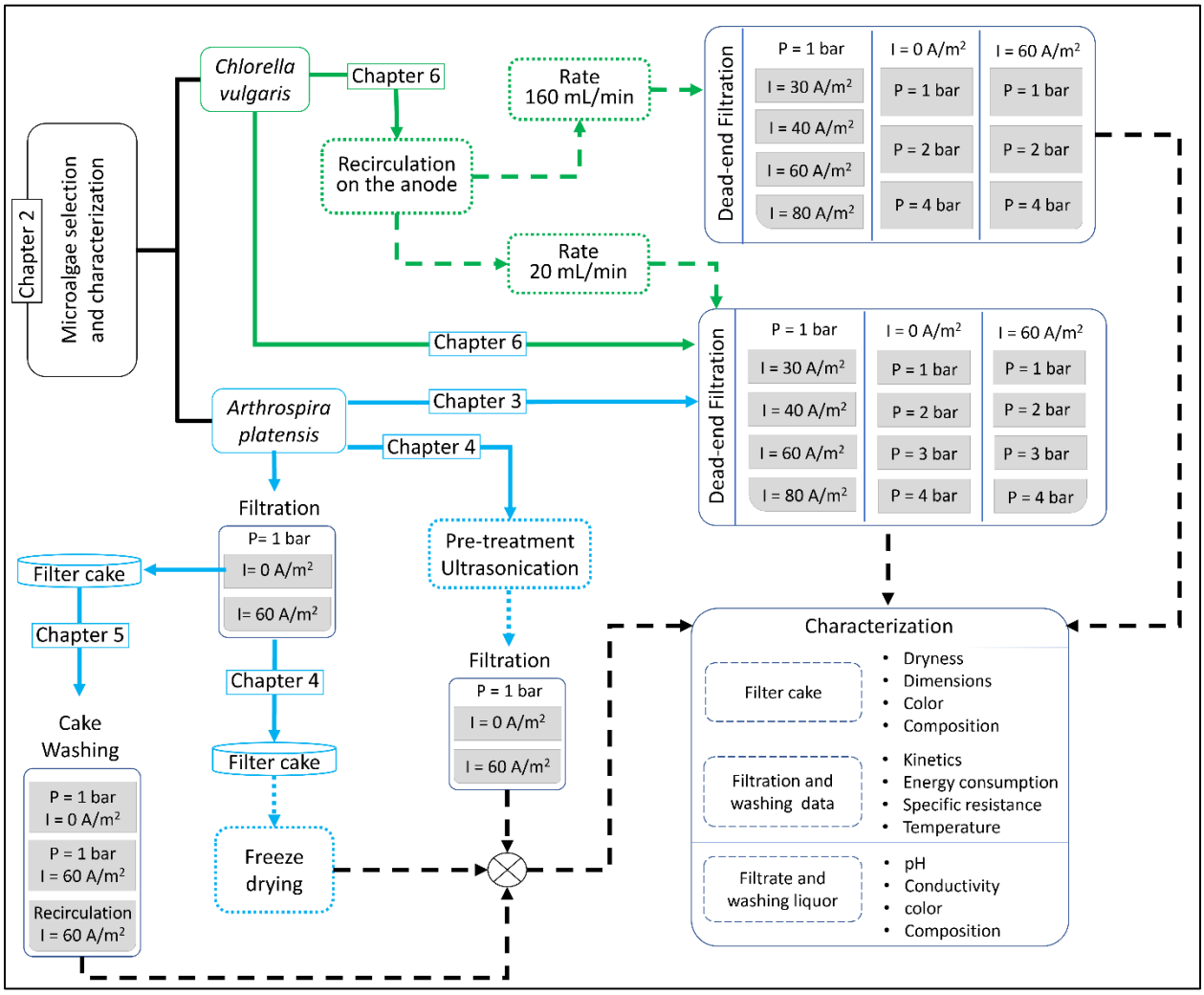

Figure 2.1. Schematic summarizing the experimental work conducted in this thesis

2.1 Studied microalgae and their properties

Two types of microalgae were studied in this thesis: *Chlorella vulgaris* and *Arthrospira platensis*, respectively purchased from Xi'an SR Bio-Engineering Co., Ltd (Weiyang District, Xi'an, China) and SAS TAM- Cyane (Plougastel-Daoulas, France). An initial concentration of 5%

by weight (hereby 5%) was used as the feed solution for both species of microalgae. For all the *A. platensis* experiments, the frozen microalgal paste was thawed at room temperature, then mixed with deionized water to form a 5% solution. For the *C. vulgaris* experiments, microalgae powder was weighed and added to deionized water, to form a 5% solution, that was then mixed until a homogeneous suspension was obtained. The properties of the studied algal suspensions are presented in Table 2.1.

Table 2.1. Characteristics of Chlorella vulgaris and Arthrospira platensis

Microalgae		*Chlorella vulgaris*	*Arthrospira platensis*
Supplier		Xi'an SR Bio-Engineering Co., Ltd (Weiyang District, Xi'an, China)	SAS TAM- Cyane (Plougastel-Daoulas, France)
Physical state		Powder	Frozen
pH*		7.8±0.1	7.06±0.3
Electrical conductivity* (mS/cm)		2.8±0.05	1.62±0.12
Zeta potential*		-23.6±1.3 mV	-17.3±0.9 mV
Average particle size (µm)- Number	d (0.1)	1.42	3.01
	d (0.5)	2.36	4.54
	d (0.9)	5.6	9.15
* Measured for the 5% solution of each microalga			

To study the effect of cell disruption on the filtration efficiency, dry products were used to simulate the filtration behavior of disrupted cells and, for previously frozen *A. platensis*, ultrasonication was used to increase the extraction yield of proteins and pigments.

2.2 Ultrasonication pretreatment

The effect of ultrasonication on the filtration and the extraction of bioactive compounds was studied by using 5% *A. platensis* suspensions that were treated by an ultrasonic processor (UP-400S, Hielscher Ultrasonics, GmbH, Germany) at 400 watts for 20 minutes. The probe was immersed in the center of the suspension to be treated, about 2 cm away from the bottom of the beaker. The temperature of the solution was controlled with an ice bath during treatment. Untreated samples were used as a control.

2.3 Filtration and electrofiltration equipment

The filtration parameters and equipment were selected based on reviewing results reported in different electrofiltration studies [1–4].

The same pieces of equipment were used for the filtration and electrofiltration experiments with minor modifications. The equipment was provided by Choquenet SAS. It consisted of a 1 L feed tank connected to a pressurized air system, a stainless steel support with a screw to secure the independent parts of the system together, and a polypropylene filtration cell (circular cross section 24.6 cm^2, volume 49.2 cm^3) equipped with a feed inlet and valve. Both sides of the filtration cell were covered with a disposable PVDF membrane (Nafion MV020T, Millipore) with a pore size of 0.2 µm, which was selected based on the particle size distribution of the *C. vulgaris* and *A. platensis* feed solutions. Prior to use, the membranes were activated by soaking them in deionized water for 30 minutes. Rubber joints were placed between any two independent parts in the filtration system to avoid any leaks. A schematic representation of the equipment is presented in Figure 2.2.

For the electrofiltration experiments, electrodes were placed in direct contact with the membrane, on the outer side of the filtration cell to avoid coming into contact with the filter cake. The electricity supply was set using the EV261 direct current generator (0–1 A, 0 –600 V, Consort, Belgium), and was monitored using a multimeter (FLUKE 45). The filtration rates were obtained by continuously weighing the obtained filtrates with two electronic balances (METTLER PM6000, max weight: 6000g, resolution: 0.01g and SARTORIUS (max weight: 600g, resolution: 0.1g).

The filtrate masses, and the applied currents and voltages were recorded by the HPVE filtration 2009 acquisition software (Electronic Service, U.T.C.). The interval between each measurement was fixed at 60 seconds. The temperature at the electrodes was measured using flexible K-type thermocouples, connected to a 4 channel thermometer (Extech Instruments).

At the end of each experiment the pH and conductivity of the filtrate were measured at room temperature (25˚C) using Consort C5010 multi-parameter analyzer.

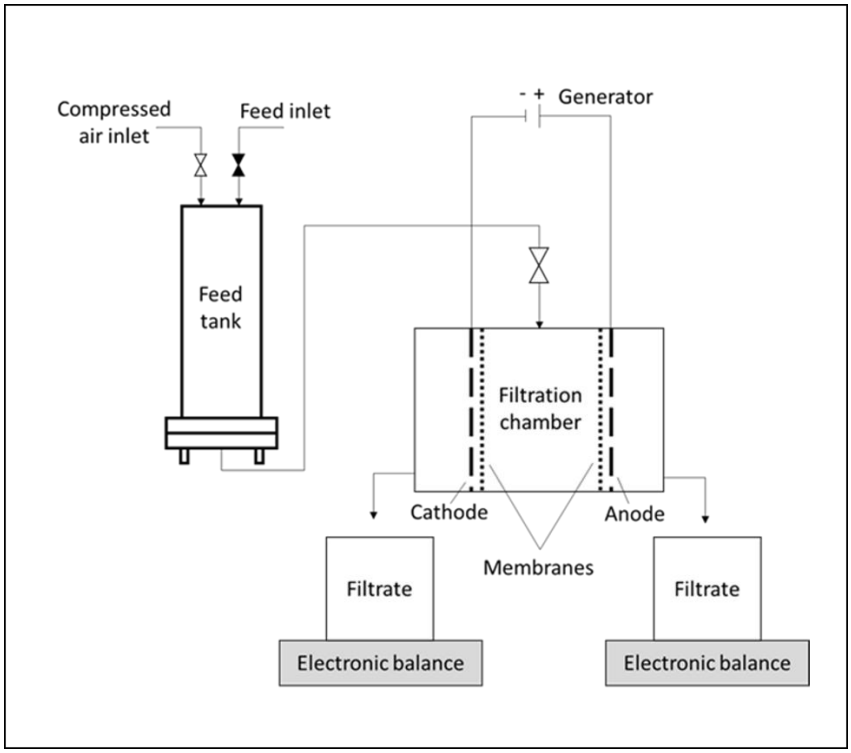

Figure 2.2. Filtration system without recirculation

For the electrofiltration experiments with fluid recirculation on the anode side, a peristaltic pump, MASTERFLEX, was used to recirculate 207 g of deionized water with the recuperated filtrate back to the anode side of the filtration chamber. The recirculation unit was used to control the temperature increase caused by ohmic heating. The use of different recirculation rates was assessed (0, 20, and 160 mL/min). Two collection systems were studied when the recirculation unit was used: a separate collection system (Figure 2.3) and a mixed collection system (Figure 2.4).

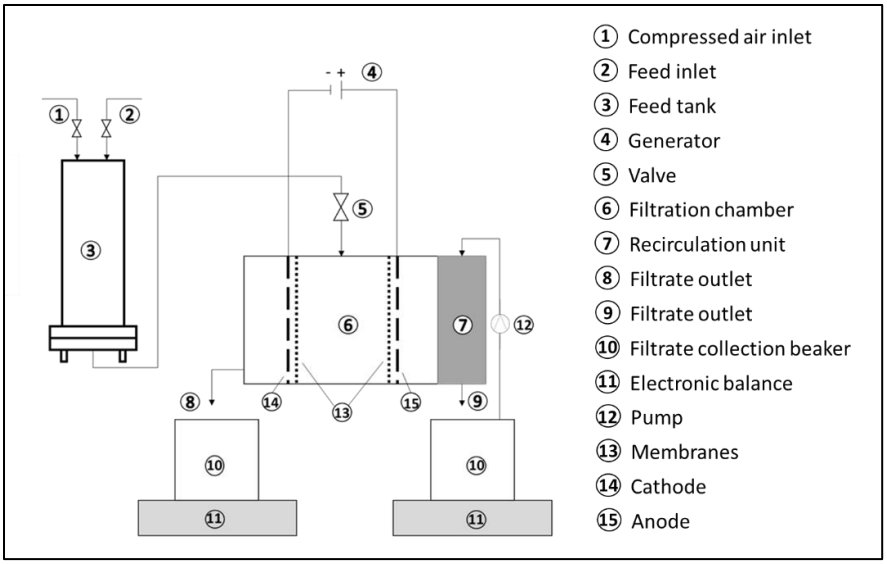

Figure 2.3. Filtration with a recirculation system at the anode side. Filtrate from the cathode and anode side are collected separately (separate collection system)

In Figure 2.3, the separate collection system entails the recirculation of the filtrate collected at the anode side mixed with deionized water.

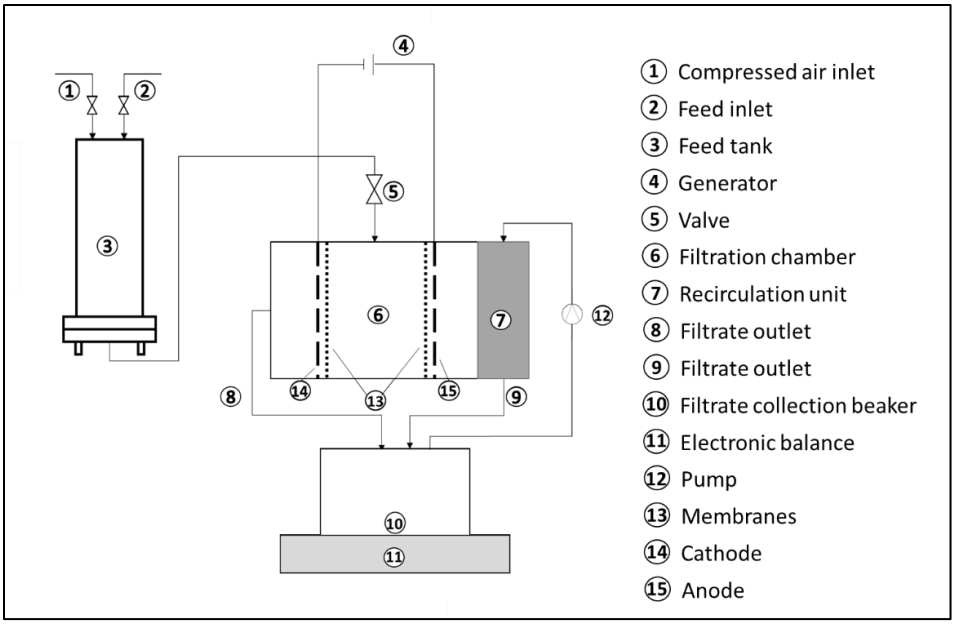

Figure 2.4. Filtration with recirculation at the anode side. The filtrate from the anode and cathode side are collected together (mixed collection system)

In Figure 2.4 the filtrate from the anode and cathode side are collected together with distilled water (that was already placed in the collection beaker) as a way to neutralize the pH of the fluid being recirculated.

Different recirculation rates were used during the filtration of *C. vulgaris* to study the effect of recirculation on the filtration rate: 20 mL/min and 160 mL/min.

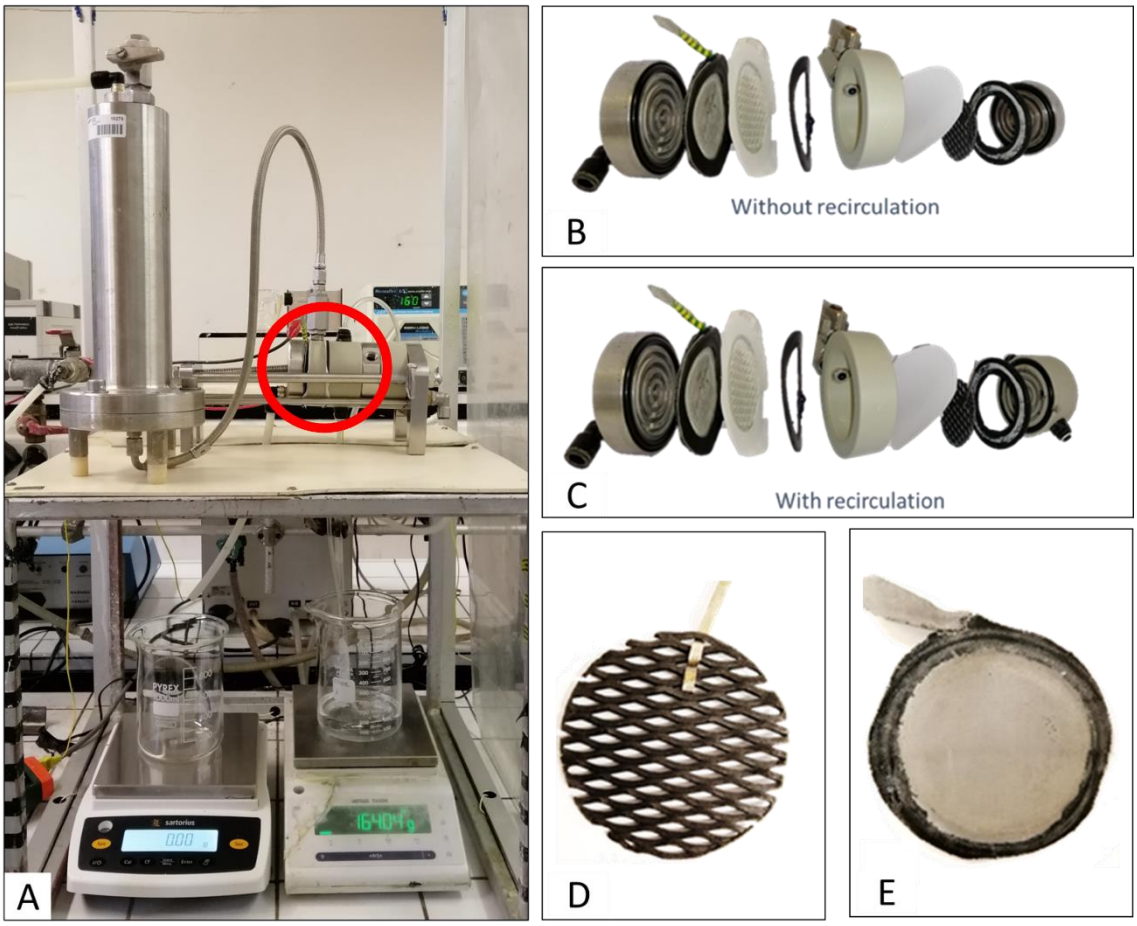

Figure 2.5. Images of the filtration equipment. (A) Experimental setup where the filtration cell is circled in red, (B) filter cell components without a recirculation unit, (C) filter cell components with a recirculation unit, (D) anode, and (E) cathode

Figure 2.5 shows the dead-end filtration equipment used in this study. The components are assembled to form one of two filtration cell configurations (Figure 2.5 B and C). For the electrically assisted experiments, two different electrodes were used: the anode was made of Titanium (dimensionally stable anode) and the cathode was made of Inox. The electrodes (Figures 2.5 D and E) are not installed in the experimental setup for the filtration experiments that do not require the application of an electric field.

2.4 Experimental conditions studied for each microalgal species

This section describes the experimental protocols used for the experiments conducted on *A. platensis* and *C. vulgaris*.

2.4.1 Arthrospira platensis

The experimental protocols used for the filtration, electrofiltration, and cake washing experiments were explained in detail in each article featured in chapters 3, 4, and 5.

2.4.1.1 Filtration and electrofiltration

Briefly, the filtration and electrofiltration experiments followed the same methodology detailed in Sections 2.4.2.1, 2.4.2.2, and 2.4.2.3.

The ultrasonication treatment (US) is described in the relevant chapter as well as Section 2.2.

We suspected that the particle size and the initial state of the microalgae (dry, fresh, frozen…) have an effect on the filtration performance. In order to determine the effect of using *A. platensis* cells with different physical states on the filtration kinetics, simple filtration and electrofiltration ($I = 60\ A/m^2$) experiments at a pressure of 1 bar were conducted for initially frozen then thawed, dry, and US treated samples (Figure 2.6).

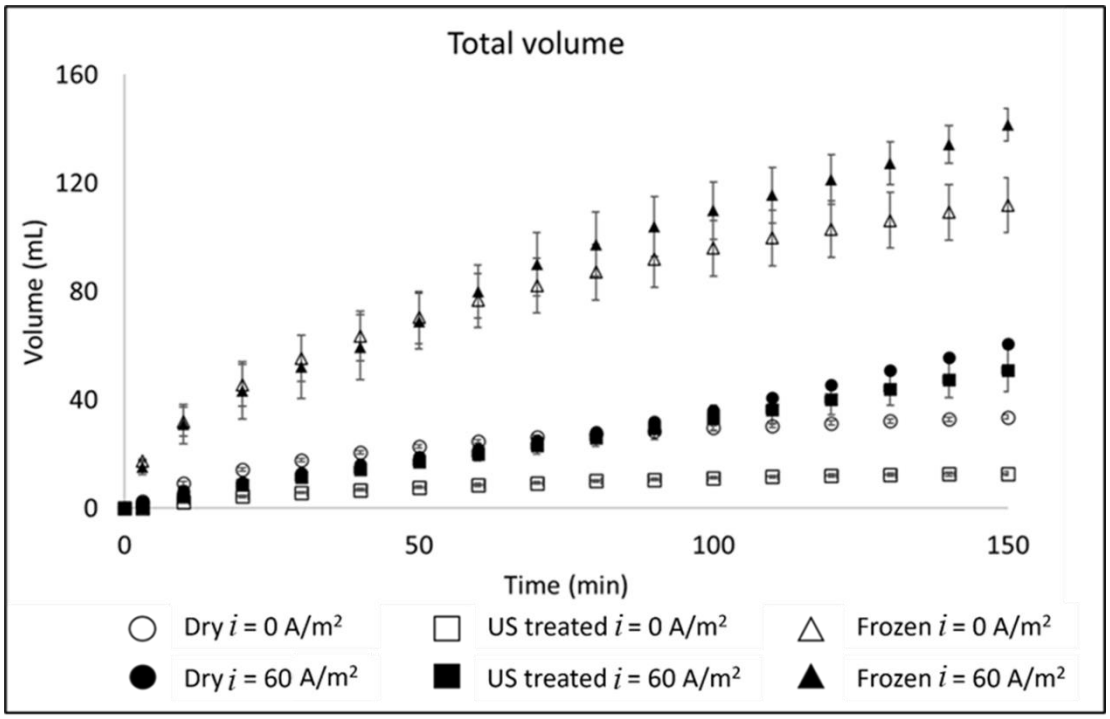

Figure 2.6. Filtration rate for 5% A. platensis feed solutions. Results for initially dry, ultrasound (US) treated, and initially frozen then thawed (Frozen) A. platensis cells

US treated *A. platensis* exhibited the slowest filtration rate without the application of an electric field. The application of an electric field drastically improved the filtration rate making it an interesting option for a feed solution. Similarly, dry *A. platensis* exhibited a slow filtration rate during simple filtration, the use of electrofiltration did not significantly improve the filtration rate, which made it a less desirable option as a feed solution. *Arthrospira platensis* that was frozen and then thawed was proven to be the most favorable type of feed solution given the filtration kinetics that was obtained by simple and electrofiltration.

Testing the use of fresh *A. platensis* would have been favorable in order to gain a better understanding of the use of filtration and electrofiltration in the context of freshly cultivated microalgae in the context of "a lab scale biorefinery". However, given the distance between the wholesaler and the university, the use of fresh microalgae was not practical due to the costs and the risks (i.e. damaging the cells) associated with transporting them over relatively long distances. Moreover, cultivating the microalgae was beyond the scope of this study.

2.4.1.2 Electrowashing procedure

Electrowashing was carried out according to the description detailed in Chapter 4 of this thesis, where the following was stated:

In order to carry out the washing procedure a well-formed cake with a relatively high specific resistance should be formed. For this reason, a feed solution of 5 % *A. platensis* was filtered at a pressure of 4 bar, in order to obtain a cake with a higher specific resistance (as demonstrated by the findings discussed in Chapter 4). The filtration time was set as 16 h.

Washing was performed in-situ within the same equipment that was used to form the cake (same as the filtration apparatus). The wash solution inlet was modified (as illustrated in Figure 2.7 A and B). Two different electrodes were used, the cathode was made out of Inox whereas the anode was made out of Titanium with a mixed metal oxide coating, also referred to as a dimensionally stable anode. Three different experimental conditions were studied: Pressure of 1 bar without an electric field (denoted PW), Pressure of 1 bar with an applied electric field of 60 A/m^2 (denoted PEW), and a recirculation system operating at 260 mL/min with an electric field strength of 60 A/m^2 (denoted EW). A peristaltic pump was used in the setup of the experiments with the recirculation system. A total of 12 samples were collected for the complete set of experiments. The first two samples were 2.5 mL each, all the other samples were 5 mL each, equivalent to a total volume of 55 mL.

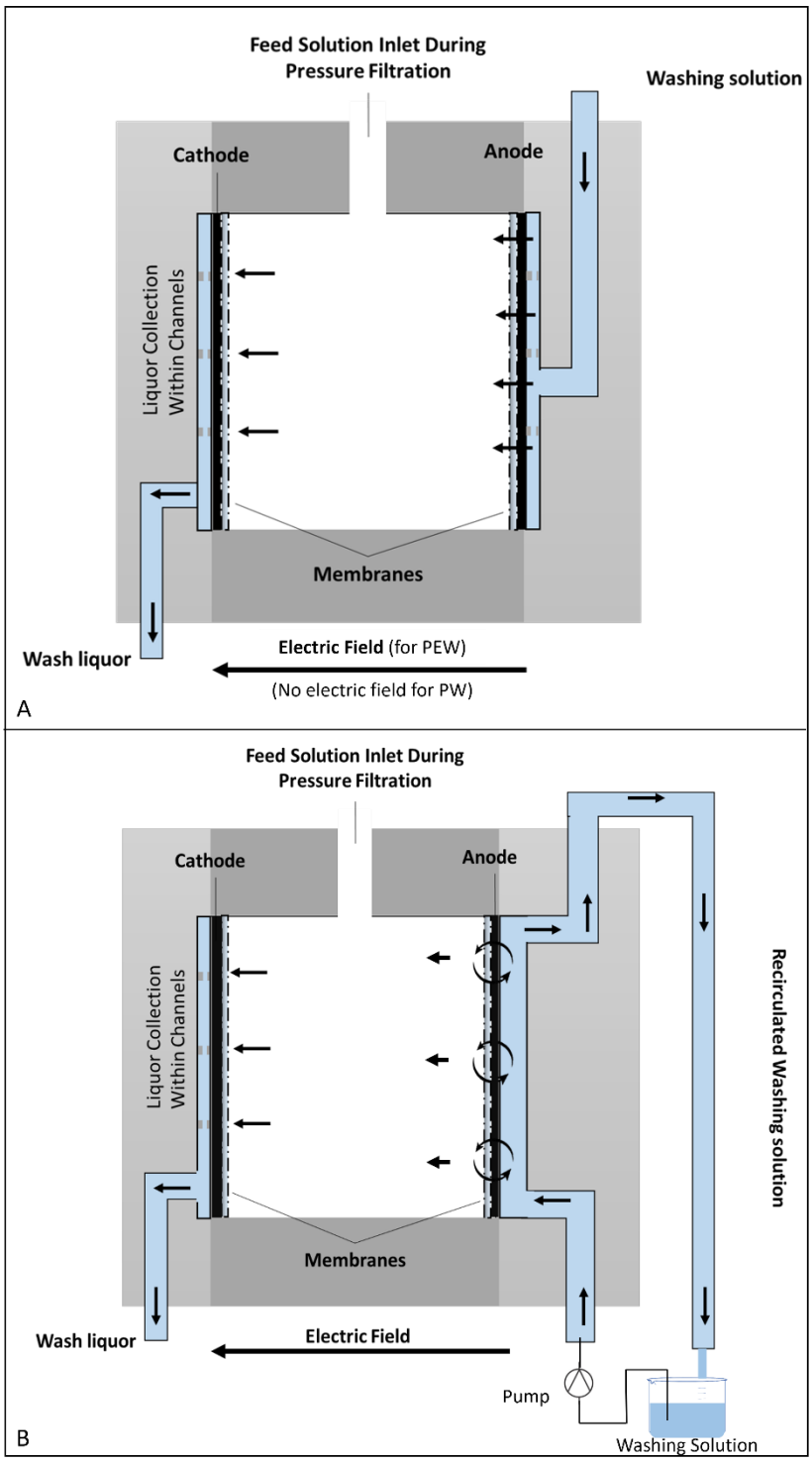

Figure 2.7. Pieces used at inlet of washing equipment, coupled by a schematic of the washing mechanism. A: Used for PW, E, and PEW (no electric field governs the transport for PW), B: used for EW

Experiments were stopped when the washing rate was found to be too slow. This was the case for PW, where a total volume of 45 mL was recovered. Tap water was used as the wash solution

(pH = 7.36, electrical conductivity σ = 0.6 mS/cm), since it is an ideal solvent to extract water soluble phycobiliproteins from *A. platensis*. The changes in temperature were measured using flexible K-type thermocouples, connected to a 4-channel thermometer (Extech Instruments). At the cathode side (outlet of the wash liquor) the temperature was measured near the electrode for an accurate representation of the temperature in the washing chamber, the temperature was not recorded on the anode side due to inevitable leaks after inserting the thermocouple near the anode.

2.4.2 Chlorella vulgaris

Different sets of experiments were performed to independently assess the effect of different parameters on the filtration efficiency. The variables taken into account were the filtration time, the pressure, the electric current density, the use of recirculation, as well as the combination of these variables.

2.4.2.1 Effect of pressure without an electric field

Suspension filtration at different pressures (1, 2, 3, and 4 bars) without the application of an electric field, referred to as filtration (F), was conducted in order to study the effect of pressure on the filtration kinetics as well as the filtrate and cake properties. The filtration time was set as 150 minutes, after which the filtration kinetics became slow. The filtrate streams obtained from the two sides of the filtration cell were collected separately.

2.4.2.2 Effect of the electric current density under constant pressure

Electrically assisted filtration, referred to as electrofiltration (EF), was carried out at a constant pressure of 1 bar and different electric current densities (30, 40, 60, and 80 A/m^2). The filtration time was set to 150 minutes for the sake of comparison with the F experiments.

2.4.2.3 Effect of pressure under the influence of an electric field

Based on the findings from the experiments described in Section 2.4.2.2, the electric current density of 60 A/m^2 was selected to study the effect of pressure on EF. Hence, EF was conducted at a constant electric current density of 60 A/m^2 for different operating pressures (1, 2, 3, and 4 bar). The experiments were also conducted for a duration of 150 minutes.

2.4.2.4 Effect of recirculation

The effect of using a recirculation unit on the anode during F and EF was assessed for different recirculation rates. Two collection configurations were studied: the collection of the filtrate from

the cathode and anode side separately (Figure 2.3) and the collection of the filtrate from the cathode and anode side mixed together in the same beaker (Figure 2.4).

2.4.2.4.1 Separate collection of the filtrate

Two recirculation rates were studied: 20 mL/min and 160 mL/min. F and EF (60 A/m^2) were conducted for 150 min at pressures of 1, 2, and 4 bar.

For the rate of 160 mL/min, EF at 60 A/m^2 was also conducted for 360 min to assess the effect of the filtration time on the filtration kinetics, cake dryness, and the pH and electrical conductivity profiles of the filtrate.

2.4.2.4.2 Mixed collection of the filtrate

F and EF at 60 A/m^2 were carried for 360 min at pressures of 1, 2, and 4 bar. The results were compared with the separate collection configuration by assessing the effect of mixing the filtrate from the anode and cathode side on the filtration kinetics, cake dryness, and the pH and electrical conductivity profiles of the filtrate.

2.5 Kinetic modeling

The kinetic models are also described in the articles presented in Chapters 3, 4, and 5.

2.5.1 Filtration (no electric field)

The specific resistance of the filter cake was calculated by applying Ruth Carman's formula (Equation 2.1):

$$\frac{t-t_0}{V-V_0} = \frac{\propto.\mu.C_0}{2A^2\Delta P}(V+V_0) + \frac{R_m.\mu}{A.\Delta P} \quad (2.1)$$

Where: t time (s), V volume of filtrate (m^3), V_0 volume of filtrate recuperated at the time t_0 which corresponds to the moment at which filtration starts to take place under a constant pressure, α specific resistance of the filter cake (m/kg), μ viscosity of water equal to 10^{-3} Pa.s, C_0 initial concentration of the feed solution (kg/m^3), A cross sectional filtration area equal to 0.00246 m^2, ΔP applied pressure (Pa), and R_m membrane resistance (m^{-1}).

2.5.2 Electrofiltration

The electrofiltration equation of suspensions with negatively charged particles considers the superposition of hydraulic and electroosmotic flows [5].

The equation on the anode side is expressed as Equation (2.2):

$$\frac{\mathrm{d}v_a}{\mathrm{d}t} = \frac{\Delta p}{\mu\alpha_a(v_a c_o + q_{ef}\cdot\varphi_s\cdot\rho_p\cdot t)+\mu R_{ma}} - P_{EO} i \quad (2.2)$$

and it is expressed as Equation (2.3) on the cathode side:

$$\frac{\mathrm{d}v_c}{\mathrm{d}t} = \frac{\Delta p}{\mu\alpha_c(v_c c_o - q_{ef}\cdot\varphi_s\cdot\rho_p\cdot t)+\mu R_{mc}} + P_{EO} i \quad (2.3)$$

where v_a and v_c are the volume of filtrate per cross sectional area of the filter surface respectively for the anode and cathode side (m^3/m^2), t is the time (s), Δp is the pressure (Pa), μ is the fluid viscosity (Pa.s), α_a and α_c are the specific cake resistance respectively for the anode and cathode side (m/kg), c_o is the mass of particles in the cake per filtrate volume in the absence of an electric field (kg/m^3), q_{ef} is the velocity of the electrophoretic movement of particles toward the anode (m/s), φ_s is the particle volume fraction in the microalgae suspension, ρ_p is the particle density (kg/m^3), R_{ma} and R_{mc} are the filter media resistance respectively for the anode and cathode side (m^{-1}), P_{EO} is the electroosmotic transfer through the cake (m^3/C), and i is the electric current density (A/m^2). In absence of electric field, $q_{ef} = 0$, $P_{EO} = 0$, $\alpha_a = \alpha_c = \alpha$, $v_a = v_c = v$, $R_{ma} = R_{mc} = R_m$ and Equations (2.3) and (2.4) can then be transformed into Equation (2.1).

2.5.3 Electrowashing

Washing and electro-washing kinetics can be modeled using Equation (2.4) [5], similarly to the electrofiltration kinetics:

$$\frac{\mathrm{d}v_w}{\mathrm{d}t} = \frac{\Delta p_W}{\mu(\alpha W + 2R_m)} + P_{eo} i \quad (2.4)$$

where v_w is the volume of wash liquor per unit of filter area (m^3/m^2), P_{EO} is the electroosmotic transfer through the cake (m^3/C), and i is the electric current density (A/m^2).

2.6 Characterization techniques

This section discusses the different techniques that were used to characterize the feed solution, filtrates, and filter cakes.

2.6.1 Filter cake: Specific resistance and compressibility

The specific resistance of the filter cake was calculated by applying Ruth Carman's formula (Equation 2.1). The slope of the curve in Equation (2.1) was obtained by plotting $(V + V_0)$ vs $\frac{t-t_0}{V-V_0}$ and selecting the portion of the curve that formed a straight line.

After obtaining the specific resistance of the filter cake for different pressure conditions the cake's compressibility was calculated based on Equation (2.5), as reported in literature [6]:

$$\alpha = \alpha_0(\Delta p/\Delta p_0)^s \tag{2.5}$$

Where α is the specific cake resistance at the pressure Δp, α_0 is the average specific resistance of the cake when $\Delta p = \Delta p_0$ and s is the compressibility index. The compressibility index s is graphically determined by plotting ln (α) vs ln ($\Delta p/\Delta p_0$) and taking the slope of the portion of the curve that forms a straight line. For values of $s > 1$ the cake has a very high compressibility [7].

2.6.2 Cake dryness

The solid content of washed and unwashed cakes was measured by drying the cake in an oven for 24 h at 105 ˚C. In some cases, the dryness profile of the cake was studied by cutting the obtained cake in different (equal) sections with the same cross sectional area, then by measuring the dryness of the different sections separately. The cake dryness was calculated as shown in Equation (2.6):

$$d = \frac{m_d}{m_w} \times 100 \tag{2.6}$$

where d is the cake or cake section's dryness (%), m_d is the mass of the dry cake or cake section (g) and m_w is the mass of the wet cake or cake section (g).

2.6.3 Zeta potential

The zeta potential is an important physical property that helps determine the behavior of a particle suspended in solution, especially the electrokinetic effects the particles are subjected to under the influence of an electric field. The zeta potential is pH sensitive.

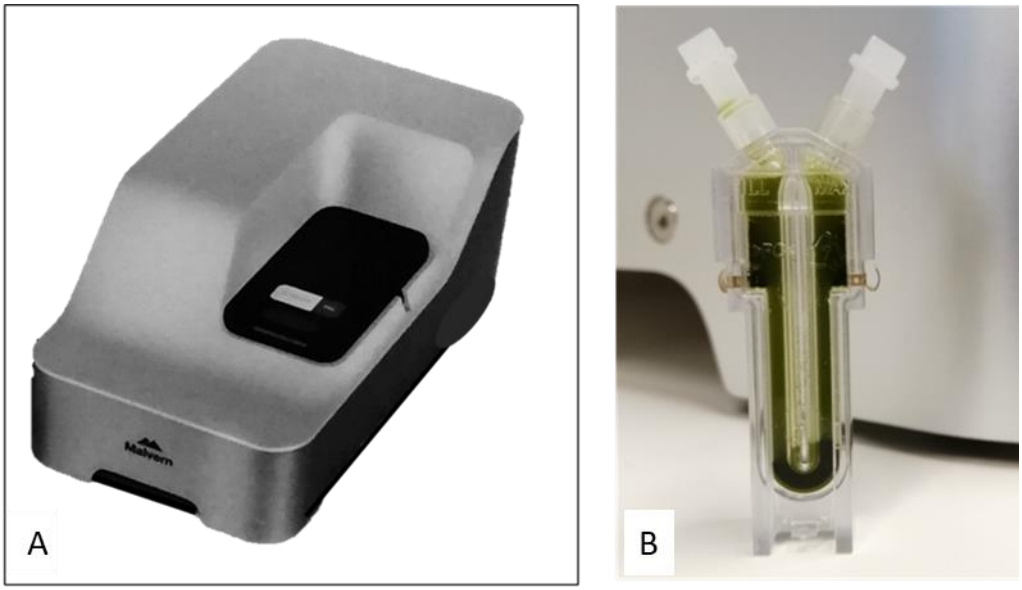

Figure 2.8. (A) Zeta sizer apparatus, (B) capillary cell

The zeta potential of *C. vulgaris* and *A. platensis* feed solutions (5% by weight) were measured using Malvern instruments Nano zeta sizer apparatus and a disposable capillary cell (Figure 2.8 A and B).

2.6.4 Particle size distribution

The particle size distribution of the feed solutions was done using Malvern Instrument Mastersizer 2000. This helped determine the adequate pore size of the membranes to be used in the filtration experiments.

The particle size distribution of the microalgal samples were measured where D(v,0.1), D(v,0.5), D(v,0.9) represent the diameters of the algal cells. D(v,0.1) indicates that 10% of the microalgae have a diameter smaller than the reported value; D(v,0.5) indicates that 50% of the microalgae have a diameter smaller than the reported value, and D(v,0.9) indicates that 90% of the particles have a diameter smaller than the reported value. Moreover, the span or the extent of the difference in values reported for the particle size distribution is an additional parameter that can be calculated, as shown in Equation 2.7.

$$\text{Span} = \frac{D(v,0.1) - D(v,0.9)}{D(v,0.5)} \tag{2.7}$$

2.6.5 Spectrophotometry

Samples were centrifuged at 13500 rpm (miniSpin Eppendorf, France) for 10 minutes, then the supernatant was collected and analyzed. This was done to characterize the feed solutions, filtrates, and in some cases the filter cakes.

2.6.5.1 Protein characterization

The protein content of the samples were determined using Bradford's method (Bradford, 1976), where 100 µL of supernatant was vortexed with 1 mL of Bradford dye reagent (Alfa Aesar, Thermo Fisher Scientific, Germany). The mixture was incubated for 10 minutes in the dark at room temperature, then the absorbance was measured at 595 nm (Biochrom Libra S32, Biochrom Ltd, UK). The blank consisted of 100 µL of deionized water vortexed with 1 mL of Bradford dye reagent. The calibration curve was obtained using bovine serum albumin (BSA) as a standard and the results were expressed as milligrams BSA equivalent per gram dry algal biomass (mg BSA equivalent/ g d.m.).

To minimize human error caused by diluting the samples to be tested, three calibration curves were developed to accommodate the absorbance ranges of the samples without dilution (Figure 2.9).

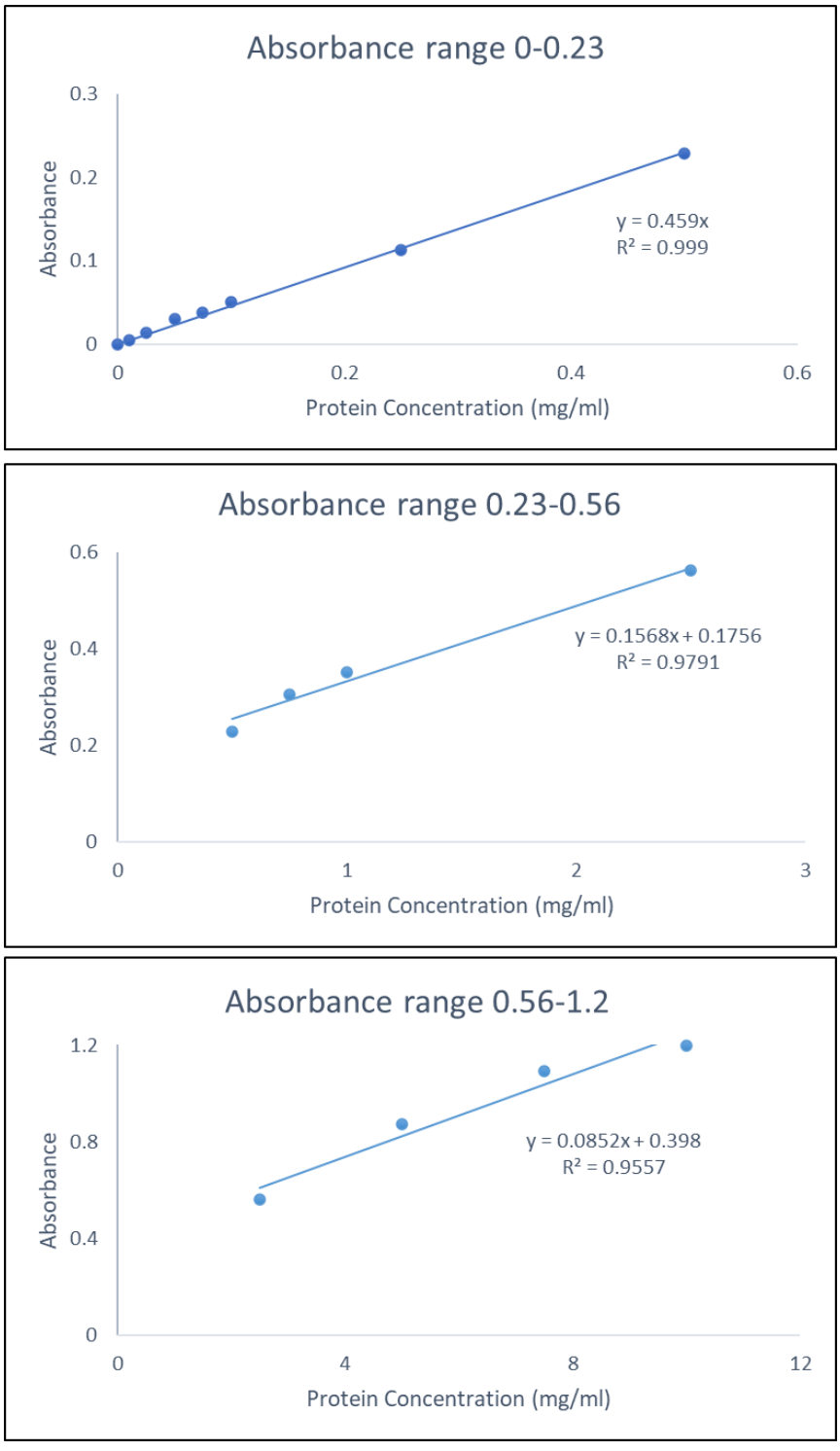

Figure 2.9. Calibration curves for protein concentration calculation

2.6.5.2 Pigment characterization for A. platensis

The phycobiliprotein content was determined by applying a modified version of the formula used by Bennett & Bogobad [8]. The C-phycocyanin, Allophycocyanin and C-phycoerythrin concentrations were respectfully calculated according to Equations 2.8, 2.9, and 2.10:

$$C_{CPC} = [A_{620} - (0.474 \cdot A_{652})]/5.34 \quad (2.8)$$

$$C_{APC} = [A_{652} - (0.208 \cdot A_{620})]/5.09 \quad (2.9)$$

$$PE = [A_{562} - (2.41 \cdot C - PC) - (0.849 \cdot APC)]/9.62 \quad (2.10)$$

Where C_{CPC} is the C-phycocyanin concentration (mg/mL), C_{APC} is the Allophycocyanin concentration (mg/mL), C_{PE} is the C-phycoerythrin concentration (mg/mL), and A_{562}, A_{620} and A_{652} are the absorbances of the sample respectively measured at 562 nm, 620 nm, and 652 nm. The concentrations were then converted to mg/ g dry *A. platensis* (hereby referred to as mg/ g d.m.).

2.6.6 Microstructure

This was measured for the initial feed solutions before and after ultrasound treatment. Scanning electron microscopy (SEM, Quanta FEG 250, FEI, Holland) was used to monitor any changes in the microstructure of the microalgal cells. A voltage of 20 kV was applied.

The SEM images of the *C. vulgaris* and *A. platensis* feed solutions are illustrated in Figure 2.10.

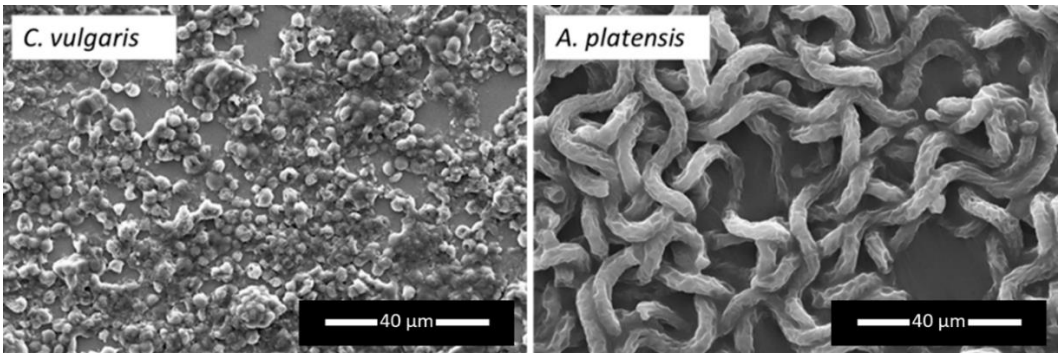

Figure 2.10. SEM images of C. vulgaris and A. platensis cells

2.7 Energy consumption

The specific energy consumption *E* was calculated during both the electrofiltration and electrowashing experiments according to Equation 2.11:

$$E = \frac{1}{M_l} \sum_{n=1}^{m} \frac{I_n \cdot U_n \cdot \Delta t}{3600} \quad (2.11)$$

E is the specific energy consumption in Wh/kg, M_l is the mass of water (filtrate or washing liquor) removed in kg, *m* is the number of measurements, I_n is the current intensity in A, U_n is the recorded voltage in V, Δt is the time interval between subsequent measurements in s. In this work, *E* is expressed in kWh/kg water removed. The water removed by filtration without an applied electric field was not taken into account in these calculations.

2.8 Statistical analyses

All the experiments were repeated at least twice. All the results are presented with the calculated standard deviation.

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Chapter 3: Dead-end filtration and electrofiltration of *A. platensis*

3.1 Introduction

Microalgae dewatering is an essential step in microalgal biorefineries: concentrating the microalgae suspensions increases the cells' shelf life and helps improve the extraction of biocompounds from the microalgae. Chapter 1 explained the advantages and disadvantages of different microalgae dewatering techniques while taking into account their energy consumption, which is usually very high. The use of dead-end filtration was found to be promising based on the conducted literature review, but this technique presented some drawbacks that needed to be addressed. In order to overcome the low filtration rate and cake dryness, dead-end electrofiltration was found to be a promising alternative to pressure driven filtration, since dead-end electrofiltration was found to enhance the filtration rate, filtrate yield, and filter cake dryness of a wide variety of suspensions (Chapter 1, Section 1.2.5). Moreover, using dead-end electrofiltration as a microalgae dewatering technique seems promising based on the analysis conducted in Chapter 1, Section 1.2.6.

Hence, the aim of this chapter is to:

- Assess the use of electrofiltration as a dewatering technique for the microalgae *Arthrospira platensis*
- Study the effect of different operational parameters on the filtration kinetics and cake dryness:
    - Pressure
    - Electric current density
    - Combination of the pressure and electric current density

The findings are presented as an article titled: "Dewatering of *Arthrospira platensis* microalgae suspension by electrofiltration". This work was submitted to and accepted by the journal "Drying Technology". The work was carried out under the direction of Prof. Eugène Vorobiev and Prof. Henri El Zakhem, in collaboration with Prof. Nabil Grimi.

3.2 Article

The article is presented on the following page.

Dewatering of *Arthrospira platensis* microalgae suspension by electrofiltration

Christa Aoude[1,2], Nabil Grimi[1], Henri El Zakhem[2], and Eugene Vorobiev[1]

[1]Université de technologie de Compiègne, ESCOM, TIMR (Transformations Intégrées de la Matière Renouvelable), Centre de recherche Royallieu - CS 60 319 - 60 203 Compiègne Cedex, France

[2] Department of Chemical Engineering, Faculty of Engineering, University of Balamand, P.O. Box 33, Amioun, Al Koura, Lebanon

Abstract

Harvesting microalgae has presented many challenges in the past, especially when taking into account the final dryness of the product and the energy requirements for the drying process. This study investigates the use of dead-end electrofiltration to dewater an *Arthrospira platensis* suspension under different pressures (1 to 4 bar) and electric current densities (30 to 80 A/m^2). Filtration without an electric field helped reach a final cake dryness in the range of 13.3-15%. Electrofiltration was found to be a more effective dewatering method, reaching a final cake dryness of up to 20.8% with an energy consumption of 0.105 kWh/kg water removed, which is significantly lower than the energy consumption reported in literature. Increasing the electric current density helped increase the cake dryness, whereas increasing the operating pressure was not effective enough due to the high cake compressibility. Electrofiltration also modifies the filtrate and cake properties due to the electrolysis reactions.

Keywords

Dewatering, electrofiltration, microalgae suspension, harvesting

1 Introduction

In microalgae biorefineries, the harvesting or dewatering step is crucial in reducing the transportation and storage costs of cultivated microalgae. However, harvesting costs are relatively high due to the high quantities of energy needed in order to separate the microalgae cells from the liquid phase they are dispersed in [1–3]. The harvesting step typically concentrates the cultured microalgae, with an initial concentration as low as 0.05%, and increases the dry weight of solids to approximately 10-25% [3]. Many studies have reported that the harvesting step contributes to 20-30% of the total costs in microalgae biorefineries [4–6]. A dry way of bio-compound recovery includes concentrating and dewatering microalgae suspensions by mechanical operations, such as flotation, sedimentation, centrifugation, and filtration [2, 3, 7]. These operations are followed by drying the concentrated microalgae suspension to obtain a powder, which is subjected to solvent extraction for the recovery of valuable compounds [1, 5, 8]. Drying costs can be significantly reduced when microalgae suspensions are concentrated by non-thermal mechanical operations.

The use of electrotechnologies for microalgae harvesting has also been investigated as a promising method to increase the harvesting efficiency and decrease the processing costs [6, 9–12]. For example, electroflotation has been used to harvest microalgae [6, 13, 14]. During electroflotation, hydrogen and oxygen bubbles are produced by electrolysis. These bubbles enable the microalgae cells in suspension to float to the water's surface. Despite the relatively high harvesting efficiency of electroflotation, this process should usually be followed by another separation technique such as centrifugation or filtration [14].

Incorporating an electric field during suspension concentration and dewatering has been found to increase the dewatering rate and the dryness of the filter cake [9, 10, 15–17]. However, studying and optimizing the use of electrofiltration for microalgae suspensions have not been extensively explored, two studies have investigated the use of electrofiltration to concentrate C*hlorella* sp. solutions [9, 10]. Kim *et al.* [9] assessed the use of cross flow dewatering at different electric current densities of 0, 2, 5, and 10 mA/cm^2, whereas Cao *et al.* [10] used dead-end electrofiltration with a piston for a duration of 1 hour and independently assessed the effect of the applied voltage (0-55 V), ionic strength of the feed solution, and pressure (0.2-0.7 MPa). Moreover, both studies assessed the use of electrofiltration for the dewatering of spherically shaped microalgae.

The aim of this study is to assess the effect of the electric current density, hydraulic pressure, and the combination of the two on the electrofiltration behavior of the helically shaped microalgae *Arthrospira platensis*. This was achieved by studying the electrofiltration kinetics, cake properties (specific resistance, compressibility, and dryness), filtrate properties, and energy consumption.

2 Materials and methods

2.1 Arthrospira platensis suspensions

Frozen *Arthrospira platensis* (*A. platensis*) microalgae was purchased from SAS TAM- Cyane (Plougastel-Daoulas, France). A 5 wt% suspension was prepared by dispersing the thawed *A. platensis* in deionized water and mixing it with a magnetic stirrer, until a homogeneous suspension was obtained. The feed solution's pH was 7.06 ± 0.3 and its electrical conductivity was 1.62 ± 0.12 mS/cm (Consort multimeter, France). The zeta potential of the solution was − 17.3 ± 0.9 mV at a pH of 7.06 ± 0.3 (Nano zeta sizer, Malvern instruments).

2.2 Electrofiltration equipment

The electrofiltration equipment (Choquenet SAS, France) was mainly composed of a 1L stainless steel feed tank connected to a pressurized air system, a stainless steel support with a screw to secure the independent parts of the system together, and a polypropylene dewatering cell (circular cross section 24.6 cm^2, volume 49.2 cm^3) equipped with a feed inlet and valve. Both sides of the dewatering cell were covered with a disposable PVDF membrane (Nafion MV020T,

Millipore) with a pore size of 0.2 µm. Prior to use, the membranes were activated by soaking them in deionized water for 30 minutes. The membrane's pore size was selected based on the particle size distribution of the *A. platensis* feed solution. The electrodes were placed in direct contact with the membrane, on the outer side of the dewatering cell to avoid coming into contact with the filter cake. Rubber joints were placed between any two independent parts in the dewatering system to avoid any leaks. Figure 3.1. serves as a schematic representation of the filtration and electrofiltration equipment.

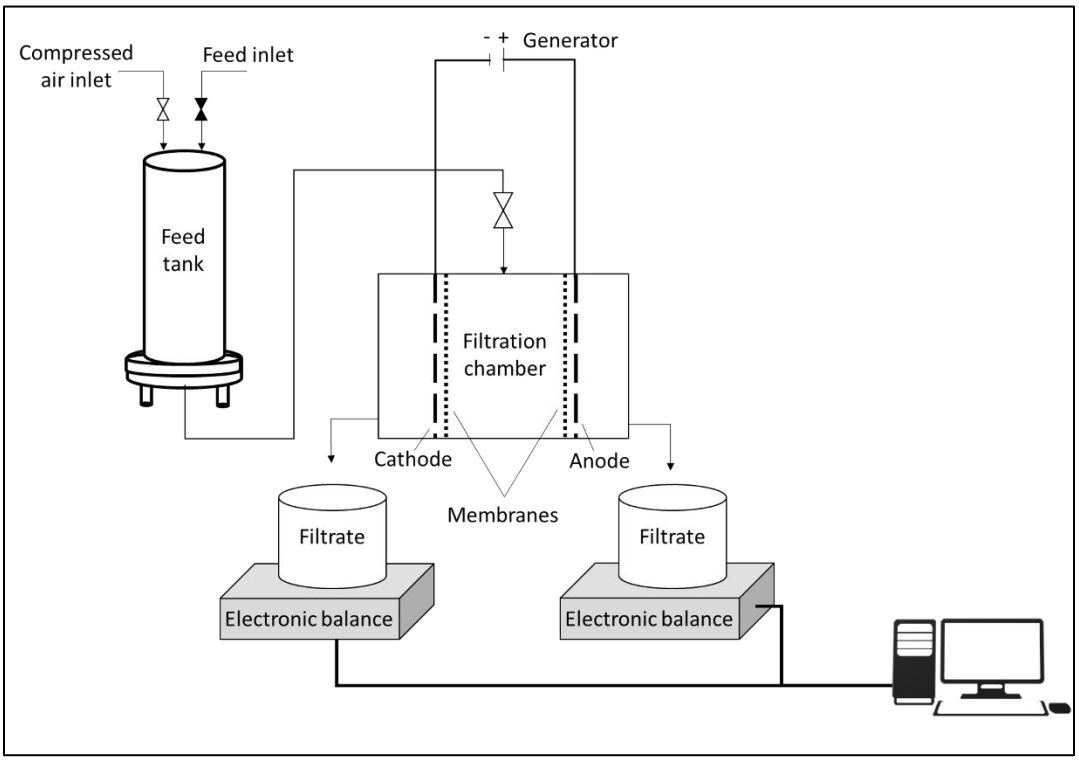

Figure 3.1. Schematic of the filtration and electrofiltration equipment

The electricity supply was set using the EV261 direct current generator (0 – 1 A, 0 – 600 V, Consort, Belgium), and was monitored using a multimeter (FLUKE 45). The filtration rates were obtained by continuously measuring the mass of obtained filtrate with two electronic balances.

The filtrate masses, as well as the applied currents and voltages were recorded by the HPVEE acquisition software (Electronic Service, U.T.C.). The interval between each measurement was fixed at 1 minute. The temperature at the electrodes was measured using flexible K-type thermocouples, connected to a 4-channel thermometer (Extech Instruments).

The gases produced by electrolysis during EF were evacuated with the filtrate from both the anode and the cathode sides of the filter chamber.

2.3 Experimental conditions

Three different sets of experiments were performed to independently assess the effect of different parameters on the filtration efficiency and product quality. The variables taken into account were the pressure and/or the electric current density. The filtrate streams obtained from the two sides of the filtration cell were collected separately for all the experiments.

2.3.1 Effect of Pressure without an electric field

Suspension filtration at different pressures (1, 2, 3, and 4 bars) without the application of an electric field, hereby referred to as filtration (F), was carried out to study the effect of pressure on the filtration kinetics as well as the filtrate and cake properties. The filtration time was set as 150 minutes, because after exceeding that time, the formed filter cake occupied the entire volume of the filtration chamber.

The specific cake resistance α for filtration (F) without the application of an electric field was calculated according to the transformed Ruth-Carman equation [18]:

$$\frac{t-t_0}{V-V_0} = \frac{\alpha.\mu.c_0}{2A^2\Delta p}(V+V_0) + \frac{R_m.\mu}{A.\Delta p} \quad (3.1)$$

Where V is the volume of filtrate (m^3), $V = Av$, v is the filtrate volume per filter surface area (m^3/m^2), A is the filter area equal to 0.00246 m^2, V_0 is the filtrate volume at the beginning of constant pressure filtration (at t_0 = 3 min), c_o is the mass of particles in the cake per filtrate volume (kg/m^3), t is the time (s), Δp is the applied pressure (Pa), μ is the filtrate viscosity (Pa·s), α is the specific cake resistance (m/kg), R_m is the filter media resistance (1/m). The values of specific cake resistance α are presented in Table 3.1. for different pressures from 1 to 4 bar. These values significantly increase with the pressure increase, which evidences a very high cake compressibility.

Table 3.1. Specific resistance of filter cakes at different pressures

Δp (bar)	**α (m/kg)**
1	1.50E+13
2	4.35E+13
3	7.75E+13
4	9.25E+13

The compressibility index can be calculated based on Equation (3.2) [19]:

$$\alpha = \alpha_0(\Delta p/\Delta p_0)^s = 1.5 \times 10^{13}(\Delta p)^s \quad (3.2)$$

where s is the compressibility index and α_0 is the average specific resistance of the cake when $\Delta p = \Delta p_0$. The compressibility index s, determined graphically by plotting $\ln(\alpha)$ vs $\ln(\Delta p/\Delta p_0)$, is presented in Figure 3.2. Values of $s > 1$ indicate a very high cake compressibility [20].

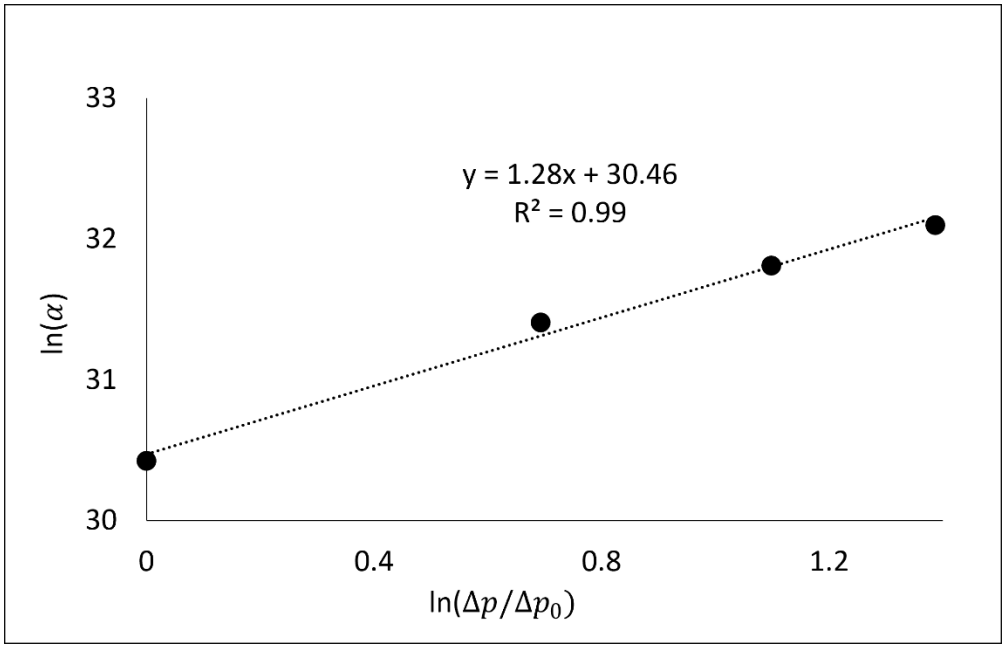

Figure 3.2. Dependence of ln(α) vs $\ln(\Delta p/\Delta p_0)$ for determination of the cake compressibility index

The value of *s* = 1.28 confirms that the studied microalgae cakes have a very high compressibility.

2.3.2 Effect of the electric current density under constant pressure

Electrically assisted filtration, hereby referred as electrofiltration (EF), was carried out at a constant pressure of 1 bar for different electric current densities (30, 40, 60, and 80 A/m^2). The filtration time was set to 150 minutes for the sake of comparison with the F experiments.

2.3.3 Effect of pressure under the influence of an electric field

Based on the findings from the experiments described in Section 2.3.2, the electric current density of 60 A/m^2 yielded promising results related to an enhancement of the filtration rate and an increase in the cake dryness. For this reason, EF was conducted at a constant electric current density of 60 A/m^2 for different operating pressures (1, 2, 3, and 4 bar). The experiments were also conducted for a duration of 150 minutes.

The effect of the electric current density was exclusively studied at a pressure of 1 bar. We suppose that modifying the filtration pressure would not modify the optimal value of the electric current density. This supposition will be verified in future work by studying EF at different electric current densities and different pressures.

2.4 Electrofiltration behavior

The electrofiltration equation of suspensions with negatively charged particles considers the superposition of hydraulic and electroosmotic flows [21].

The equation on the anode side is expressed as Equation (3.3):

$$\frac{\mathrm{d}v_a}{\mathrm{d}t} = \frac{\Delta p}{\mu\alpha_a\left(v_a c_o + q_{ef}\cdot\varphi_s\cdot\rho_p\cdot t\right)+\mu R_{ma}} - P_{EO}\,i \tag{3.3}$$

and it is expressed as Equation (3.4) on the cathode side:

$$\frac{\mathrm{d}v_c}{\mathrm{d}t} = \frac{\Delta p}{\mu\alpha_c\left(v_c c_o - q_{ef}\cdot\varphi_s\cdot\rho_p\cdot t\right)+\mu R_{mc}} + P_{EO}\,i \tag{3.4}$$

where v_a and v_c are the volume of filtrate per cross sectional area of the filter surface respectively for the anode and cathode side (m^3/m^2), c_o is the mass of particles in the cake per filtrate volume in the absence of an electric field (kg/m^3), α_a and α_c are the specific cake resistance respectively for the anode and cathode side (m/kg), q_{ef} is the velocity of the electrophoretic movement of particles toward the anode (m/s), φ_s is the particle volume fraction in the microalgae suspension, ρ_p is the particle density (kg/m^3), R_{ma} and R_{mc} are the filter media resistance respectively for the anode and cathode side (1/m), P_{EO} is the electroosmotic transfer through the cake (m^3/C), and i is the electric current density (A/m^2). In the absence of an electric field, $q_{ef} = 0$, $P_{EO} = 0$, $\alpha_a = \alpha_c = \alpha$, $v_a = v_c = v$, $R_{ma} = R_{mc} = R_m$ and Equations (3.3) and (3.4) can then be transformed into Equation (3.1).

2.5 Cake dryness

The formed cake was weighed then dried in an oven at 105 ˚C for 24 hours. The mass of each cake before and after drying was recorded and the dryness was calculated based on Equation (3.5):

$$d = \frac{m_d}{m_w} \times 100 \tag{3.5}$$

where d is the cake dryness (%), m_w is the mass of the wet cake (g) and m_d is the mass of the dry cake (g).

2.6 Cake microstructure

Scanning electron microscopy (SEM, Quanta FEG 250, FEI, Holland) with an applied voltage of 20 kV was used to view the microstructure of the algal cake.

2.7 Filtrate characterization

The pH and conductivity of the filtrate were measured at t = 150 min using Consort C5010 multi-parameter analyzer (France).

2.8 Energy consumption

For the EF experiments, the specific energy consumption was calculated using Equation (3.6):

$$E = \frac{1}{M_l}\sum_{n=1}^{m}\frac{I_n \cdot U_n \cdot \Delta t}{3600} \quad (3.6)$$

where E is the specific energy consumption (Wh/kg) of the filtration process, M_l is the mass of water removed (kg), I_n is the current intensity (A), U_n is the recorded voltage (V), Δt is the time interval between subsequent measures (s). n and m are the number of subsequent measurements, with n being the first one. The energy was converted from Wh/kg to kWh/kg.

When calculating the energy, two cases were considered, calculating the energy required to remove water by: (1) F combined with EF and (2) EF alone.

3 Results and discussion

3.1 Effect of pressure on electrofiltration

3.1.1 Characteristics of the filtrates and filter cakes

Figure 3.3. shows the photos of the filter cakes and filtrates obtained after F and EF at different pressures ranging from 1 to 4 bar. All the filter cakes seem to be well structured. Regardless of the applied pressure, the thickness of the obtained filter cake was nearly equal to 2 cm, which is the same thickness as the filtration chamber. Hence the cakes completely filled the filtration chamber after 150 minutes of filtration. The color of the filtrate obtained by F indicates the presence of pigments, probably phycobiliprotein, C-phycocyanin and others, which is typical for the microalgae *Arthrospira platensis* [22, 23]. On the contrary, the color of the filtrates obtained by EF is clearly different. It has a lighter hue from the anode side and a yellow hue from the cathode side, which can be a consequence of the electrolysis reactions that take place at the electrodes and subsequently lead to pH changes (Table 3.2.).

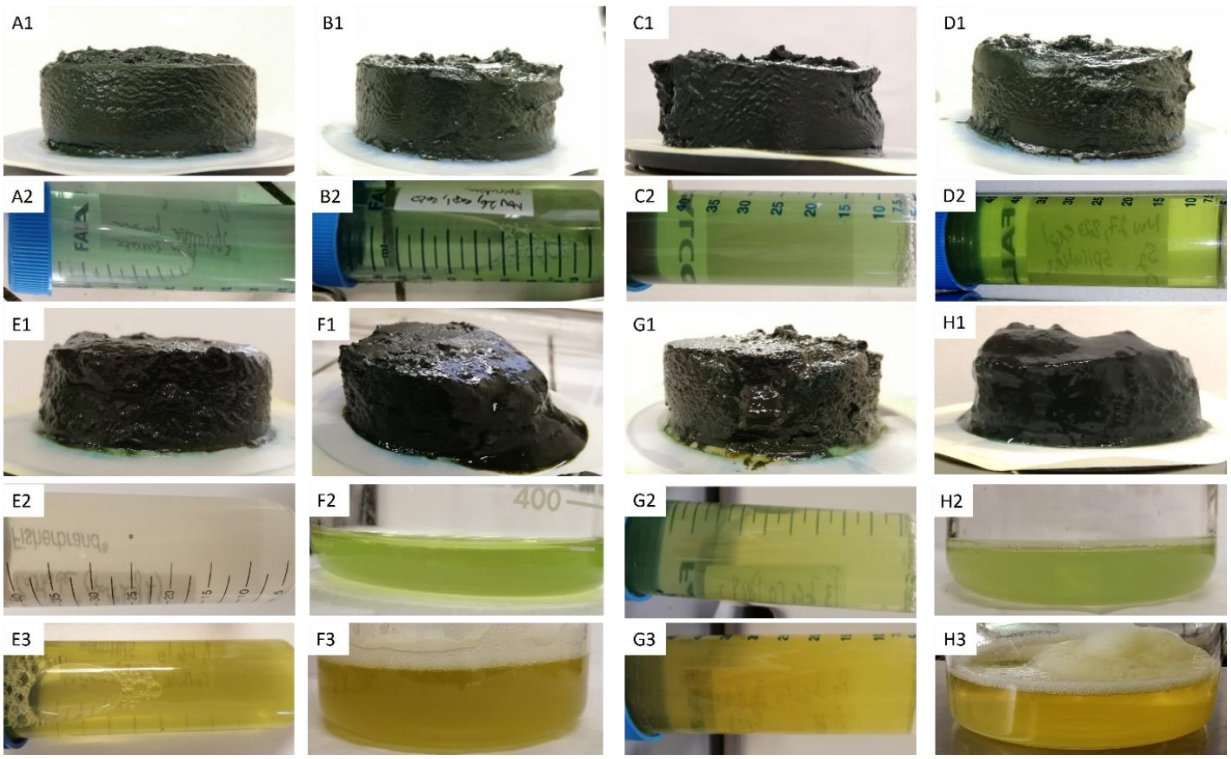

Figure 3.3. Filter cakes (A1, B1, C1, and D1) and filtrates (A2, B2, C2, and D2) obtained by F respectively at the pressures of 1, 2, 3, and 4 bar. Filter cakes (E1, F1, G1, and H1) and filtrates from the anode side (E2, F2, G2, and H2) and from the cathode side (E3, F3, G3, and H3) obtained by EF respectively at the pressures of 1, 2, 3, and 4 bar, and i = 60 A/m^2

Table 3.2 shows the changes in the filtrate conductivity and pH due to the presence of salts and ions. Without the application of an electric field, regardless of the applied pressure, the filtrate was found to have a pH of 7.35 ± 0.15 and a conductivity of 2.15 ± 0.07 mS/cm. The application of an electric field resulted in obtaining a more acidic pH on the anode side and a more alkaline pH on the cathode side (Table 3.2). The electrical conductivity of the filtrate obtained on both the anode and the cathode sides was modified. This change was generally more important on the cathode side. The electrical conductivity depends on the concentration of both positively and negatively charged ions within a sample, while pH is the measurement of hydrogen ions. There is no direct relationship between the pH and conductivity. However, the presence of hydrogen ions in a solution would have an impact on its conductivity.

Table 3.2. Filtrate conductivity and pH for F and EF at i = 60 A/m^2 in function of different pressures

	Pressure (bar)		1	2	3	4
F	Conductivity (mS/cm)		2.15 ± 0.07			
	pH		7.35 ± 0.15			
EF	Conductivity (mS/cm)	Anode	4.64 ± 0.7	3.99 ± 0.2	2.85 ± 0.59	2.96 ± 0.42
		Cathode	6.71 ± 0.27	9.75 ± 0.15	8.85 ± 0.58	9.11 ± 0.69
	pH	Anode	2.70 ± 0.02	3.42 ± 0.12	3.78 ± 0.1	3.70 ± 0.06
		Cathode	12.3 ± 0.02	12.0 ± 0.07	12.2 ± 0.01	12.0 ± 0.08

The deviation of the filtrate pH values from a neutral to a more acidic or alkaline range has been linked to the degradation of the phycobiliprotein C-phycocyanin, which is characterized by its blue color [24–26].

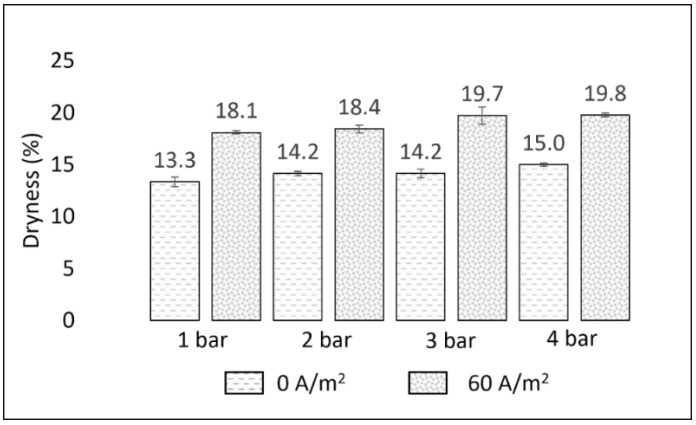

Figure 3.4. Total dryness of filter cakes obtained by F and EF at the different pressures

The total dryness of the microalgae filter cakes obtained by F slightly increased with pressure as shown in Figure 3.4 (from the value of 13.3% at Δp = 1 bar to the value of 15.0% at Δp = 4 bar). This can be explained by the very high compressibility of the microalgae filter cake formed by F (compressibility index s = 1.28, Figure 3.2). The application of an electric field led to a more noticeable increase in the cake dryness. EF at 60 A/m^2 increased the total dryness of the microalgae filter cakes up to 18.1% and 19.8% respectively under the pressures of 1 and 4 bar. The use of EF facilitated the elimination of an even more important amount of water compared to F. EF at 60

A/m^2 was able to eliminate an additional 4.8% (from 13.3 to 18.1% and from 15.0 to 19.8%) of water from the cakes for both pressures of 1 bar and 4 bar when compared to F.

Table 3.3 presents the local dryness determined in different sections of the filter cakes obtained by EF at the pressures of 1 and 4 bar and electric current density of 60 A/m^2. Section 1 and 4 were respectively adjacent to the cathode and anode, and sections 2, 3 were intermediate sections between the cathode and anode. Data in Table 3.3 show that the cake dryness gradually increases in the cake when measured from the cathode to the anode side.

Table 3.3. Local cake dryness d (%) in different sections of the filter cakes obtained by EF at pressures of 1 and 4 bar and an electric current density of i = 60 A/m^2

	Pressure (bar)	1	4
d (%)	Cake section 1 (near cathode)	13.6 ± 0.55	13.3 ± 0.14
	Cake section 2	17.8 ± 1.1	18.5 ± 0.44
	Cake section 3	19.0 ± 2.46	20.7 ± 0.9
	Cake section 4 (near anode)	27.5 ± 1.86	29.2 ± 2.75

For instance, at a pressure of 1 bar, the cake dryness in section 1, which is adjacent to the cathode, is 13.6% and increases up to the value of 27.5% in section 4, which is adjacent to the anode. Uneven dryness of the cake between the cathode and anode was indicated for other types of suspensions and was explained by the more important ohmic heating of the anode during EF and the different cake resistance [15, 17, 27].

Figure 3.5 presents the SEM images of the filter cakes formed by EF on the anode (A) and cathode (B) sides of the filter chamber. Cake structure and properties on the anode and cathode sides can be different due to the electrolysis reactions near the electrodes.

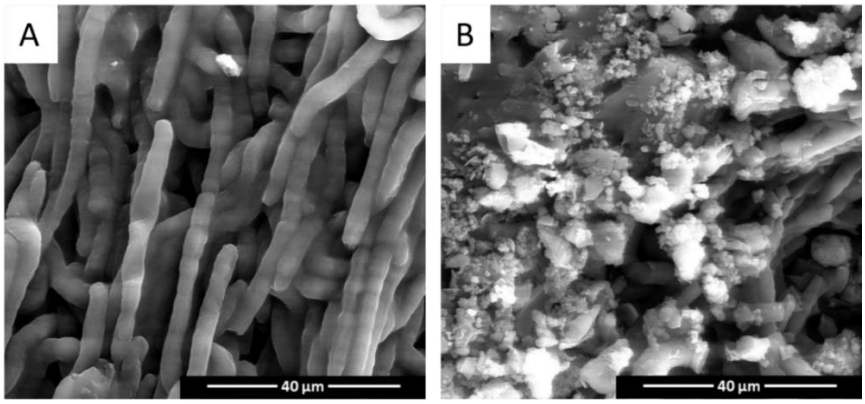

Figure 3.5. SEM images of filter cakes formed by EF on the anode (A) and cathode (B) side

For instance, salt complexes, which are absent in the SEM images of the cake formed near the anode (Figure 3.5 A), can be easily detected on the SEM images of the cake formed near the cathode (Figure 3.5 B). This is also in line with the higher filtrate conductivity on the cathode side (Table 3.2).

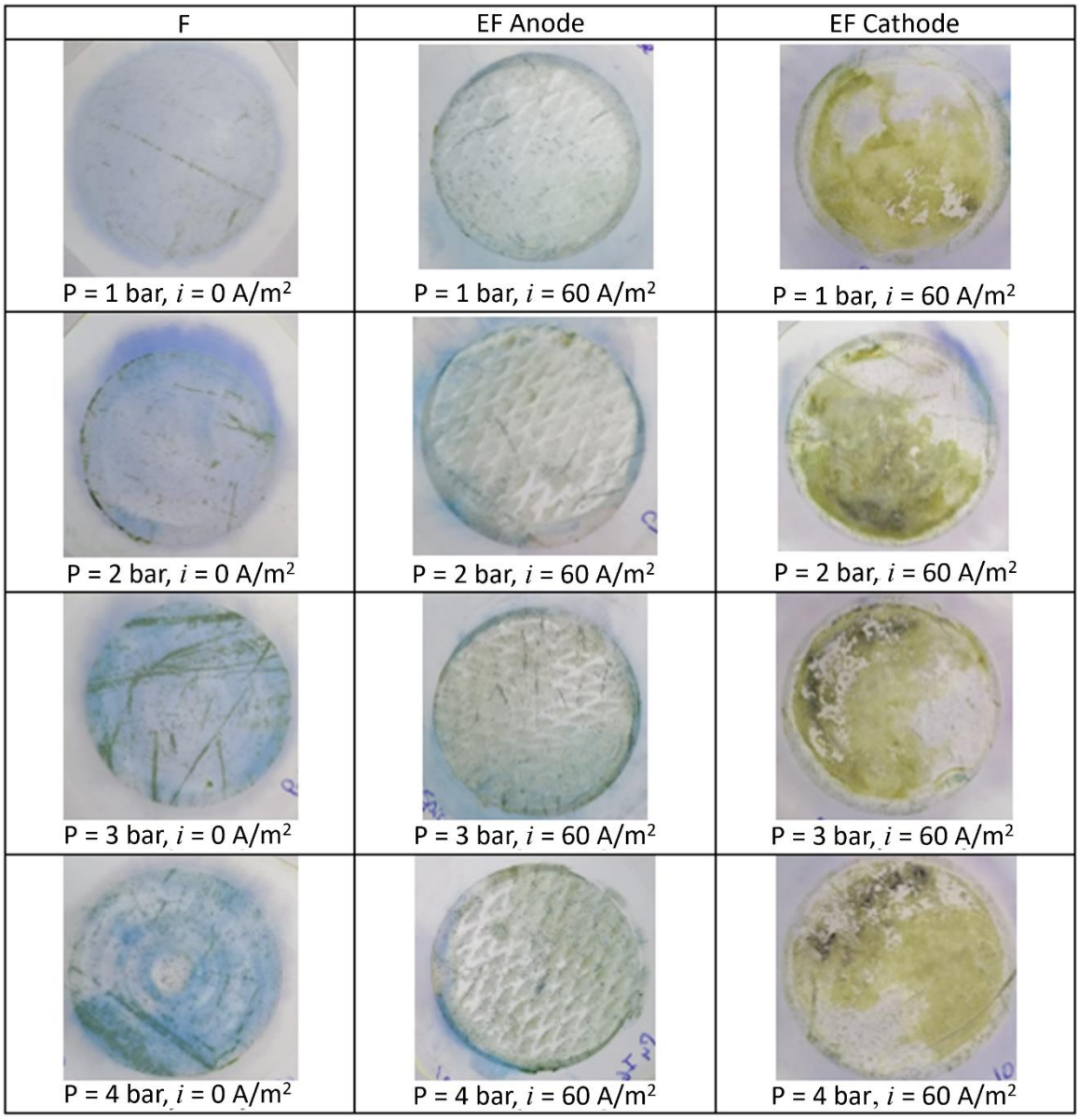

Figure 3.6. Images of the spent membranes after filtration (i = 0 A/m^2) and electrofiltration

The chemical changes due to the electrolysis reactions near the electrodes also led to the modification of the color of the compounds retained by the filtration membrane as illustrated in Figure 3.6. The visual presence of pigments on the surface of the membranes also indicates the possibility of membrane fouling.

3.1.2 Kinetics of electrofiltration at different pressures

The effect of pressure on the filtration rate during F and EF at 60 A/m^2 is shown in Figure 3.7.

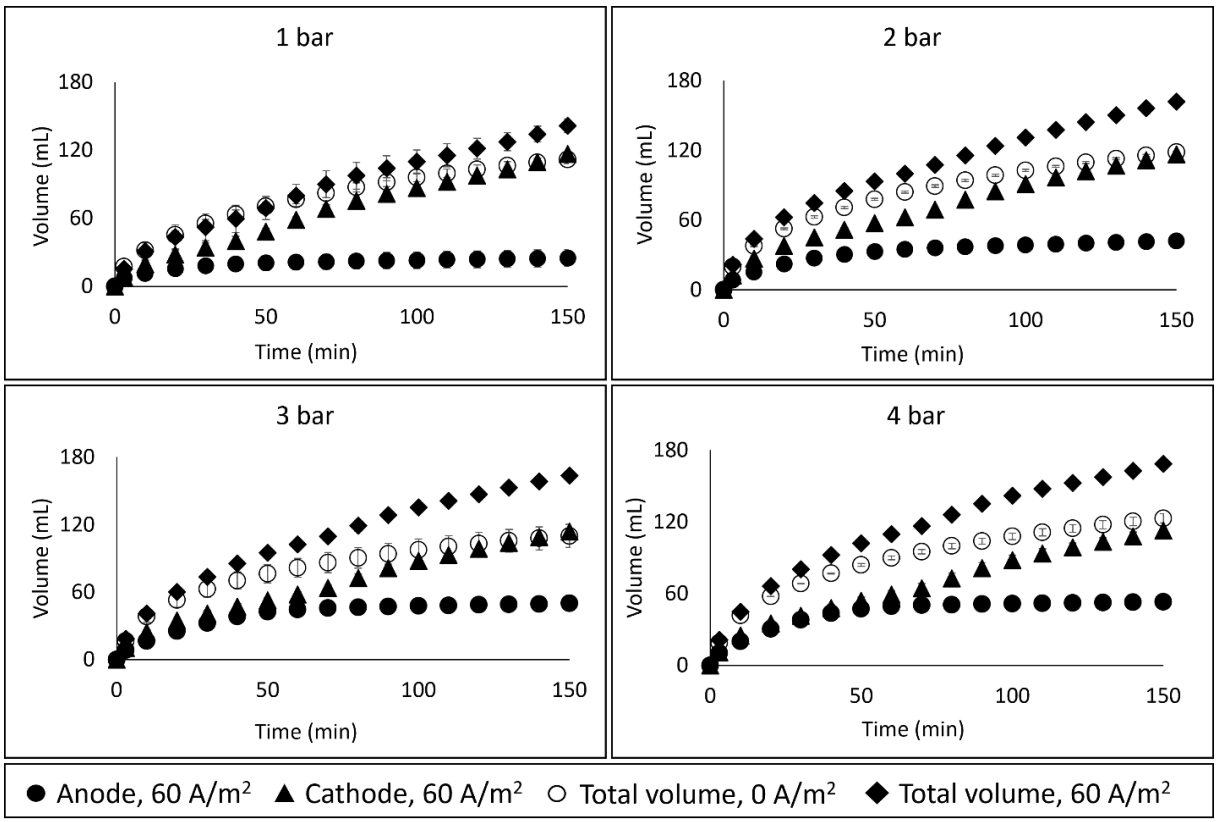

Figure 3.7. Filtration kinetics during F and EF at different pressures and electric current density of i = 60 A/m^2

Without the application of an electric field, increasing the pressure had a very small effect on the filtration rate and on the total volume of filtrate obtained. For the filtration experiments without the application of an electric field (F), the total volume of filtrate recorded after 150 minutes was 112 ± 10.2 mL and 123 ± 3.92 mL for the pressures of 1 and 4 bar respectively. This corresponds to a 9.8% increase in the filtrate volume by increasing the pressure by 4 folds. The small effect of pressure on the filtration rate can be explained by the very high compressibility of the microalgae cake (s = 1.28). The application of an electric current density of 60 A/m^2 increased the filtration rate with a preferential flow of filtrate from the cathode side. This is explained by the electrophoretic movement of particles towards the anode and its congruency with the directions of the hydraulic and electroosmotic flows (based on Equation (3.4)). For EF, the total amount of filtrate after 150 minutes increased by 18.3% with the increase in pressure from 1 to 4 bar, respectively reaching volumes of 142 ± 6.09 mL and 168 ± 3.49 mL.

On the contrary, the flow rate from the anode side considerably decreased due to the electrophoretic movement of particles towards the anode, which is in the opposite directions of the hydraulic and electroosmotic flows (based on Equation (3.3)). This corresponds to the typical

electrofiltration behavior of suspensions containing negatively charged particles [15–17, 21, 28, 29]. With the pressure increase from 1 to 4 bar, the final volumes of filtrate obtained from the anode side respectively reached 24.9 ± 7.45 mL and 53.1 ± 2.34 mL. The combined effect of the electric current density of 60 A/m^2 with pressure showed an increase in the total volume of filtrate by 26.5%, 36.9%, 47.2%, and 36.8% respectively for operating pressures of 1, 2, 3, and 4 bar when compared to filtration without an electric field. An anomalously low increase of the total volume of filtrate by 36.8% was observed under the operating pressure of 4 bar, which can be explained by a counterbalance of the flow of particles: (1) towards the cathode (due to the pressure of 4 bar) and (2) from the cathode to the anode (due to the electrophoretic force). As a result, a thicker filter cake layer is formed on the cathode side at a higher pressure of 4 bar when compared to that formed on the cathode side at a lower pressure of 3 bar. Figure 3.7 confirms that the filtration rate from the cathode side was higher at the pressure of 3 bar (thinner cake) than at the pressure of 4 bar (thicker cake). The ratio of the filtrate volume obtained from the cathode side by EF and F were 2.25 and 1.83 respectively at the pressure of 3 and 4 bar. Also, the lower efficacy of EF under the pressure of 4 bar may be explained by a higher cake compressibility at these conditions and a more important clogging of the filter cloth. Additional studies are required to verify the latter.

3.2 Effect of electric current density

3.2.1 Characteristics of the filtrates and filter cakes

Since the pressure was found to slightly influence the filtration kinetics, a pressure of 1 bar was selected to study the effect of the electric current density on EF behavior. Figure 3.8 shows the photos of the filter cakes and filtrates obtained by EF at 1 bar and different electric current densities of 30, 40, 60, and 80 A/m^2. The side of the filter cakes that is facing upwards (Figure 3.8) was adjacent to the cathode and seems to be more humid in the cakes obtained at lower electric current densities of 30 and 40 A/m^2. The color of the filtrates obtained by EF at different electric current densities does not visually indicate a significant change in the quantity of the extracted pigments. The filtrates obtained from the anode side have a very light color whereas the filtrates obtained from the cathode side have a yellow hue, which can be a consequence of the electrolysis reactions that take place near the electrodes.

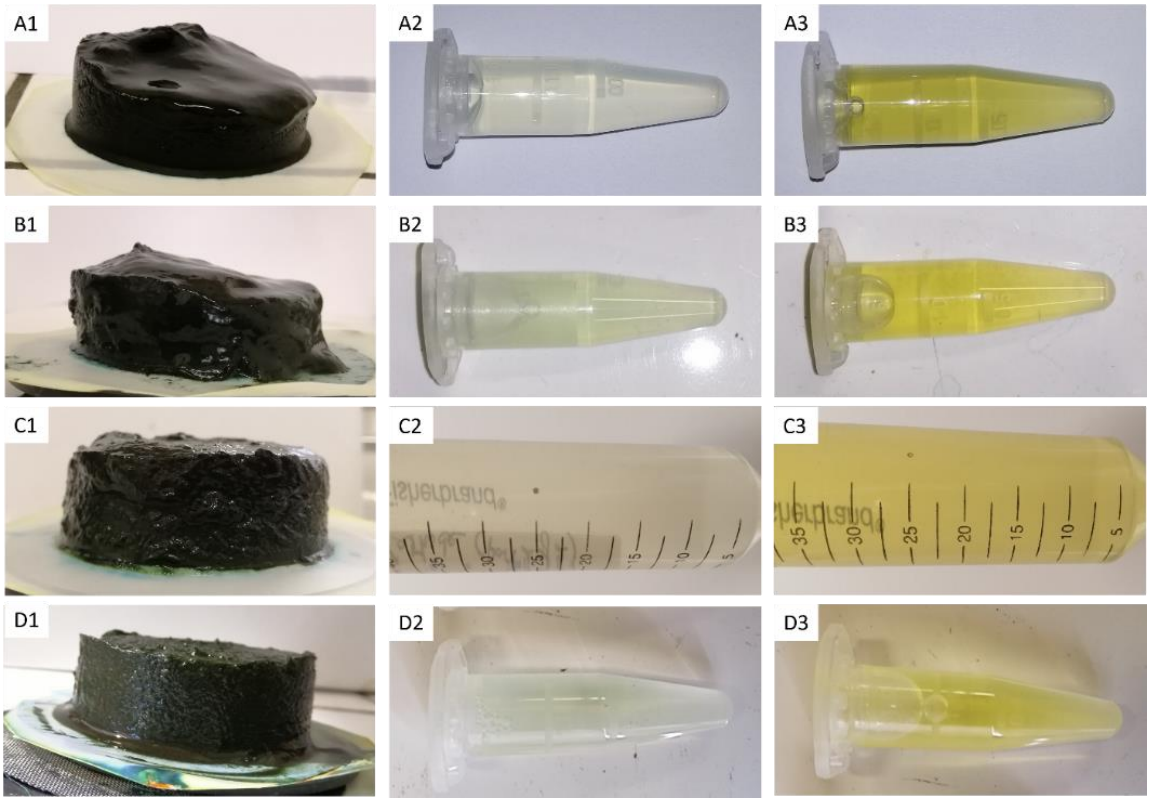

Figure 3.8. Filter cakes (A1, B1, C1, and D1), filtrates from the anode side (A2, B2, C2, and D2), and filtrates from the cathode side (A3, B3, C3, and D3) obtained by EF respectively at the electric current densities of i = 30, 40, 60, and 80 A/m^2, and a pressure of 1 bar

The set of data presented in Table 3.4 shows that by increasing the electric current density from 30 to 80 A/m^2, the conductivity of the filtrate on the anode side was found to respectively increase from 1.77 ± 0.33 mS/cm to 5.9 ± 2.7 mS/cm, whereas it decreased on the cathode side from 12.9 ± 0.3 mS/cm to 8.63 ± 0.87 mS/cm.

Table 3.4. Filtrate conductivity, pH, and cake dryness for EF at 1 bar and different electric current densities

Current density I (A/m^2)		0	30	40	60	80
Conductivity (mS/cm)	Anode	2.15 ± 0.07	1.77 ± 0.33	1.72 ± 0.39	4.64 ± 0.7	5.90 ± 2.7
	Cathode		12.9 ± 0.3	10.2 ± 2.45	6.71 ± 0.27	8.63 ± 0.87
pH	Anode	7.35 ± 0.15	4.76 ± 0.3	4.64 ± 0.2	2.70 ± 0.02	3.38 ± 0.7
	Cathode		12.0 ± 0.02	12.0 ± 0.04	12.3 ± 0.02	12.1 ± 0.2
Cake dryness (%)		13.3	15.5 ± 1.57	17.9 ± 0.93	18.1 ± 0.16	20.8 ± 0.23

The total cake dryness reached values of (15.5 ± 1.57)%, (17.9 ± 0.93)%, (18.1 ± 0.16)%, and (20.8± 0.23)% for the respective electric current densities of 30, 40, 60 and 80 A/m^2 (Table 3.4). This was higher than the cake dryness obtained by F at 1 bar (13.3%). However, the part of the cake close to the cathode was more humid at the electric current densities of respectively 30 and 40 A/m^2 due to the uneven dryness distribution in the different cake sections, similarly to the data presented in the Table 3.3. The use of EF facilitated the elimination of additional quantities of water compared to F. For instance, EF at 1 bar was able to eliminate an additional 2.2, 4.6, 4.8, and 7.5% of water from the formed cake respectively for the electric current densities of 30, 40, 60, and 80 A/m^2, when compared to F at 1 bar (13.3% in Figure 3.4).

3.2.2. Kinetics of electrofiltration at different electric current densities

The effect of the electric current density on the filtration kinetics during EF at 1 bar is shown in Figure 3.9. Filtrate volume increases with the increase of the electric current density. Compared to F at 1 bar, the application of an electric current density of 30, 40, 60, and 80 A/m^2 was respectively able to increase the total yield of filtrate by 1.27%, 42.4%, 26.6%, and 50.6%. It is known that the use of higher electric field intensities leads to a higher increase in the total yield of filtrate [21, 28, 30]. This can be explained by both the electrophoretic movement of particles from the cathode to the anode side and the flow of electroosmotic liquid through the cake pores from the anode in the direction of the cathode. Both of these phenomena lead to the formation of a thinner filter cake on the cathode side, which result in having a higher filtration rate obtained on the cathode side of the filter chamber.

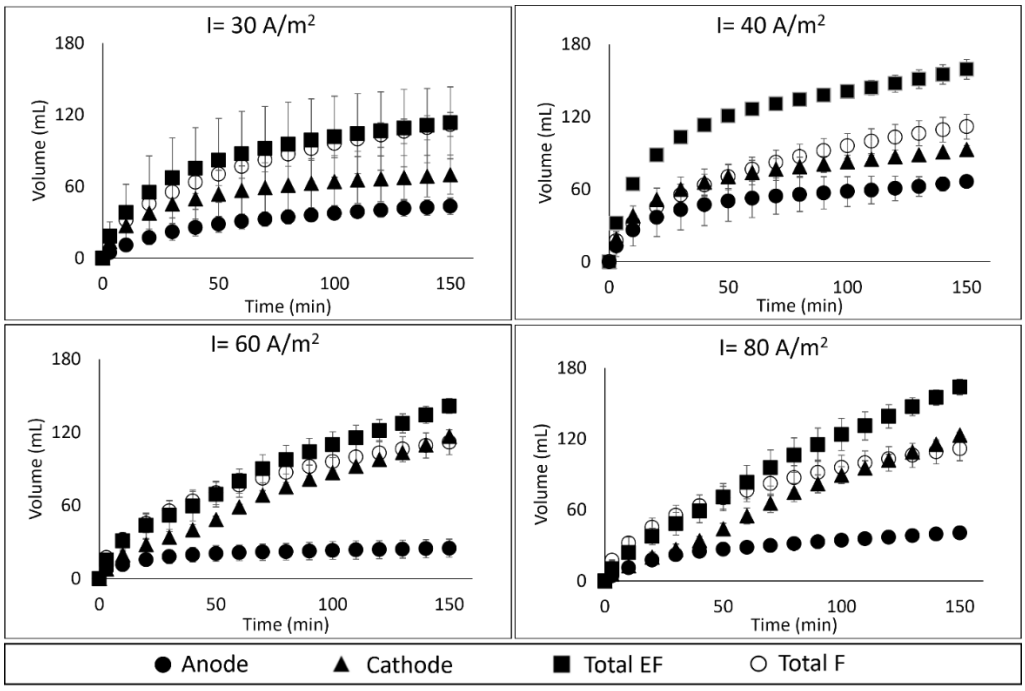

Figure 3.9. Filtration kinetics during EF at different electric current densities and a pressure of 1 bar

In our work, compared to the filtrate obtained on one side by F the enhancement of the filtrate yield at the cathode side by EF was approximately 21, 61, 102, and 114% respectively at the electric current densities of 30, 40, 60, and 80 A/m^2. On the contrary, electrophoretic movement of particles towards the anode leads to the formation of a thicker filter cake on the anode side. Moreover, on the anode side, the electroosmotic flow of liquid is in the opposite direction of the filtrate flow under the pressure difference Δp. Therefore, both electrophoretic and electroosmotic phenomena lead to the lower filtration rate obtained from the anode side of filter chamber. In our work, compared to the filtrate obtained on one side by F the decrease in the filtrate yield on the anode side during EF was as follows 19.8, 53.9, and 25.2% respectively for the electric current densities of 30, 60, and 80 A/m^2, but at the electric current density of 40 A/m^2 the filtrate yield increased by 22.5% instead of decreasing. The anomaly in the observed trend requires more study in order to be properly explained. In general, with the increase in the electric current density, the resulting filtrate yield followed an increasing tendency for the filtrate obtained from the cathode side and a decreasing tendency for the filtrate obtained from the anode side. The total filtrate yield mostly increased with the increase in the electric current density, as shown in Figure 3.7. However, the increase in the filtration rate from the cathode side was partly counterbalanced by the decrease in the filtration rate from the anode side. This may depend on many factors such as the different structures of the filter cake formed notably on the cathode and anode sides, different local cake dryness, etc. It may be speculated that the smaller extent of enhancement of the filtrate yield (decreased from 42.4 to 26.6%) with the increase in the electric current density from 40 to 60 A/m^2 is explained by such counterbalance between filtration rates from the cathode and anode sides of filter chamber.

The preferential flow of filtrate from the cathode side was more prevalent for electric current densities of 60 A/m^2 and 80 A/m^2. For instance, for the electric current density of 80 A/m^2, 74.6% of the total volume of filtrate flowed towards the cathode side. For the lower electric current densities of 30 and 40 A/m^2, the electrophoretic force responsible for the particles movement towards the anode decreased and did not significantly exceed the hydrodynamic force, which guaranteed the cake formation on the cathode side. Moreover, the electroosmotic liquid flow towards the cathode was weaker at the lower electric current densities, which led to the decrease in the flow of liquid from the cathode side and increased the flow of liquid from the anode side of the filter chamber. Equations (3.3) and (3.4) quantitatively explain these phenomena. When the electric current density i decreases, the second term in each of these equations also decreases, which in turn increases the flow rate $\frac{\mathrm{d}v_a}{\mathrm{d}t}$ towards the anode (Equation (3.3)) and decreases the flow rate $\frac{\mathrm{d}v_c}{\mathrm{d}t}$ towards the cathode (Equation (3.4)). Additional factors such as the difference in the structure of the cake segments formed near the anode and the cathode (Figure 3.5) as well as the different extent of membrane fouling on the anode and cathode sides (Figure 3.6) may influence the values of the specific cake resistances α_a and α_c, and membrane resistances R_{ma} and R_{mc}. As a result, the EF kinetics may also change since they depend on these parameters.

3.2.3. Ohmic heating and energy consumption

EF led to ohmic heating within the filtration cell and increased the temperatures near the electrodes, which was demonstrated by the temperature measurements made using flexible K-type thermocouples (Figure 3.10). Ohmic heating was more pronounced with higher electric current densities. For instance, the temperatures on the anode side reached 23.3, 25.0, 34.3, and 44.9 °C after 150 min of EF with electric current densities of respectively 30, 40, 60, and 80 A/m^2. Ohmic heating was less important on the cathode side, where the temperatures reached 22.7, 23.9, 28.1, and 36.6 °C after 150 min of EF respectively for 30, 40, 60, and 80 A/m^2. More important heating on the anode side compared to the cathode side during EF was reported in different studies [31–33] and can be eliminated by electrode flushing [15]. In our study the preferential anode heating possibly contributed to obtaining a higher cake dryness on the anode side (Table 3.3).

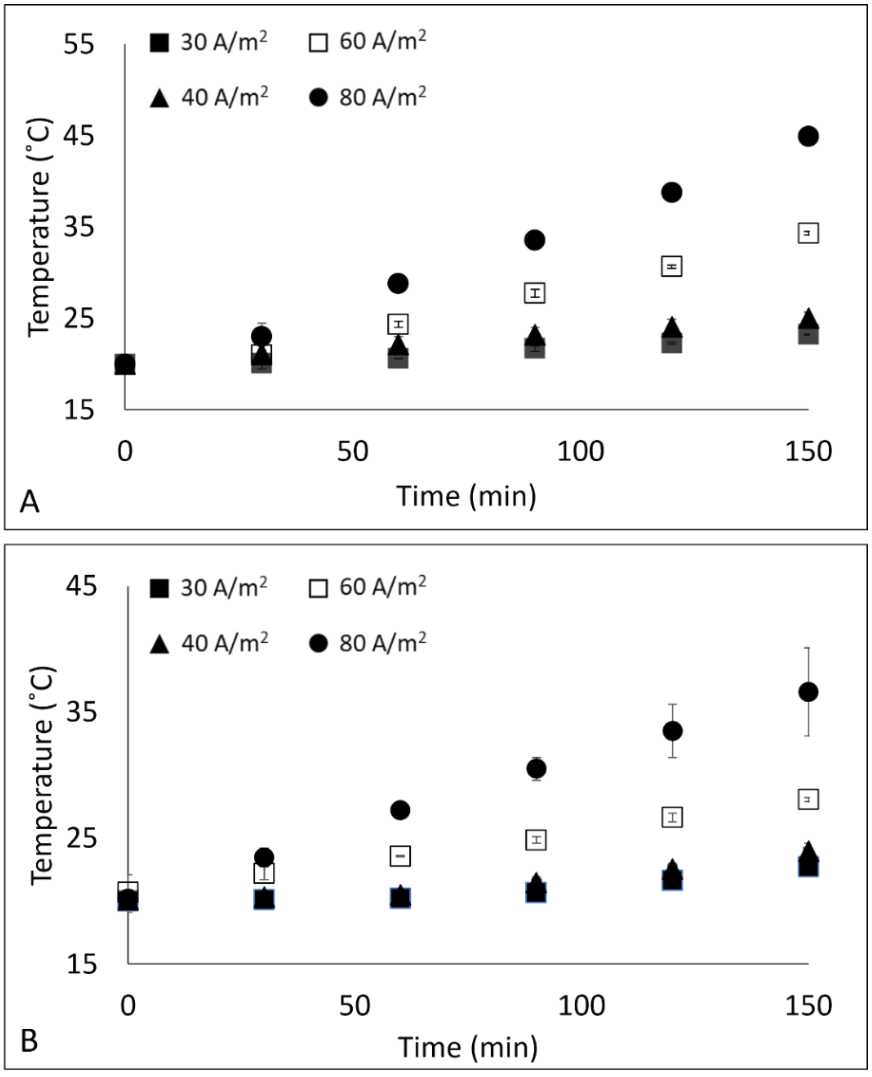

Figure 3.10. Increase in temperature on the anode (A) and cathode (B) side of filter chamber at different electric current densities

Figure 3.11 presents the specific energy consumption during EF at 1 bar for different electric current densities versus EF time, without eliminating the volume obtained by F during the first 3 minutes of filtration before applying an electric field. Logically, the specific energy consumption increases with the increase of the electric current density, reaching values of 0.019, 0.024, 0.067, and 0.105 kWh/kg water removed respectively for the electric current densities of 30, 40, 60, and 80 A/m^2 after 150 min of EF.

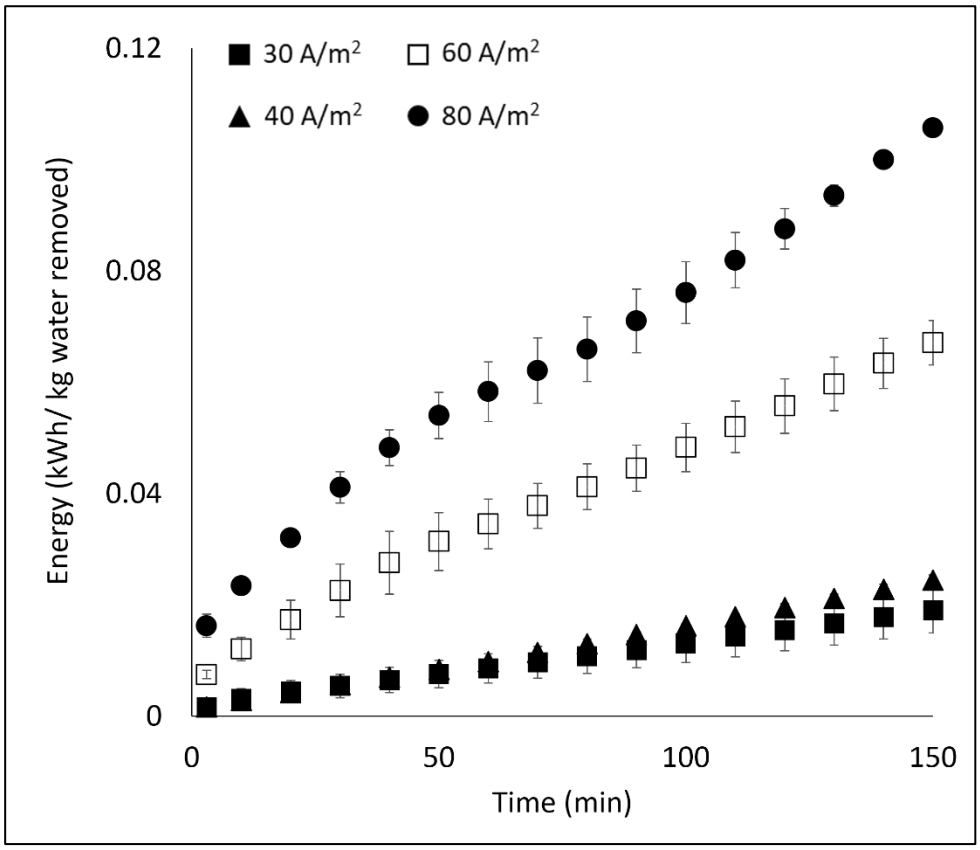

Figure 3.11. Specific energy consumption over time for EF at different electric current densities and a pressure of 1 bar

When the specific energy was calculated by taking into account the volume of filtrate the was removed exclusively by EF (eliminating the volume removed by F during the calculations), the following specific energy consumption was observed: (0.022 ± 0.003), (0.03 ± 0.002), (0.074 ± 0.004), and (0.112 ± 0.001) kWh/kg water removed respectively for the electric current densities of 30, 40, 60, and 80 A/m^2 after 150 min of EF.

Such values for the specific energy consumption are considerably lower than the energy needed for thermal and in some cases non thermal dehydration of *A.* platensis, which could reach up to 2.35 kWh/kg water removed by solar drying and 0.75 kWh/kg water removed by vacuum drying [34]. This shows the competitiveness of the EF process, especially if it is used during the first stage of microalgae dehydration before undergoing additional thermal drying processes.

4 Conclusion

Dead-end filtration does not lead to a better dewatering of the microalgae *A. platensis* simply by increasing the operating pressure because of the very high cake compressibility.

Electrofiltration can be an effective method for the non-thermal dewatering of *A. platensis* cells. Increasing the electric filed strength increases the cake dryness but it also leads to a higher energy consumption. Nevertheless, the energy consumption needed for the EF of *A. platensis* remains considerably lower than that needed for the thermal dehydration of this microalgae.

EF also modifies the filtrate and cake properties due to the electrolysis reactions that take place. This can modify the qualitative properties of the extracted compounds that could be separated, unfolded, or deteriorated due to the electric field exposure, hence the composition of the filtrates from the anode and cathode sides should be studied in depth in future work. The use of a special setup for the EF equipment, that includes a recirculation unit for electrode flushing, could decrease the extent of contamination of the cake and filtrate by the electrolysis products and better preserve the properties of the extracted microalgae compounds.

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Declaration of interest statement

The authors report that there are no competing interests to declare.

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3.2 Conclusion

Chapter 3 focuses on studying the effect of pressure and electric current density during dead-end filtration for the dewatering of the microalgae *Arthrospira platensis*. Increasing the pressure slightly increased the filtration kinetics during filtration without an electric field (F), this was related to the high compressibility of the microalgal cake. The use of electrofiltration (EF) increases the filtration kinetics. However, when compared to F, EF altered the properties of the filtrate (color, pH, and conductivity) due to the electrokinetic phenomena that take place in the presence of an electric field. The observed alterations in the filtrate properties highlighted the need to study the effect of EF on the biocompounds (proteins, CPC, and APC) present in both filtrate streams (from the anode and the cathode) as well as the formed filter cake. These research gaps were studied in the work presented in Chapter 4.

Chapter 4: Effect of electrofiltration on the extraction of biocompounds from *A. platensis*

4.1 Introduction

The effectiveness of using electrofiltration as a dewatering method applied to the microalgae *Arthrospira platensis* was demonstrated in Chapter 3. Electrofiltration was able to enhance the filtration kinetics, thereby increasing the filtrate yield as well as the cake dryness. However, the use of electrofiltration changed the filtrate properties: during EF the filtrate was acidic and alkaline respectively from the anode and cathode sides of the filtration cell. Whereas compared to F the pH of the filtrate was neutral. Given the pH and temperature sensitivity of the phycobiliproteins produced by *A. platensis*, Chapter 4 studies the effect of electrofiltration on the concentration of bioactive compounds (proteins, APC, and CPC) present in the filtrates and the cake.

Hence, the aim of this chapter is to assess the effect of electrofiltration on the biocompounds extracted in the filtrate streams and retained in the filter cake. The chapter also studied the effect of using ultrasonication (based on the literature review in Chapter 1 Section 1.1.3.3) as a cell disruption technique before filtration and electrofiltration as a method to increase the yield of biocompound recovery. And lastly, the use of freeze drying to dry the dewatered cake was explored. Each technique was accompanied by the characterization of the final product(s) obtained (filtrate, concentrated wet microalgae cake, and the dried microalgae cake).

The findings are presented as an article titled: “Effect of electrofiltration on the extraction of biocompounds from *Arthrospira platensis*”. This work is prepared for submission to a scientific journal. The work was carried out under the direction of Prof. Eugène Vorobiev and Prof. Henri El Zakhem, in collaboration with Prof. Nabil Grimi.

4.2 Article

The article is presented on the following page.

Effect of Electrofiltration on the Dewatering Kinetics of Arthrospira platensis and Biocompound Recovery

Christa Aoude[1,2], Nabil Grimi[1], Henri El Zakhem[2], and Eugene Vorobiev[1]

[1] Sorbonne University, University of Technology of Compiegne, ESCOM, EA 4297 TIMR, Royallieu Research Center, CS 60319, 60203 Compiegne Cedex, France

[2] Department of Chemical Engineering, Faculty of Engineering, University of Balamand, P.O. Box 100, Tripoli, Lebanon

Abstract

Arthrospira platensis (*A. platensis*) is a microalgae with a wide range of commercial uses. One of the main concerns that needs to be addressed in microalgae biorefineries is the costs associated with the harvesting and concentration steps. Filtration has been shown to be an effective technique for concentrating microalgae and recent studies have attempted to enhance membrane filtration by applying an external electric field to the filtration cell. This study consisted in assessing the use of electrically assisted filtration (electrofiltration) at 60 A/m^2 and 1 bar for the dewatering of *A. platensis*, as well as the effect of pretreating the microalgae with ultrasounds (US) on the filtration process. Untreated *A. platensis* exhibited better filtration kinetics than US treated *A. platensis* and electrofiltration was found to increase the cake dryness. More protein and pigments were present in the US treated microalgae solution compared to the untreated microalgae, which led to the presence of higher concentrations of protein and pigments in the filtrate streams after pressure filtration at 1 bar without the application of an external electric field. Electrofiltration was found to consume less energy compared to traditional drying techniques used for *A. platensis*. However electrofiltration degrades the biocompounds present in the filtrate and cake due to pH changes and other electrophoresis phenomena, which shows the need to optimize the process in future work.

Keywords

Microalgae *Arthrospira Platensis*, dewatering, filtration, electrofiltration, phycocyanin, protein

1 Introduction

Arthrospira platensis (*A. platensis*), commercially referred to as *Spirulina*, is a strain of microalgae that is categorized as a type of cyanobacteria. This microalgal strain has been associated with many benefits and potential applications [1–6]. It is mainly known for its ability to produce a blue pigment called phycocyanin that presents many benefits due to its color, antitumor, anti-inflammatory, and antioxidant properties [7]. Even though the phycobiliprotein phycocyanin offers many benefits and can be used in applications such as food and pharmaceuticals, it also presents many limitations. The main issue related to the use of

phycocyanin in different contexts is its sensitivity to certain temperatures, pH values, alcohol concentrations, ionic strengths, and light conditions [7–10].

After the cultivation of microalgal cells under the desired conditions to accumulate high concentrations of the bio-compounds of interest [11–13], the microalgae needs to be harvested and processed to recover these compounds [14–18]. A dry way of bio-compound recovery is most often used. It includes the concentration of microalgal suspension by flotation [19–23] or centrifugation [24–27] and eventually further dewatering by cross-flow microfiltration [28–32]. This is followed by drying the concentrated suspension to obtain a microalgal powder, that would then undergo a selective solvent extraction to recover the compounds of interest from the dried microalgae [33–35]. Alternatively, a wet pathway for microalgae compound recovery can be applied, including preliminary cell disruption, followed by solid-liquid extraction and selective separation of valuable compounds. Both dry and wet processing methods have their own significant shortcomings. While the dry way of microalgae processing is highly energy consuming, the wet processing pathway includes a complex separation stage to purify the obtained solution [33,34,36,37].

Dead-end filtration can be used to better dehydrate different sludges and increase the filter cake dryness [38–40]. Preliminary mechanical concentration of microalgae suspension by dead-end filtration can decrease the energy consumption required for the subsequent thermal drying of the filter cake. This can increase the global effectiveness of the dry way of microalgae processing. In spite of existing examples of the industrial implementation of filtration equipment [41–45], dead-end filtration of microalgae suspensions is poorly studied [32,46–49]. The high specific cake resistance of the microalgal filter cake leads to the low filtration velocity. This factor hinders the implementation of filtration techniques in microalgae processing. Electrofiltration has been found to enhance filtration velocity. The use of electrofiltration has been studied for different industrial sludges [38,39,50–53] and biopolymers [54,55]. Two studies assessed the use of electrically assisted filtration of the microalgae *Chlorella vulgaris* by: cross-flow filtration under a constant or periodic electric field [56] and the use of a cylindrical filter press at a pressure of 0.6 Mpa for 1h [57].

The aim of this work is to compare the behavior of dead-end filtration and electrofiltration, without any additional mechanical pressure, to improve the dewatering of the microalgae *Arthrospira platensis* while causing minimal damage to biocompounds of interest. Untreated and ultrasound treated (US) microalgae suspensions were used for dead-end filtration and electrofiltration. The US treated *A. platensis* was used to extract more biocompounds from wet biomass and create a more difficult to filter feed solution. Filter cakes obtained by the filtration of untreated *A. platensis* were freeze dried and the obtained powder was qualitatively and quantitatively assessed. This allowed us to study the effect of the order of the processing steps for the recovery and purification of bioactive compounds from *A. Platensis*. Filtration characteristics of the filter cakes (specific cake resistance and cake dryness) as well as qualitative and quantitative attributes of the electrically treated and untreated filtrates were evaluated.

2 Materials and methods

2.1 *Arthrospira platensis* suspensions

The microalgae *A. platensis* was used in this study. The algae was purchased from SAS TAM-Cyane (Plougastel-Daoulas, France), as a frozen algae paste (≈14 ± 1.2% dry weight content) to prevent its spoilage during its transportation to Compiègne, France. The frozen *A. platensis* paste was stored at −20 °C. The pastes were thawed at ambient temperature and diluted with deionized water to prepare algal solutions with a concentration of 5% by weight dry matter (henceforth %). The feed 128olutionn had a pH of 7.06 ± 0.3, a conductivity of (1.62 ± 0.12) mS/cm, and a zeta potential of -17.3 ± 0.9 mV (Zetasizer, Malvern Panalytical ltd). An *A. platensis* feed solution that did not undergo further treatment was used for control experiments hereby referred to as untreated.

Scanning electron microscopy (SEM, Quanta FEG 250, FEI, Holland) was used to monitor any changes in the microstructure of the algal cells, with an applied voltage of 20 kV. The SEM image of the untreated feed solution is shown in Figure 4.1 a.

To study the effect of preliminary cell disruption on the filtration and electrofiltration behavior as well as its effect on the extractability of biocompounds, *A. platensis* suspensions were pretreated by an ultrasonic processor at 400 watts for 20 minutes (UP-400S, Hielscher Ultrasonics, GmbH, Germany). *A. platensis* cells were disrupted into cell debris after the US pretreatment as shown by the SEM image in Figure 4.1 b. The untreated and US treated solutions had the same pH values of 7.7 ± 0.1, whereas the electrical conductivity increased from (1.03 ± 0.12) mS/cm to (2.49 ± 0.24) mS/cm after the US treatment due to the release of cellular compounds.

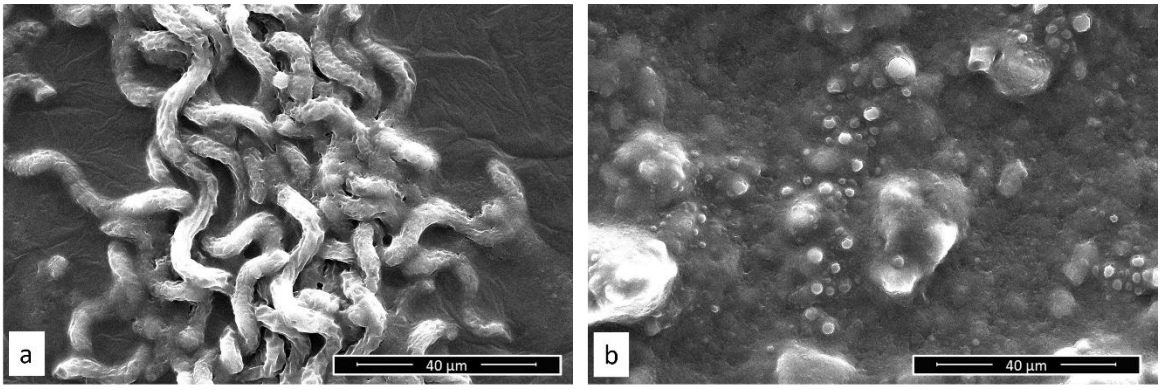

Figure 4.1. SEM images of the untreated (a) and US treated (b) suspensions of *A. platensis* microalgae

2.2 Dead-end filtration and electrofiltration

Two types of dead-end filtration experiments were carried out: pressure filtration (F) at a constant pressure of 1 bar and electrofiltration (EF) at a constant electric current of 60 A/m^2 and the same pressure of 1 bar. The filtration equipment (Figure 4.2) consisted of a 1L feed tank

connected to a pressurized air system, a stainless-steel support with a screw to secure the independent parts of the system together, and a polypropylene filtration cell (circular cross section 24.6 cm^2, volume 49.2 cm^3) equipped with a feed inlet and valve. Both sides of the filtration cell were covered with a disposable PVDF membrane (Nafion MV020T, Millipore) with a pore size of 0.2 µm. Prior to use, the membranes were activated by soaking them in deionized water for 30 minutes. The wire mesh electrodes made of titanium (anode) and inox (cathode) were placed on the outer side of the filtration cell in a way that would prevent them from being in direct contact with the filter cake.

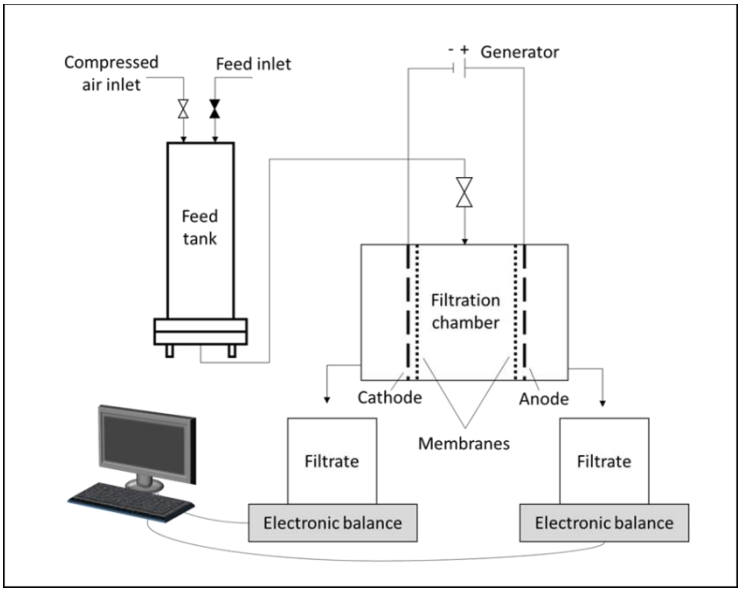

Figure 4.2. Schematic of the dead-end filtration/electrofiltration equipment

The filtration time of 150 minutes was needed to fill the filtration cell by the cake in F conditions. The graph *t/V* vs *V* curve presented in Figure 4.3 deviates from the straight line at the filtration time $t > \sim 150$ min indicating that the filtration cell is completely filled by the cake. This was assessed based on Ruth-Carmen's filtration model [44] as presented in Equation 4.1:

$$\frac{t-t_0}{V-V_0} = \frac{\propto.\mu.C_0}{2A^2\Delta P}(V+V_0) + \frac{R_m.\mu}{A.\Delta P} \quad (4.1)$$

Where t is the time (s), V is the total volume of filtrate (m^3), α is the specific resistance of filter cake (m/kg), A is the total cross sectional filtration area, $\mu=10^{-3}$ Pa.s is the filtrate viscosity, C_0 is the concentration of the feed solution (kg/m^3), ΔP is the applied pressure (Pa), R_m is the filter media resistance (m^{-1}), V_0 is the initial volume of filtrate recuperated at the time t_0 needed to attain stabilized filtration regime. The specific resistance of the filter cake α obtained by F at 1 bar was found to be equal to 1.94E+13 m/kg for the untreated sample (Figure 4.3) and 3.87E+15 m/kg for the US treated sample. Similarly, the high specific cake resistances of the order of 1.0E+14 m/kg were recorded for the filtration of powdered *Chlorella vulgaris* microalgae [32].

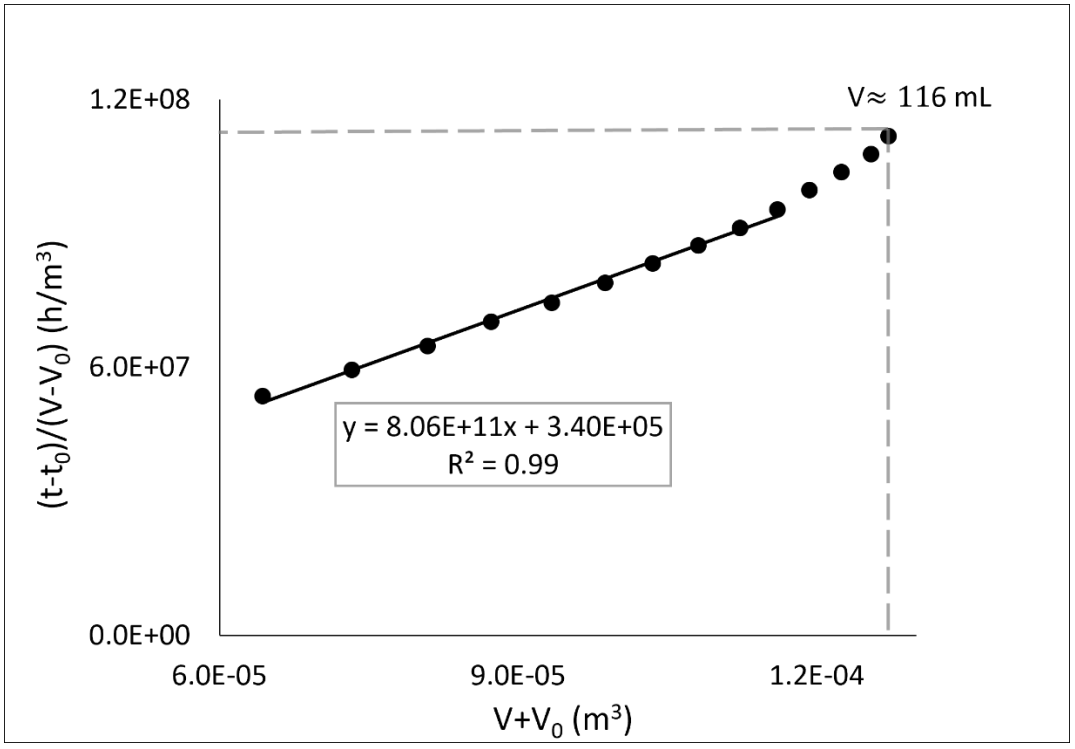

Figure 4.3. Typical example of filtration data for the untreated *A. platensis* samples

The increase in the specific cake resistance α after US treatment is related to the disruption of *A. platensis* cells.

The same experimental setup was used for both F and EF experiments. Filtrates from each outlet of the filtration cell were collected in separate beakers. The electricity supply was set using the EV261 direct electric current generator (0–1 A, 0 –600 V, Consort, Belgium), and was monitored using a multimeter (FLUKE 45). The filtration rates were obtained by continuously measuring the mass of the obtained filtrates with two electronic balances (METTLER PM6000, max weight: 6000g, resolution: 0.01g and SARTORIUS (max weight: 600g, resolution: 0.1g). The filtrate masses, and the applied currents and voltages were recorded by the HPVEE filtration acquisition software (Electronic Service, UTC, France). The interval between each measurement was fixed at 60 seconds. The temperature at the electrodes was measured using flexible K-type thermocouples, connected to a 4-channel thermometer (Extech Instruments). The pH and conductivity of the filtrate were measured using a Consort multimeter.

2.3 Freeze drying of the filter cake

For the experiments using untreated microalgae, filter cakes obtained by the F and EF were freeze-dried. The samples were initially frozen at -20 °C, they were then placed on a pre-cooled shelf at ≈ -20°C in a SMH 15 freeze-drier (Usifroid, Maurepas, France) and freeze-dried until each sample reached a constant weight, indicating that they were completely dry.

2.4 Filtrate and filter cake characterization

Filtrates and dispersed filter cake samples were centrifuged at 13500g for 10 minutes, then the supernatants were collected and analyzed. The freeze-dried cakes were hand pulverized into a finer powder, then the obtained powder was dispersed into deionized water and vortexed.

2.4.1 Protein characterization

The protein content of the samples was determined using Bradford's method [58]. The 100 µL of supernatant was vortexed with 1 mL of Bradford dye reagent (Alfa Aesar, Thermo Fisher Scientific, Germany). Then the mixture was incubated for 10 minutes in the dark at room temperature and the absorbance was measured at 595 nm (Biochrom Libra S32, Biochrom Ltd, UK). The blank consisted of 100 µL of deionized water with 1 mL of Bradford dye reagent. The calibration curve was obtained using Bovine Serum Albumin (BSA) as a standard and the results were expressed as milligrams BSA equivalent per gram dry algal biomass (mg BSA equivalent/ algae).

2.4.2 Pigment characterization

The phycobiliprotein content was determined by applying a slightly modified version of the formulas developed by Bennett and Bogorad [59], as shown in Equations 4.2, 4.3, and 4.4:

$$C_{C-PC} = [A_{620} - (0.474\ A_{652})] / 5.34 \quad (4.2)$$

$$C_{APC} = [A_{652} - (0.208\ A_{620})] / 5.09 \quad (4.3)$$

$$C_{PE} = [A_{562} - (2.41\ C_{C-PC}) - (0.849\ C_{APC})\ ] / 9.62 \quad (4.4)$$

where C_{C-PC} is the C-phycocyanin concentration (mg/mL), C_{APC} is the Allophycocyanin concentration (mg/mL), C_{PE} is the C-phycoerythrin concentration (mg/mL), A_{562}, A_{620} and A_{652} are, respectively, the absorbances of the sample at 562 nm, 620 nm, and 652 nm. The concentrations were then converted to mg/ g dry *A. platensis* (hereby referred to as mg/ g d.m.).

2.4.3 Filter cake dryness

To determine the dryness of filter cake, the wet cake was placed in an oven at 105 ˚C for 24 hours. The filter cake's dryness was calculated based on the following equation:

$$\%dryness = \frac{m_{wet\ cake}}{m_{dry\ cake}} \times 100 \quad (4.5)$$

where $m_{wet\ cake}$ and $m_{dry\ cake}$ are respectively the masses of wet and dry filter cake, (g).

2.5 Energy consumption

The specific energy consumption during electrofiltration was calculated using Equation 4.6:

$$E = \frac{1}{M_l}\sum_{j=1}^{Z}\frac{I_j \cdot U_j \cdot \Delta t}{3600} \quad (4.6)$$

where E is the specific energy consumption (kWh/kg water removed), M_l is the mass of water removed due to the application of an electric field (kg), I_j is the current intensity (A), U_j is the voltage (V), Δt is the time interval between subsequent measurements (s).

2.6 Statistical analyses

All the experiments were repeated at least three times. All the results are presented with the calculated standard deviation.

3 Results and Discussion

3.1 Filtration and electrofiltration behavior

Filtration (F) and electrofiltration (EF) kinetics for the untreated *A. platensis* microalgae are presented in Figure 4.4. The quantity of filtrate obtained during electrofiltration from the anode side of filter cell was very small (24.93 ± 7.45 mL), while the quantity of filtrate obtained from the cathode side of filter cell was considerably larger (116.6 ± 0.96 mL). This is explained by the negative charge of the microalgae particles, which migrate towards the anode due to the electrophoresis forces. As a result, the filter cake is more intensively built near the anode, which in turn decreases the filtration velocity on the anode side. Simultaneously, electroosmotic forces in the pores of filter cake push the liquid flow towards the cathode, thus increasing the quantity of filtrate obtained from the cathode side. Similar observed behavior during electrofiltration has been reported in literature for different types of suspensions [38,50,55,60]. The total quantity of filtrate obtained after 150 minutes of electrofiltration (EF-total) was higher (141.52 ± 6.09 mL) than that obtained by pressure filtration (F-total) (111.84 ± 10.18 mL).

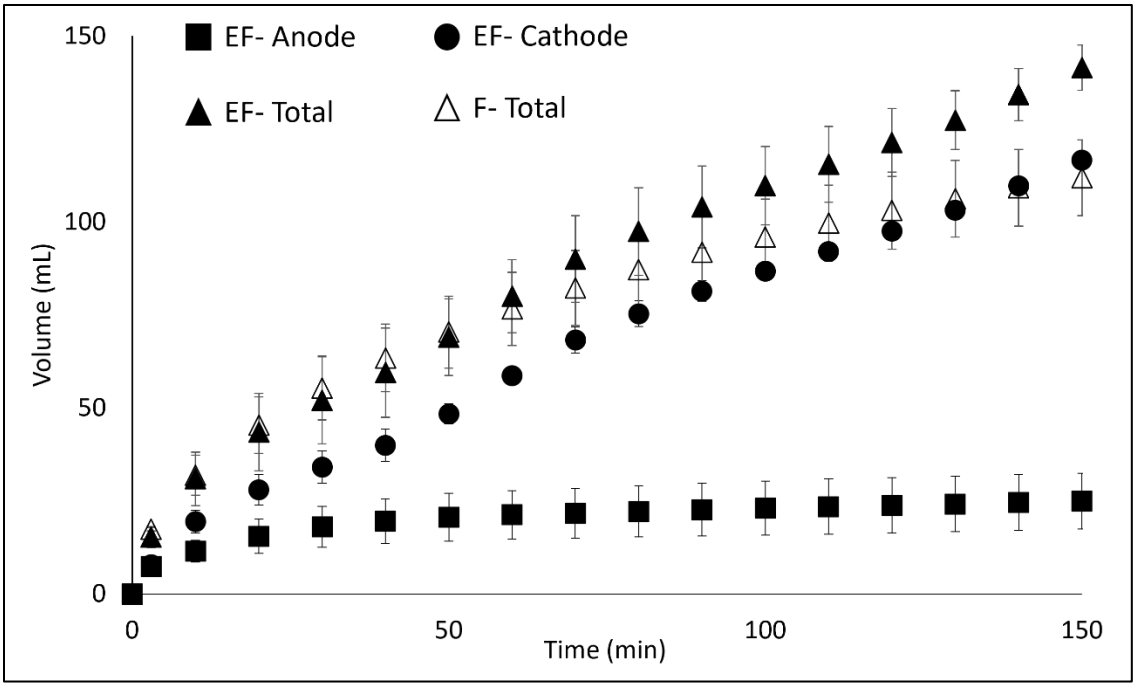

Figure 4.4. Filtrate volume obtained from the anode side (EF-anode), cathode side (EF-cathode), and both sides (EF-total) during electrofiltration of the untreated A. platensis suspension. F-total is the total filtrate volume obtained during pressure filtration

The filtration and electrofiltration kinetics for the *A. platensis* microalgae pretreated by US are presented in Figure 4.5. US pretreatment reduces the size of the microalgae particles and destroys the cells' structure as revealed by the SEM imaging (Figure 4.1 b). Consequently, cellular compounds are better extracted after the US pretreatment. However, US pretreatment considerably decreases the filtration rate due to the higher specific resistance of the formed filter cake, which increased by approximately 200 times in our case (from 1.94E+13 to 3.87E+15 m/kg). Moreover, cell debris and the released intracellular compounds can lead to membrane fouling by pore blocking [48,56,61–63]. During the filtration of *A. platensis* the polysaccharides, cell debris, and exopolymeric materials secreted from the microalgal cells were the main cause of membrane fouling [64,65].

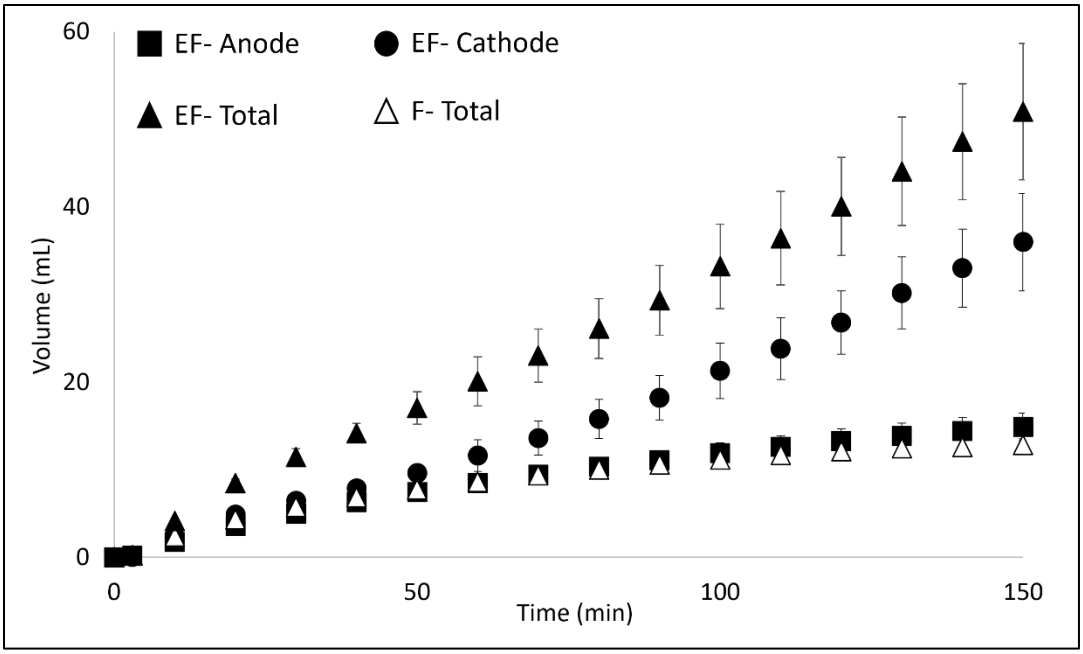

Figure 4.5. Filtrate volume obtained on the anode side (EF-anode), cathode side (EF-cathode), and both sides (EF-total) during electrofiltration of the US treated A. platensis suspension. F-total is the total filtrate volume obtained during pressure filtration

The quantity of filtrate obtained during pressure filtration (F) of US treated *A. platensis* was very small, reaching a total volume of 12.84 ± 0.71 mL. Approximately the same volume of filtrate was obtained from the anode side of filter cell during electrofiltration of US treated *A. platensis* (EF-anode). Electrofiltration considerably increased the filtration rate from the cathode side of filter cell (EF-cathode). Consequently, the final total volume of filtrate obtained by electrofiltration (EF-total) was 4 times larger than that obtained by filtration (F-total).

Figure 4.6 presents the photos of filter cakes formed by F and EF. Filter cakes formed by both F and EF of the untreated microalgae suspension have a thickness of 2 cm and occupy the entire volume of the filter chamber after a filtration time of 150 min (Figure 4.6 a and 4.6 b).

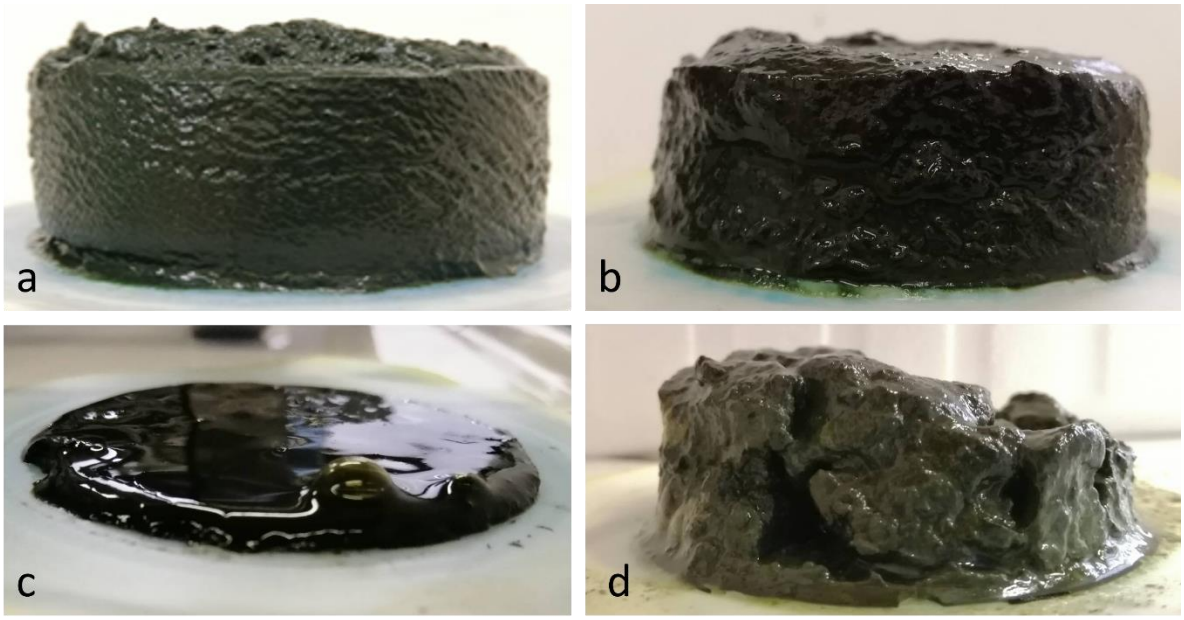

Figure 4.6. Filter cakes formed from the untreated A. platensis suspension by F (a) and electrofiltration (b). Filter cakes formed from the US treated A. platensis suspension by F (c) and electrofiltration (d)

The dryness of filter cake formed by EF is somewhat higher (16.04 ± 0.2) % than that of the filter cake formed by F (13.0 ± 0.47) %. Filter cakes formed from the US treated *A. platensis* suspension incompletely occupy the volume of the filter chamber (Figure 4.6 c and 4.6 d). This is more prominently observed with the filter cake formed by F (Figure 4.6 c), which remains in liquid form and has a dryness of (6.75 ± 0.02) %. The filter cake formed by EF is better structured (Figure 4.6 d) and has a higher dryness (10.07 ± 0.32) %. The difference observed between the cakes formed using untreated and US treated *A. platensis* can be associated to the difference in the particles' shape and size as clearly illustrated in the SEM imaging (Figure 4.1 a and 4.1 b). Many studies have investigated the influence of the particle shape and size on filtration kinetics and the properties of the filter cake [60,66–68]. The higher cake dryness reported for the EF experiments compared to the F experiments was expected, since the application of an electric filed during filtration has been proven to increase the cake dryness due to the electrokinetic phenomena that take place [39,40,50,69].

Figure 4.7 presents the specific energy consumption over time during EF of the untreated and US treated *A. platensis* suspension calculated using Equation (4.6). It is observed that the energy consumption increases more rapidly during the electrofiltration of US pretreated microalgae. As a result, the final energy consumption was 0.24 kWh/kg water removed for the electrofiltration of US pretreated *A. platensis*, while it was just 0.07 kWh/kg water removed for the electrofiltration of the untreated *A. platensis*. This is easily explained by the higher electric resistance of the filter cake as well as the higher voltage during the electrofiltration of US pretreated *A. platensis*. For instance, the initial value of the voltage (at the constant electric current I = 60 A/m^2) was U_0 = 4.51 V. At the end of the electrofiltration process at I = 60 A/m^2 the value of the voltage increased up

to (38.61 ± 1.77) V and (50.37 ± 5.01) V respectively for the untreated and US pretreated microalgae. A study had also reported that electrically assisted filtration became more efficient with an increase of voltage and/or ionic strength [57]. The temperature increase measured near the electrodes was moderate for both untreated (up to ≈ 32°C) and US pretreated (up to ≈ 35°C) *A. platensis*.

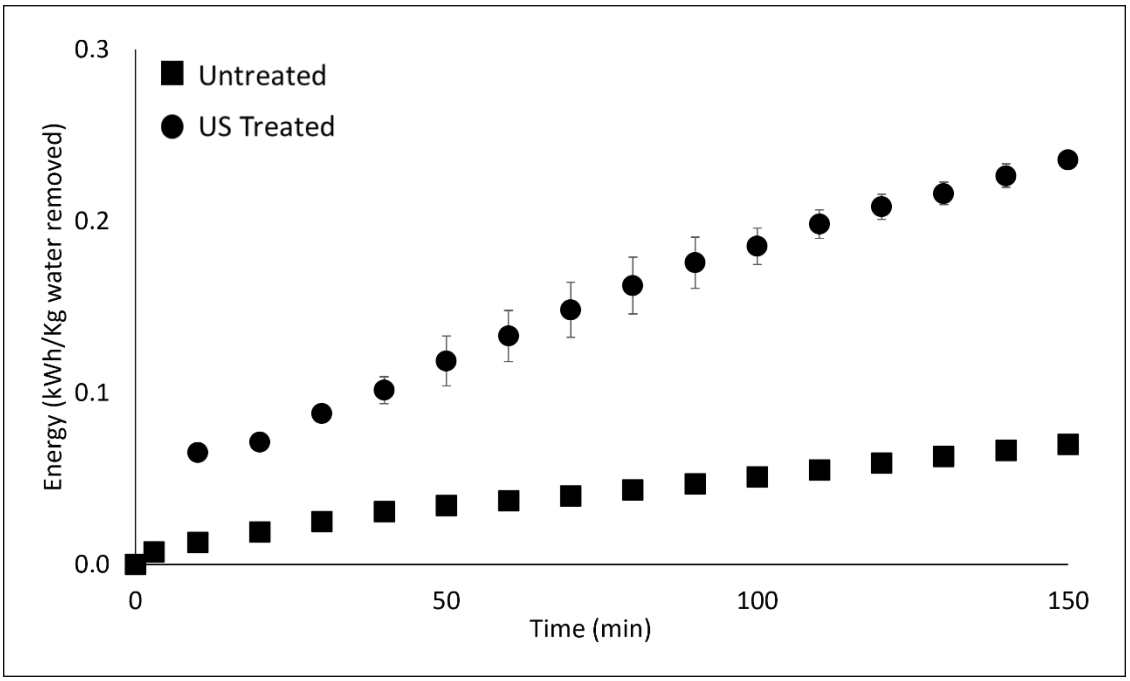

Figure 4.7. Specific energy consumption over time during EF of the untreated and US treated suspension of A. platensis

Data presented in Figure 4.7 show that the electrofiltration remains less energy consuming for the dewatering of microalgae in comparison with thermal processing. For instance, drum drying of microalgae has an energy consumption of 0.9 kWh/kg water removed, and spray drying has an even higher energy consumption of 1.09 kWh/kg water removed [70].

3.2 Qualitative characteristics of extract solutions and filter cakes

Table 4.1 shows the characteristics of the untreated and US pretreated *A. platensis* feed solutions used for the F and EF experiments. The untreated and US treated feed solutions had similar pH values which were close to being neutral, whereas the conductivity increased by a factor of 2.4, i.e. from (1.03 ± 0.12) mS/cm for the untreated solution to (2.49 ± 0.24) mS/cm for the US treated feed solution.

Table 4.1. Characteristics of the untreated and US treated *A. platensis*

Feed solution	Untreated	US treated
pH	7.87 ± 0.06	7.38 ± 0.13
Conductivity (mS/cm)	1.03 ± 0.12	2.59 ± 0.3
Protein concentration (mg/ g d.m.)	15.69 ± 0.79	27.18 ± 2.38
C-PC concentration (mg/ g d.m.)	2.65 ± 0.96	3.17 ± 0.3
APC concentration (mg/ g d.m.)	1.07 ± 0.3	2.12 ± 0.33
PE concentration (mg/ g d.m.)	0.12 ± 0.08	1.25 ± 0.07

The change in conductivity for US treated microalgae can be directly related to the release of bioactive compounds from the cells into the medium after cell disruption. This is further proven by the spectrophotometric analyses (Table 4.1). For instance, after the US treatment the concentrations of protein, phycocyanin concentration (C-PC), Allophycocyanin concentration (APC), and phycoerythrin concentration (PE) in the feed solution were respectively increased by approximately 1.73, 1.20, 1.98, and 10.4 times.

Table 4.2 presents the qualitative characteristics of filtrates obtained by F and EF of the untreated and US pretreated *A. platensis* suspensions. Electrofiltration significantly modified the characteristics of the filtrates obtained from the cathode and anode sides of the filter chamber. The filtrate obtained from the anode side was acidic with a pH respectively equal to 2.7 ± 0.02 and 4.05 ± 0.09 for the untreated and US pretreated *A. platensis*. On the contrary, filtrate obtained from the cathode side was basic with approximatively the same pH of 12.1-12.3 for both untreated and US pretreated *A. platensis* microalgae. The observed pH changes are related to electrolysis reactions on the electrodes, and are in accordance with the findings reported in literature for EF of microalgal solutions [56] as well as for other types of solutions [50,54,71].

Table 4.2. Qualitative characteristics of filtrates obtained by filtration (F) and electrofiltration (EF) of the untreated and US pretreated *A. platensis* microalgae

		Untreated		US treated	
		F	EF	F	EF
pH	Anode	7.43 ± 0.19	2.71 ± 0.02	7.73 ± 0.25	4.05 ± 0.09
	Cathode		12.3 ± 0.02		12.1 ± 0.08
Conductivity (mS/cm)	Anode	2.19 ± 0.21	5.66 ± 0.76	2.98 ± 0.14	10.37 ± 4.24
	Cathode		6.71 ± 0.27		16.2 ± 1
Protein concentration (mg/g d.m.)	Anode	1.37 ± 0.27	0.28 ± 0.01	15.56 ± 1.5	negligible
	Cathode		4.88 ± 0.05		2.71 ± 0.2
C-PC concentration (mg/g d.m.)	Anode	0.43 ± 0.04	negligible	0.21 ±0.02	negligible
	Cathode		negligible		negligible
APC concentration (mg/g d.m.)	Anode	negligible	negligible	0.17 ± 0.03	negligible
	Cathode		negligible		negligible
PE concentration (mg/g d.m.)	Anode	negligible	negligible	negligible	negligible
	Cathode		negligible		negligible

The conductivity of the filtrates obtained by EF was significantly higher than the conductivity of the filtrates obtained by F, especially for US pretreated *A. platensis*. The quantity of proteins detected in the filtrate obtained by F was very low for the untreated microalgae: (1.37 ± 0.27) mg/g d.m. and it significantly increased after the US treatment: (15.56 ± 1.5) mg/g d.m. PVDF membrane with a pore size of 0.2 μm used in this paper may retain just a small part of protein molecules, as many studies have found that different extents of protein binding can occur when using PVDF membranes [72–75]. The formed *A. platensis* filter cake, which has a very important specific resistance, may also hinder the passage of protein to the filtrate. The concentration of C-phycocyanin was lower in the filtrate obtained by F than in the feed solution. However, the blue color was clearly visible for the filtrates obtained by F of both the untreated (Figure 4.8 a) and US treated (Figure 4.8 b) microalgae. The concentration of other pigments in the filtrate was very low and can be considered negligible. Electrofiltration led to the extraction of different concentrations of protein in the filtrate obtained from the anode and cathode sides of the filter cell. The quantity of proteins obtained in the filtrate on the cathode side was somewhat higher (in comparison with the filtrate on the anode side) but it remained lower than the concentration detected in the feed solution. Other microalgae compounds that are present in the filtrate were detected in negligible amounts, which explains the absence of the blue color for the filtrates obtained by EF (Figure 4.8 c, d, e, f).

The extraction of negligeable amounts of phycoerythrin (PE) was expected, given the initially lower concentration of PE detected in the feed solution compared to the other biocompounds that were extracted. This has been observed in a study extracting phycocyanin and phycoerythrin from

A. platensis using protic ionic liquids and it was also associated to the lower concentrations of PE initially present in the algal cells compared to the more abundantly present phycocyanin [76].

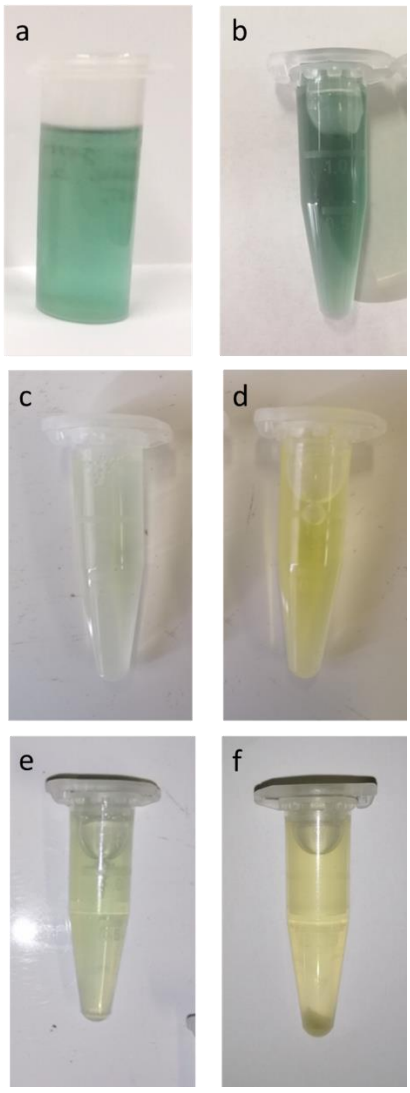

Figure 4.8. Filtrates obtained by F from the untreated (a) and US treated (b) microalgae suspensions. Filtrates obtained by EF from the untreated (c: anode side, d: cathode side) and US treated (e: anode side, f: cathode side) microalgae suspensions

The filter cakes obtained by F and EF of untreated *A. platensis* were analyzed after they had been freeze-dried (Table 4.3). This helped preserve the residual microalgae compounds within the cake by eliminating the use of high drying temperatures, which have been associated to pigment and protein denaturation [77–80]. It is evident from the data presented in Table 4.3 that the protein, C-phycocyanin, Allophycocyanin, and C-phycoerythrin were conserved in the filter cake obtained by filtration. However, protein and other microalgae compounds were detected in very low concentrations in the freeze-dried filter cake obtained by electrofiltration. This could be explained by protein denaturation for more basic and acidic pH values of 11 and 4.5 as interpretated in previous studies [78,81].

Table 4.3. Qualitative characteristics of freeze-dried filter cakes obtained by F and EF of untreated *A. platensis*

Cake	F	EF
Protein concentration (mg/ g d.m.)	164.5 ± 0.57	1.81 ± 0.02
C-PC concentration (mg/ g d.m.)	43.2 ± 0.12	0.33 ± 0.01
APC concentration (mg/ g d.m.)	18.14 ± 0.06	0.28 ± 0
PE concentration (mg/ g d.m.)	0.6 ± 0.41	0.09 ± 0

Figure 4.9 shows the images of the freeze-dried filter cakes obtained by F (a) and EF (b) from the untreated microalgae. Blue color can be easily detected on the surface of freeze-dried filter cake obtained by F. However, the surface of the filter cake obtained by EF has brown and dark green tints, as well as a white residue, which could indicate the presence of salts. These visual attributes are probably due to the formation of electrolysis products.

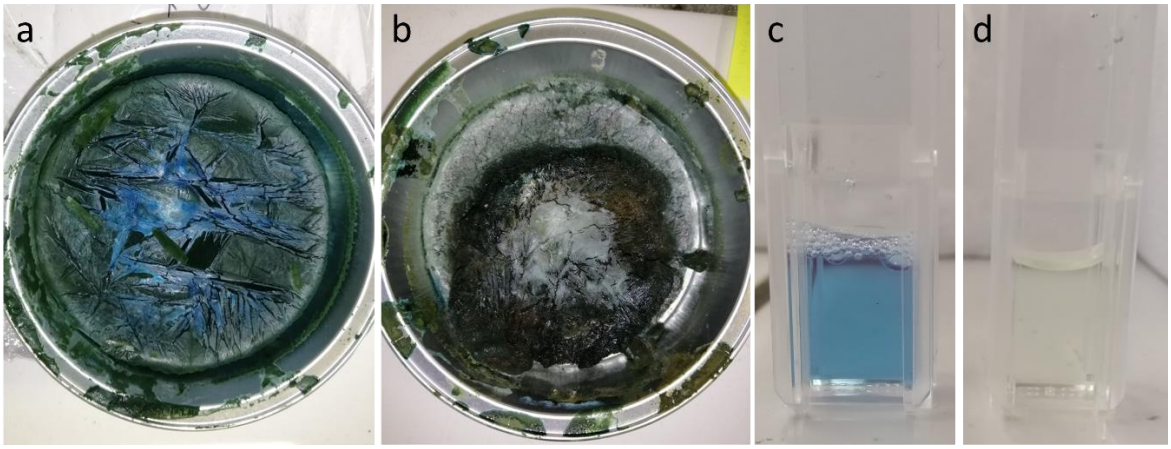

Figure 4.9. Images of freeze-dried filter cakes obtained by F (a) and EF (b) from the untreated microalgae and the same freeze-dried cakes dispersed in water for F (c) and EF (d)

Dispersing the freeze-dried cakes obtained by F (Figure 4.9 a) and EF (Figure 4.9 b) provided further visual evidence that very low amounts of C-phycocyanin were present in the EF treated cake compared to the relatively higher amount present in the F treated cake, as quantitatively demonstrated in Table 4.3.

4 Conclusion

Dead-end filtration is an effective method to mechanically dehydrate microalgal suspensions. Filtration (F) at 1 bar was able to increase the dry matter of untreated *A. platensis* from 5 to 13%, which in turn can significantly decrease the energy required during a subsequent drying step. At the same time, for the filtration of untreated *A. platensis*, small quantities of proteins and other microalgal compounds were released into the filtrate streams, whereas the majority of these

compounds were mostly retained in the filter cake. Therefore, the obtained filtrate is poor in microalgal which eliminates the need to let it undergo any additional separation steps.

US pretreatment was somewhat more effective in increasing the quantity of released microalgae compounds in the filtrate streams. However, this quantity remained rather small and insufficient to justify the wet way of extraction from microalgae using US as a pretreatment followed by F. Moreover, the filter cake formed during the F of US treated microalgae has a very high specific resistance and low dryness, making the filtration process less efficient.

Electrofiltration of the untreated *A. platensis* enhanced filtration kinetics when compared to pressure filtration without an electric field, it also helped increase the cake dryness, reaching values up to approximately 16%. The specific energy consumption during electrofiltration of the untreated A. platensis was considerably low when compared to the energy consumption associated with thermal drying techniques, reaching 0.07 kWh/kg water removed.

Furthermore, the microalgae compounds were denatured during electrofiltration, probably due to the extreme pH conditions and electrolysis phenomena. Electrofiltration of US treated microalgae is also effective for enhancing the filtration kinetics and increasing the cake dryness (up to approximately 10%). However, this process consumes more energy (0.27 kWh/kg) and does not have any additional advantages in comparison with the electrofiltration of untreated microalgae.

Due to electrofiltration's ability to enhance the filtration kinetics and improve the cake dewatering process compared to pressure filtration without the application of an external electric field, further studies should be conducted to optimize the processing conditions and prevent the denaturation of biocompounds of interest. Particularly, electrofiltration should be performed at neutral pH conditions, which can be achieved by filtrate recirculation [50,54,55].

Declaration of competing interest

The authors declare that they have no conflicts of interest.

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4.3 Conclusion

Chapter 4 showed that dead-end electrofiltration decreased the total concentration of proteins and pigments present in the obtained filtrates when compared to pressure driven dead-end filtration. Disrupting the microalgae cells by ultrasonication before filtration increased the concentration of proteins and pigments in the filtrate stream by both dead-end filtration and electrofiltration. However, the filtration kinetics were severely reduced when the cells were disrupted in comparison to untreated intact cells. In both cases, the use of electrofiltration did lead to the deterioration of the biocompounds present in the filtrates and the microalgal cake. Electrofiltration also caused a change in the appearance (color and structure) of the filtrates and the formed cake. Freeze drying the microalgae cakes preserved the retained biocompounds, nevertheless the cakes obtained by electrofiltration retained a smaller concentration of biocompounds when compared to the cakes obtained by pressure driven dead-end filtration. The decline in the biocompound concentration was linked to their denaturation after being exposed to a medium with an alkaline or acidic pH. This shows the need to prevent the changes in pH to better preserve the extracted biocompounds (explored in Chapter 6). The caked also retained biocompounds (either in the filtrate trapped in the pores or the cells themselves), this requires additional study to further recover biocompounds trapped in the formed cake (explored in Chapter 5).

Chapter 5: Filter cake washing and electrowashing

5.1 Introduction

Chapter 4 studied the use of dead-end filtration and electrofiltration for the dewatering of microalgal cakes. The study found that biocompounds are retained in the formed cakes and that higher concentrations were detected in the cakes formed by pressure driven dead-end filtration without the application of an electric field. As discussed in Chapter 1, Section 1.3, cake washing and electrowashing are efficient methods for the recovery of compounds trapped in filter cakes.

The aim of this chapter is to assess the use of different cake washing and electrowashing configuration for the recovery of bioactive compounds trapped in an *A. platensis* filter cake.

The findings are presented as an article titled: “Electrowashing of microalgae *Arthrospira platensis* filter cake”. This work was submitted to the journal “Separation Science and Technology”. The work was carried out under the direction of Prof. Eugène Vorobiev and Prof. Henri El Zakhem, in collaboration with Prof. Nabil Grimi.

5.2 Article

The article is presented on the following page.

Electrowashing of microalgae *Arthrospira platensis filter cake*

Abstract

Cake washing has been used to remove compounds trapped in the pores of a filter cake. These compounds could be desired products that should be recovered. Cake washing and electrowashing have been studied and found to present many benefits, but in some cases washing filter cakes can be a slow process. Moreover, electrowashing of microalgal cakes has not been studied yet. In this paper, an *Arthrospira platensis* filter cake formed by constant pressure dead-end filtration was washed by pressure washing (PW), electrowashing (EW), and pressure electrowashing (PEW) processes. Washing was carried out to extract desired biocompounds (CPC, APC and proteins) from the filter cake. The study showed that the use of a constant direct current (60 A/m^2) coupled with the effect of an applied hydraulic pressure was an effective way to increase the cake washing kinetics. It also demonstrated that it was possible to extract proteins and pigments by applying the washing by displacement technique.

Keywords: *Arthrospira platensis*, Electrowashing, Extraction, Filter cake washing, Microalgae cake.

1 Introduction

Microalgal biorefineries use multiple processing steps, including cultivating the microalgae, harvesting and solvent extraction to recover valuable bio-compounds, e.g. carbohydrates, proteins, lipids, pigments [1–7]. Often, two-step harvesting is used. During the first step, sedimentation or flotation can be used to increase the total solid concentration to 2 -7 % w/v. This is followed by a second step, where the suspension can be further dewatered by centrifugation or filtration to concentrate the microalgal biomass to 15 – 25% w/v before performing other processing techniques such as drying and solvent extraction [8–10]. Extraction of valuable microalgal compounds can be achieved by a dry or wet way of extraction. The dry way, which is widespread, consists in microalgae drying followed by organic solvent extraction. In general, drying techniques consume high amounts of energy. This is why the wet way of extraction, including performing an initial mechanical or physical disruption of cells (e.g., by high pressure homogenization, bead milling, pulsed electric field, ultrasound), is also explored [11,12]. This non thermal way consumes less energy, but it requires the use of complex purification techniques to separate the extracts from cell debris and other impurities [13–18]. While centrifugal sedimentation is used for the concentration of microalgal suspensions, filtration can also be used as an alternative technique [19–25]. Crossflow filtration efficiently concentrates microalgal suspensions, but it can only reach a limited extent of microalgal slurry dehydration [21,26,27]. Dead-end (cake) filtration using a frame or belt filter-presses leads to a better extent of slurry dewatering. Moreover, this technique allows the subsequent use of cake washing techniques to remove soluble compounds that are

trapped within the pores of the formed filter cake [28–32]. Cake washing could be used to extract some microalgal biocompounds released during harvesting. Unfortunately, dead-end filtration of microalgae has a low filtration yield due to the high specific resistance of the formed filter cake. For instance, the filter cake obtained by dead-end filtration of the microalgae *Chlorella* has a specific resistance in the range of (2.8 - 6.5)*10^{14} m/kg [33], which decreases the filtration efficiency over time, especially when processing large quantities of microalgal suspensions. As an alternative, the use of electrofiltration, electrodewatering, and electrowashing with a DC electric field enhances the flow of liquid inside filter cakes with low permeabilities due to the electroosmotic phenomenon that takes place [34–39]. To the best of our knowledge, cake washing and electrowashing have not been studied yet, for the recovery of valuable microalgal compounds trapped within a microalgal cake [31,40–43]. This paper explores the potential of using washing and electrowashing to remove soluble compounds trapped in a microalgal cake before the subsequent cake drying step.

2 Materials and Methods

2.1 Microalgal feed solution

Frozen *A. platensis* paste (15% by weight dry matter) was purchased from SAS TAM- Cyane (Plougastel-Daoulas, France). The paste was thawed and diluted with deionized water into a 5% suspension (pH = 7.87 ± 0.06, σ = 1.03 ± 0.12 mS/cm) to form the feed solution for the filtration experiments. The number-based particle size distribution of the sample was measured using a laser diffraction particle size analyzer (Malvern Mastersizer 2000, France), the average particle size distribution shows that 10% of the particles were smaller than 3.01 µm, less than 50% were smaller than 4.54 µm, and less than 90% were smaller than 9.15 µm.

2.2 Filtration-washing setup

Filtration was carried out for 16h at a pressure of $\Delta P_F = 4$ bar in a batch filtration cell with a circular cross sectional area of 24.6 cm^2 and a volume of 49.2 cm^3 (Choquenet SAS, France) (Figure 5.1). Both sides of the filtration cell were covered by a PVDF membrane (Nafion MV020T, Millipore) with a pore size of 0.2 µm. Prior to their use, the membranes were activated by soaking them in deionized water for 30 minutes. A filter cake with a thickness of 2 cm was formed by dead-end constant pressure filtration.

Filter cake washing was then performed in the same filtration cell. During the electrowashing experiments (Figure 5.1), two different electrodes were used, where the cathode was made out of Inox and the anode was made out of Titanium. Three different experimental conditions were investigated: 1) washing under a washing pressure $\Delta P_W = 1$ bar without an electric field (denoted as pressure washing PW), 2) electrowashing at 60 A/m^2 under a pressure $\Delta P_W = 1$ bar (denoted as pressure electrowashing PEW), and 3) electrowashing at 60 A/m^2 with recirculation of washing liquid at a flow rate of 260 mL/min with $\Delta P_W = 0$ bar (denoted as electrowashing EW). The first and second washing conditions are presented in Figure 5.1 A. The third washing condition is

presented in Figure 5.1 B. A peristaltic pump was used for the EW experiments to ensure a recirculating flow rate of 260 mL/min. Tap water was used as the wash solution (pH = 7.36, electrical conductivity σ = 0.6 mS/cm). A total of 12 samples of wash liquor were collected during PEW and EW, whereas in the case of PW the washing rate was found to be too slow and hence the experiments were stopped after the collection of 10 samples. The first two collected samples were 2.5 mL each, while all the other samples were 5 mL each. Therefore, during PEW and EW a total volume of 55 mL of wash liquor was recovered, and a total volume of 45 mL was recovered during PW. The changes in temperature were measured on the cathode side (outlet of wash liquor) using flexible K-type thermocouples, connected to a 4 channel thermometer (Extech Instruments). The temperature was not recorded on the anode side due to inevitable liquid leaks after inserting the thermocouple near the anode.

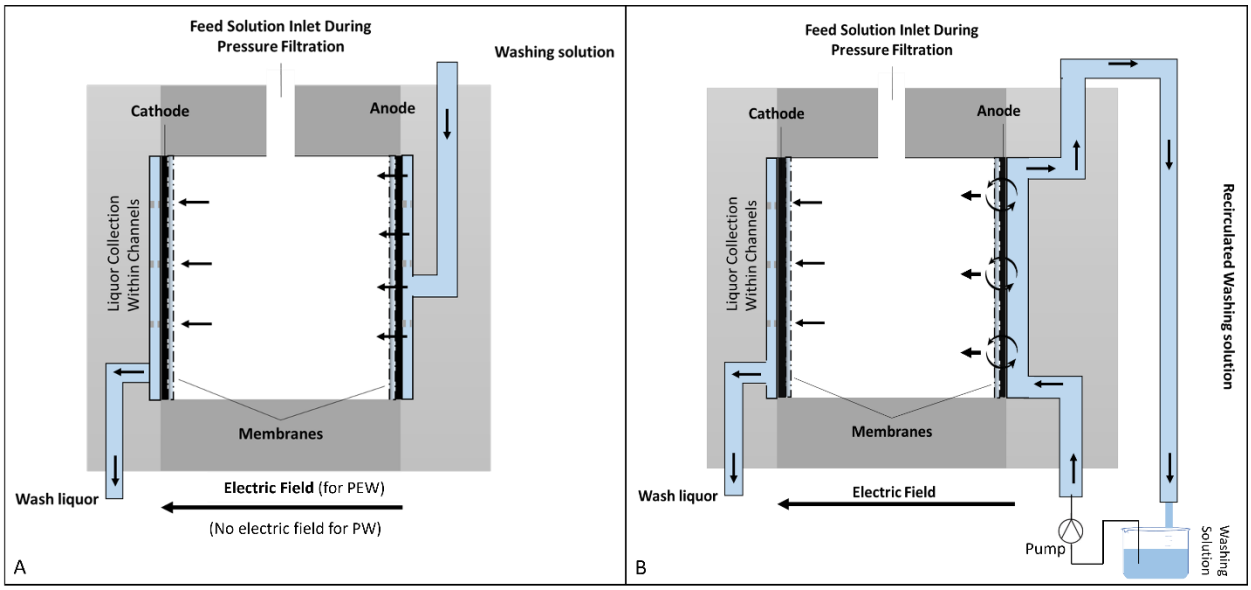

Figure 5.1. Representation of the filtration-washing cell, A: Washing without recirculation (PW and PEW), B: Washing with recirculation (EW)

The specific resistance of the filter cake was calculated by applying Equation (5.1):

$$\frac{t - t_0}{V - V_0} = \frac{\propto . \mu . C_0}{2A^2 \Delta P_F}(V + V_0) + \frac{R_m . \mu}{A . \Delta P_F} \qquad (5.1)$$

where t is the time (s), V is the volume of filtrate (m^3), V_0 is the volume of filtrate recuperated after establishment of the stabilized filtration process (at t_0 = 180 s), α is the specific resistance of the filter cake (m/kg), μ is the liquid viscosity ($\mu = 10^{-3}$ Pa.s), C_0 is the concentration of the feed solution (C_0 = 50 kg/m^3), A is the total filtration area ($A = 4.92*10^{-5}$ m^2), ΔP_F is the pressure during filtration ($\Delta P_F = 4*10^5$ Pa), and R_m is the membrane resistance (m^{-1}).

2.3 Cake dryness

The dryness of the studied filter cakes was measured by drying the cake in an oven for 24 h at 105 ˚C. The washed cakes were cut into three circular cross sections (with the same cross sectional area of the cake), each section had an equal thickness that was equivalent to the total thickness of the cake divided by 3. The dryness of each cake section was determined separately based on Equation (5.2).

$$d = \frac{m_d}{m_w} \times 100 \tag{5.2}$$

where d is the cake section's dryness (%), m_w is the mass of the wet cake section (g) and m_d is the mass of the dry cake section (g).

2.4 Kinetic modeling

Washing and electrowashing kinetics can be modeled using Equation (5.3) [44], similarly to the electrofiltration kinetics:

$$\frac{\mathrm{d}v_w}{\mathrm{d}t} = \frac{\Delta p_W}{\mu(\alpha W + 2R_m)} + P_{eo} i \tag{5.3}$$

where v_w is the volume of wash liquor per unit of filter area (m^3/m^2), P_{EO} is the electroosmotic transfer through the cake (m^3/C), and i is the electric current density (A/m^2).

2.5 Energy consumption

The change in voltage was recorded and used to calculate the energy consumption based on Equation (5.4):

$$E = \frac{1}{V_l} \sum_{\mathrm{j}=1}^{\mathrm{z}} \frac{I_j * U_j * \Delta t}{3600} \tag{5.4}$$

where E is the electric energy (kWh/ kg wash liquor removed), V_l is the volume of wash liquor removed (L), z is the number of measures, I_j is the electric current intensity at each measurement (A), U_j is the voltage at each point j (V), Δt is the time interval between subsequent measurements (s).

2.6 Ionic compounds and pH

The extraction of ionic compounds during the washing process was monitored by measuring the electric conductivity of the wash liquor, using a multi-parameter analyzer with a conductivity electrode (Consort C5010, Belgium). The conductivity was measured at 23 °C for all the samples.

The pH of each sample of wash liquor was measured using a multi-parameter analyzer (Consort C5010, Belgium) with a pH electrode at 23 °C.

2.7 Pigment and protein characterization

2 mL of the samples to be tested were centrifuged using a miniSpin plus Centrifuge (Eppendorf, Germany) at 13500 rpm for 10 min and the supernatants were collected. The absorbances of the samples were measured using a spectrophotometer (Biochrom Libra S32, Biochrom Ltd, UK).

The phycobiliprotein content was determined by applying an adjusted version of the formulas developed by Bennett and Bogorad [45], as shown in Equations (5.5) and (5.6) :

$$C_{C-PC} = [A_{620} - (0.474 \cdot A_{652})]/5.34 \quad (5.5)$$

$$C_{APC} = [A_{652} - (0.208 \cdot A_{620})]/5.09 \quad (5.6)$$

where C_{C-PC} is the C-phycocyanin concentration (mg/mL), C_{APC} is the Allophycocyanin concentration (mg/mL), A_{620} and A_{652} are, respectively, the absorbances of the sample at 620 and 652 nm. The concentrations were then converted in mg/ g dry *A. platensis* (hereby referred to as mg/ g d.m.).

The protein content of the samples was determined using Bradford's method [46]: 100 µL of supernatant was vortexed with 1 mL of Bradford dye reagent (Alfa Aesar, Thermo Fisher Scientific, Germany). The mixture was incubated for 10 minutes in the dark at room temperature, then the absorbance was measured at 595 nm (Biochrom Libra S32, Biochrom Ltd, UK). The blank consisted of 100 µL of deionized water mixed with 1 mL of Bradford dye reagent. The calibration curve was obtained using bovine serum albumin (BSA) as a standard and the results were expressed in mg BSA equivalent/ g dry *A. platensis* (hereby referred to as mg BSA equivalent/ g d.m.).

2.8 Statistical analysis

Experiments were at least tested in triplicates. Data are expressed as mean ± standard deviations. The error bars on the figures correspond to the standard deviations. Standard deviations below 0.1 were considered to be negligeable and do not appear on the graphs.

3 Results and discussion

3.1 Filtration stage and filter cake properties

Filtration behavior corresponded to the cake filtration law yielding a straight line for a segment of the curve $\frac{t-t_0}{V-V_0}$ vs $(V + V_0)$ (Figure 5.2). The average specific cake resistance (α) was calculated based on Equation 5.1, according to the slope obtained for this straight line, $\alpha = (4.27 \pm 0.1).10^{14}$ m/kg. At the end of the filtration experiment a total filtrate volume of (159 ± 19.7) mL was recovered, and the cake had a dryness of (17.9 ± 0.13) %. The cake completely filled the cell, having a thickness of 2 cm and a diameter of 5.6 cm, without any visible cracks or fissures on the surface.

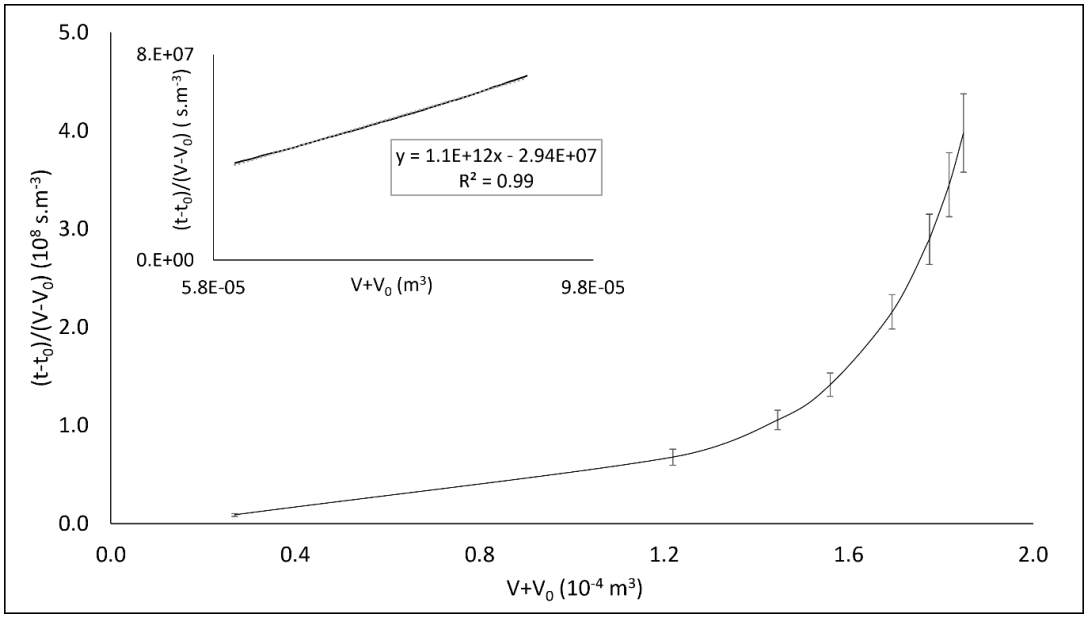

Figure 5.2. Filtration curve for the total volume of filtrate based on the Ruth formula

3.2 Washing and electrowashing kinetics

Since the *A. platensis* cells have a negative zeta potential, electroosmotic flow through the cake occurred from the positively charged anode towards the negatively charged cathode, as predicted. This has also been demonstrated in many other studies on electrically assisted dewatering [47–49].

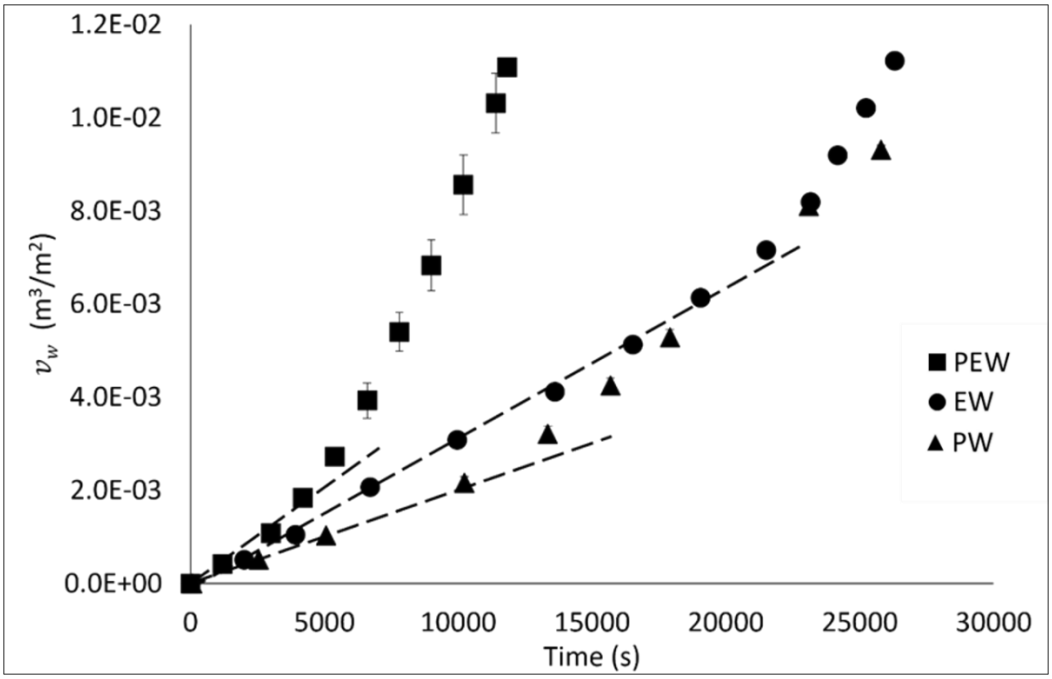

Figure 5.3. Washing kinetics

Figure 5.3 shows washing kinetics during PEW, EW, and PW processes. Dashed lines approximate the initial part of the washing curves when washing occurred under a constant flow rate $\frac{\mathrm{d}v_w}{\mathrm{d}t}$ according to Equation (5.3). The time required to recover 55 ml of wash liquor (v_w = 0.011 m^3/m^2) was the shortest for PEW, taking 187 minutes on average. EW was found to be the second most time-consuming method, taking about 439 minutes to yield 55 mL of wash liquor. Whereas PW was the most time-consuming method, taking 431 minutes to yield only 45 ml of wash liquor (v_w = 0.009 m^3/m^2). The slow flow rate during PW is explained by the very high specific resistance of the cake formed by the microalgae *Arthrospira platensis* ($\alpha = 4.27.10^{14}$ m/kg). EW and especially PEW are capable of increasing the washing rate. Electroosmotic phenomenon is the main factor that enhanced the washing rate. Equation (5.3) quantitatively explains this phenomenon. For the PW process, the second term in Equation (5.3) is absent and the estimated initial washing flow rate $\frac{\mathrm{d}v_{pw}}{\mathrm{d}t} = 4.93 \cdot 10^{-7}\ \frac{m^3}{m^2 s}$ mainly depends on the washing pressure Δp_W and the filter cake characteristics. For the EW process, the first term in Equation (5.3) is absent and the initial washing flow rate $\frac{\mathrm{d}v_{ew}}{\mathrm{d}t} = 6.24 \cdot 10^{-7}\ \frac{m^3}{m^2 s}$ depends on the electric current density i. For the PEW process, the total washing flow rate $\frac{\mathrm{d}v_{pew}}{\mathrm{d}t} = 8.15 \cdot 10^{-7}\ \frac{m^3}{m^2 s}$ depends on both the first and second terms of Equation (5.3). After the initial period of constant washing velocity, a more rapid increase of the washing rate occurs (Figure 5.3). This may be explained by structural modifications of the filter cake during the washing process. In addition, the liquor's viscosity decreases during the EW and PEW operations, due to the observed temperature increase over time. This also contributes to the enhancement of the washing rate. Electroosmotic transfer through the filter cake can be estimated from Equation (5.3) under EW conditions, $\frac{\mathrm{d}v_{ew}}{\mathrm{d}t} = P_{EO} i$. Then $P_{EO} = 1.03 \cdot 10^{-8}\ m^3/C$. Unfortunately, simple summarization of PW and EW flow rates does not permit the calculation of PEW flow rate, which probably depends on other factors that lead to the modification of the wash liquor and cake characteristics.

3.3 Characteristics of wash liquors and washed filter cakes

The pH of the wash liquor is presented in Figure 5.4. It is rather close to the neutral values for the PW. However, it is heavily alkaline (about 12) for the EW and changes from heavily to moderately alkaline (about 10) for the PEW.

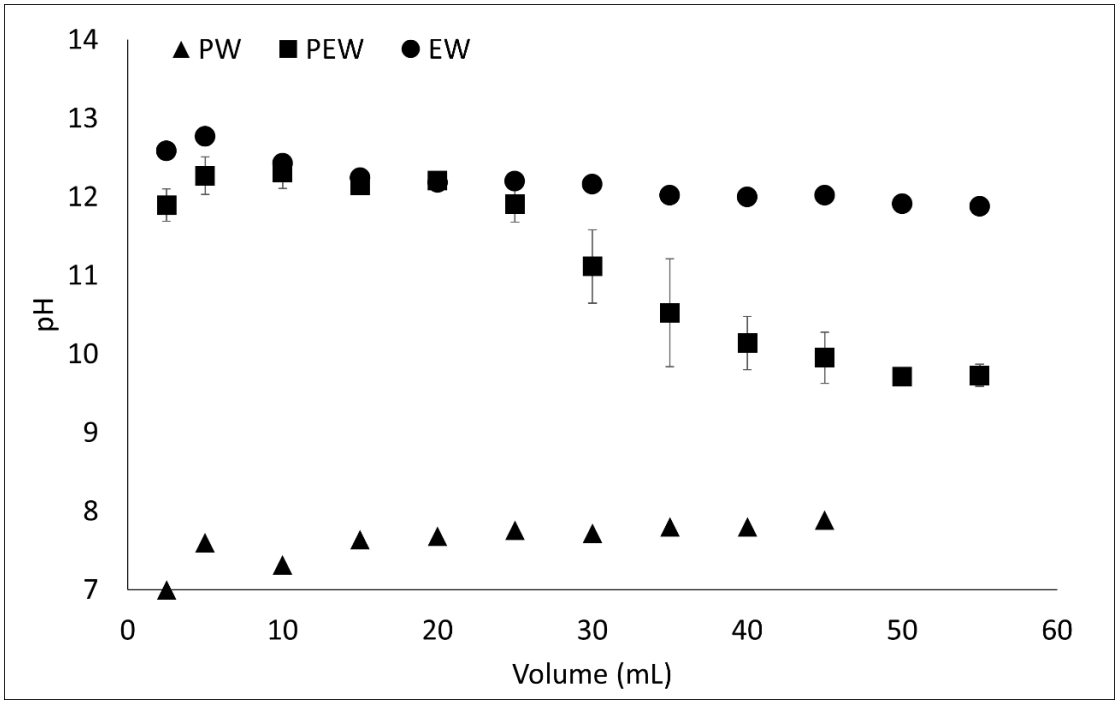

Figure 5.4. pH of the wash liquor in function of the volume recovered

It was reported in literature the heavily alkaline pH values of the filtrates obtained from the cathode during electrically assisted filtration and dewatering [34,50]. This is mainly due to the electrochemical reactions, i.e. water electrolysis, that take place during the process.

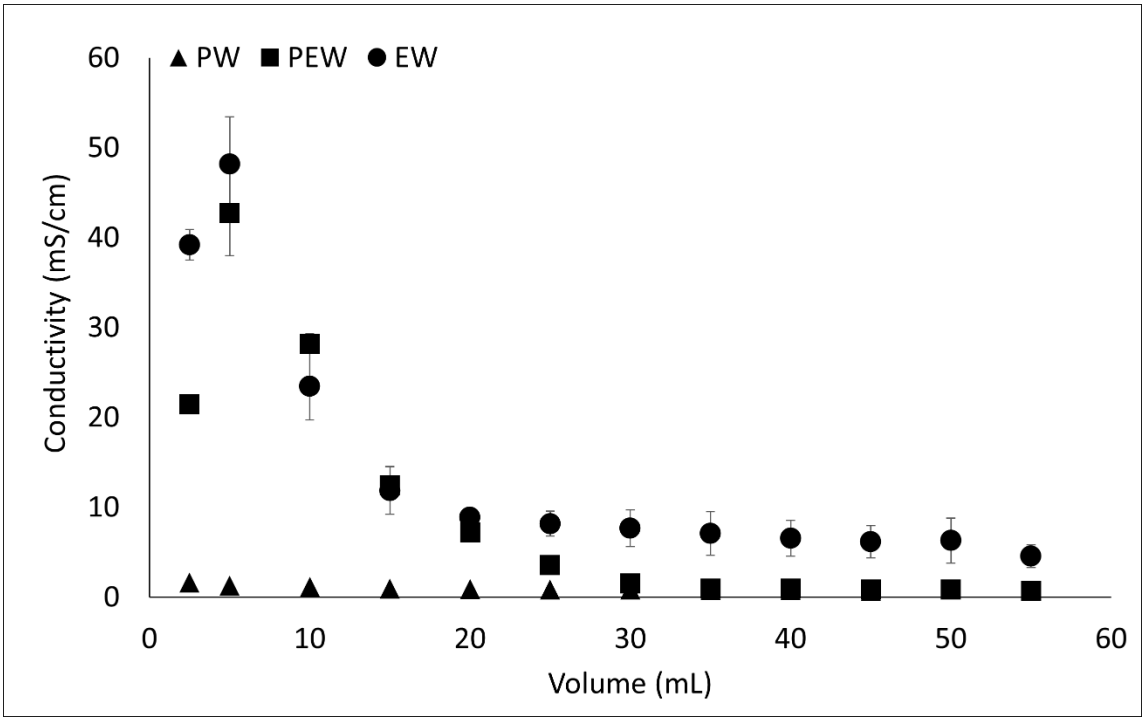

Figure 5.5. Electrical conductivity of the wash liquor in function of the volume recovered

Figure 5.5 presents the electrical conductivity of the wash liquor. The electrical conductivity of the wash liquor was equal to that of tap water, (Ϭ = 0.6 mS/cm) for PW, whereas the electrical conductivity of the liquor obtained at the beginning of EW and PEW exhibited a sharp increase (reaching up to 40 – 50 mS/cm). Over time, the electrical conductivity of the wash liquor was found to have a decreasing tendency, this is probably due to the evacuation of the electrolysis products. The decrease in the electrical conductivity was especially noteworthy during PEW, demonstrating the better efficiency of washing.

Figure 5.6 shows the temperature of the wash liquor for the EW and PEW processes. The increase of the liquors' temperatures is related to the ohmic heating phenomenon, and it is more important during the EW process. The higher temperature observed during EW can be partly responsible for the higher electrical conductivity values of the wash liquor when compared to PW and PEW. The temperature during PW remained constant throughout the washing process (approximately 23 ˚C) which was also the room temperature. The temperature during PEW and EW respectively reached (42.5 ± 0.1) ˚C and (63.4 ± 0.1) ˚C by the end of the washing process.

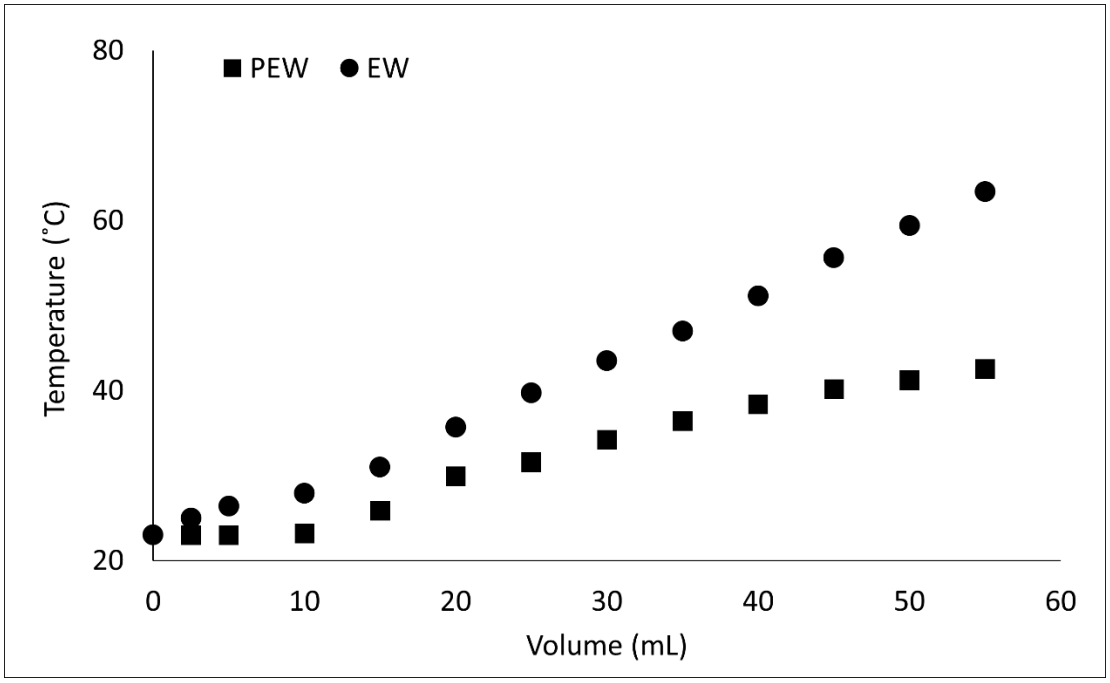

Figure 5.6. Temperature of the wash liquor in function of the volume recovered

Figure 5.7 shows the photos of the feed solution (A), and wash liquors obtained during PW (B), PEW (C) and EW (D). The same figure shows the photos of the filter cakes obtained during PW (E), PEW (F) and EW (G). The appearance of the wash liquors and the washed filter cakes was modified by the application of an electric field. The blue color of the supernatant recovered from the feed solution (Figure 5.7 A) and the first liquor samples (Figure 5.7 B) obtained by PW indicates the presence of pigments, such as phycobiliprotein, C-phycocyanin and others, which is typical for the microalgae *Arthrospira platensis* [51–54]. These pigments are progressively washed away when the liquid solution trapped in the cake's pores is replaced by water, which in turn led

to the gradual discoloration of the wash liquor over time (Figure 5.7 B). On the contrary, the blue color is absent in wash liquors obtained by PEW and EW. The yellow and transparent hues of these wash liquors can be a consequence of the electrolysis reactions [55].

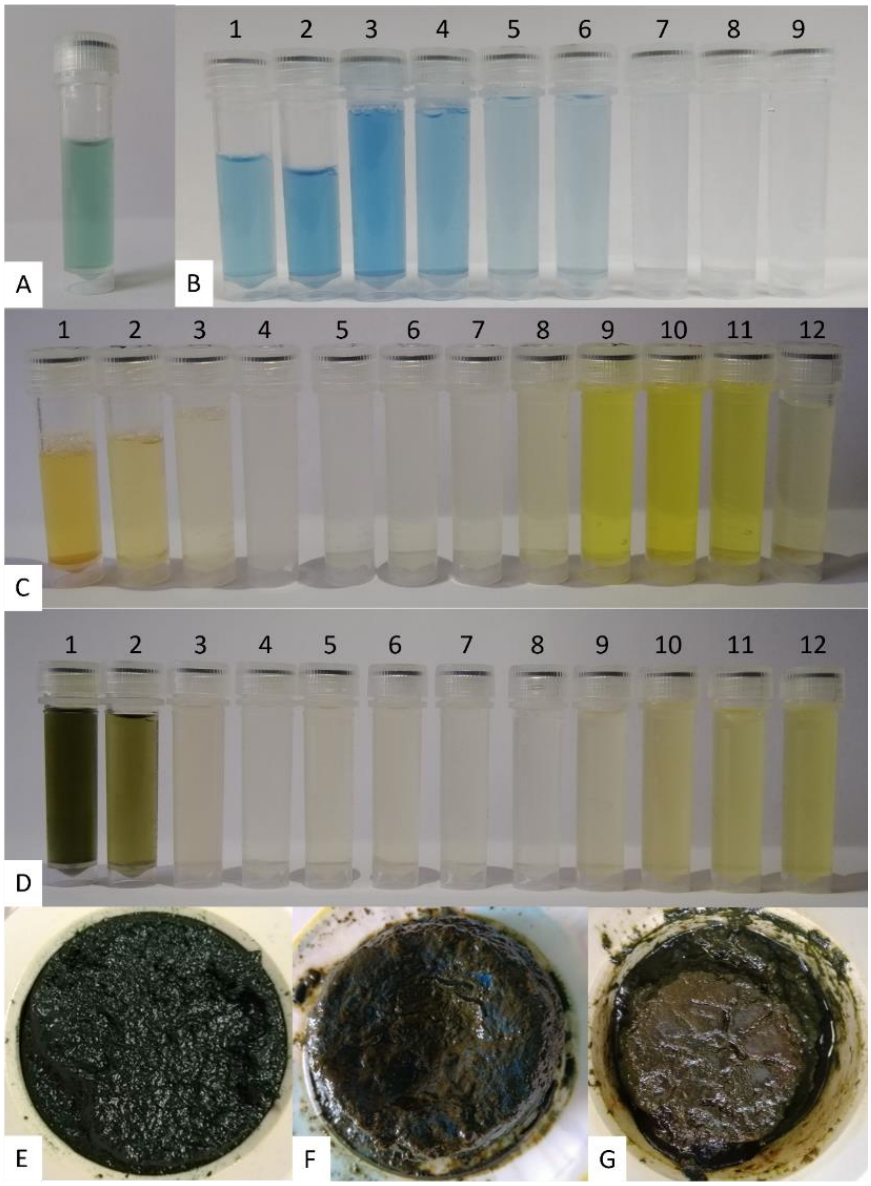

Figure 5.7. Photos of: feed solution (A); wash liquors obtained during PW (B), PEW (C), and EW (D); and filter cakes obtained during PW (E), PEW (F), and EW (G)

PW exhibited an even distribution of dryness throughout the 3 cake sections (18.2 ± 0.27) %, which was nearly the same as the dryness of the filter cake before washing (17.9 ± 0.13) %. However, PEW and EW yielded a considerably better dehydrated filter cake with a dissimilar dryness distribution. For instance, the cake dryness after PEW was (42.4 ± 0.2) % for the section on the anode side, (60.5 ± 0.15) % for the middle section, and (39 ± 0.34) % for the section on the cathode side. After EW, the cake dryness was (29.6 ± 0.08) % at the anode side, (38.2 ± 0.1) % in

the middle, and (25.9 ± 0.27) % at the cathode side. Non uniform cake dryness has been reported after electroosmotic dewatering with a higher dryness near the anode. This was explained by the liquid outflow from the anode towards the cathode and by the worse contact between the anode and the filter cake, leading to a higher temperature increase near the anode [56–58]. The increase in cake dryness has not been described in previous cake washing studies, however, changes in the cake porosity have been reported. Kilchherr *et al.* [29] studied the porosity of a filter cake during electrowashing at a constant electric current of 20 V and found that the porosity decreased from an initial value of 0.57 to 0.47 after washing the cake for 1000 s. Similarly, Tarleton *et al*. [38] reported a decrease in cake porosity with the increase in electrowashing time. Figures 5.7 F and 5.7 G show that the filter cake had somewhat shrunk after PEW and especially after the EW operation, which explains the cakes' higher dryness, when compared to PW (Figure 5.7 E). This phenomenon was accompanied by several shrinkage cracks on the cake surface, which usually leads to a less successful cake washing procedure because the washing solution would preferentially flow through the cracks [59,60]. Regardless of the cake washing performance, the significant increase in the dryness of the electrically washed filter cakes is an interesting result, which may lead to lower energy requirements for the subsequent thermal drying of the microalgae filter cake, hence allowing an overall decrease in the energy consumption for the concentration of *A. platensis*. Studying the use of mechanical dewatering combined with electrowashing may prevent the formation of cracks within the cake during washing. The additional mechanical pressure can potentially help form a well consolidated cake with a better washing capacity.

Figure 5.8 presents the cumulative content of CPC, APC, and proteins extracted by PW, PEW, and EW processes. Around 10 times more CPC was extracted by PW (0.21 mg/g d.m.) compared to PEW (0.024 mg/g d.m.) and EW (0.025 mg/g d.m.). The amount of APC extracted by PW (0.08 mg/ g d.m.) was around 4 times larger than that extracted by PEW (0.024 mg/g d.m.) and EW (0.025 mg/g d.m). Conversely, the highest concentration of proteins was extracted by PEW (14.6 ± 0.16 mg BSA equivalent/g d.m.), the lowest was extracted by EW (6.16 ± 0.59 mg BSA equivalent/g d.m.) compared to (9.4 ± 0.21) mg BSA equivalent/g d.m. that was extracted by PW.

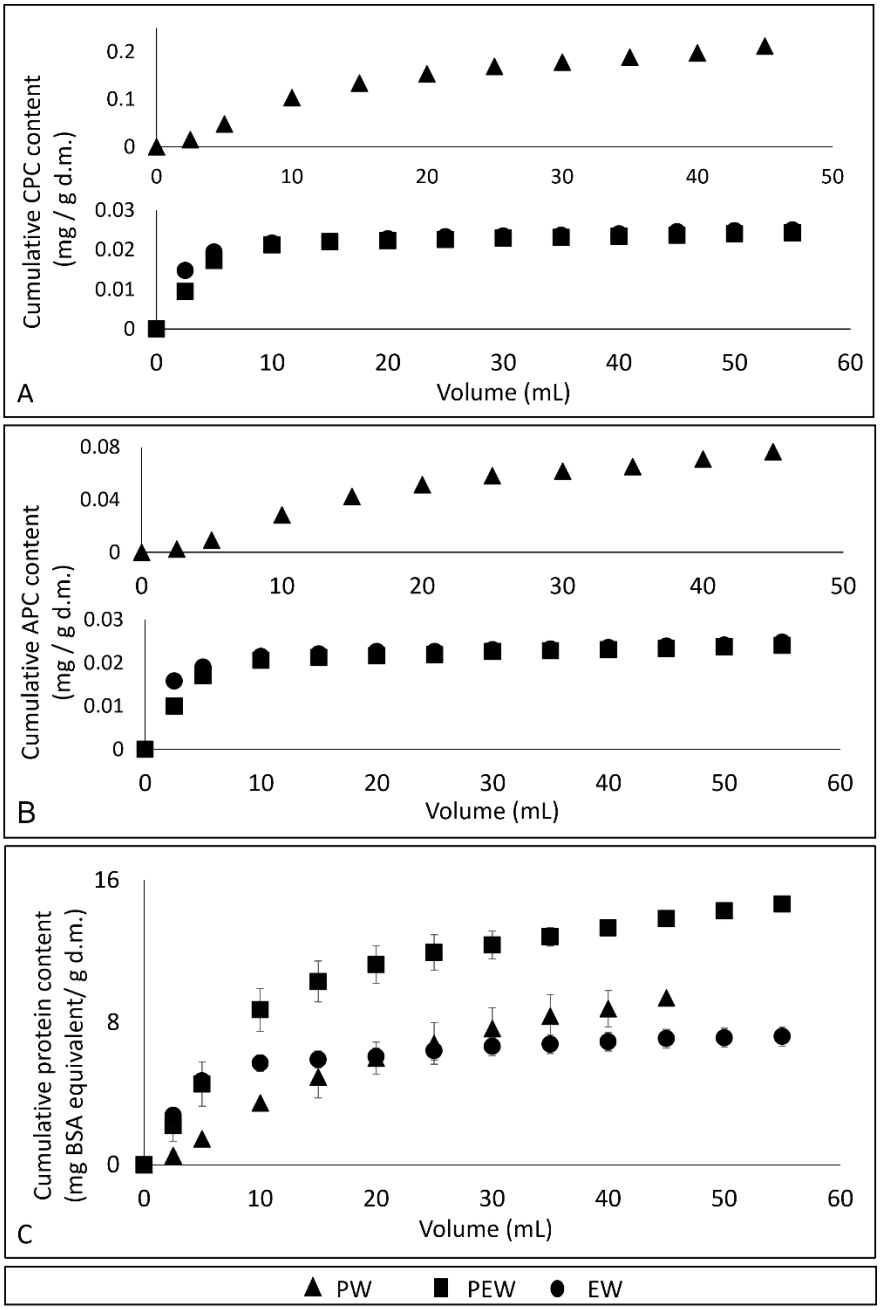

Figure 5.8. Cumulative content of CPC (A), APC (B), and proteins (C) in the wash liquor

Applying an electric field during the washing procedure led to a decrease in the quantities of APC and CPC extracted respectively by a factor of 3.3 and 0.024 for PEW and a factor of 3.2 and 8.4 for EW. This corroborates with the absence of blue color in the wash liquors obtained by PEW and EW, which can be explained by the electrode reactions that occur during electrowashing. The observed results for the pigments and proteins could be explained by the pH and temperature values that were discussed earlier; as studies have shown that APC and CPC are pH and temperature sensitive, and that pH values outside the range of 2.5 to 6 can lead to their denaturation [61–63]. Another factor that was found to influence the stability of APC and CPC is their

interaction with proteins present in the medium [61,62]. However, electrowashing by PEW was able to increase the amount of protein extracted by a factor of 1.55 compared to PW, EW resulted in the extraction of 1.53 times less protein than PW. Many factors could be responsible for this observed difference, such as the concentration of ionic compounds present in the liquor and the extent of the temperature increase recorded during the electrowashing processes [64,65].

3.4 Energy consumption

The increase in the energy consumption was less significant for PEW compared to EW (Figure 5.9). In order to recover 55 mL of wash liquor, PEW and EW respectively consumed 0.36 and 1.25 kWh/ kg wash liquor removed.

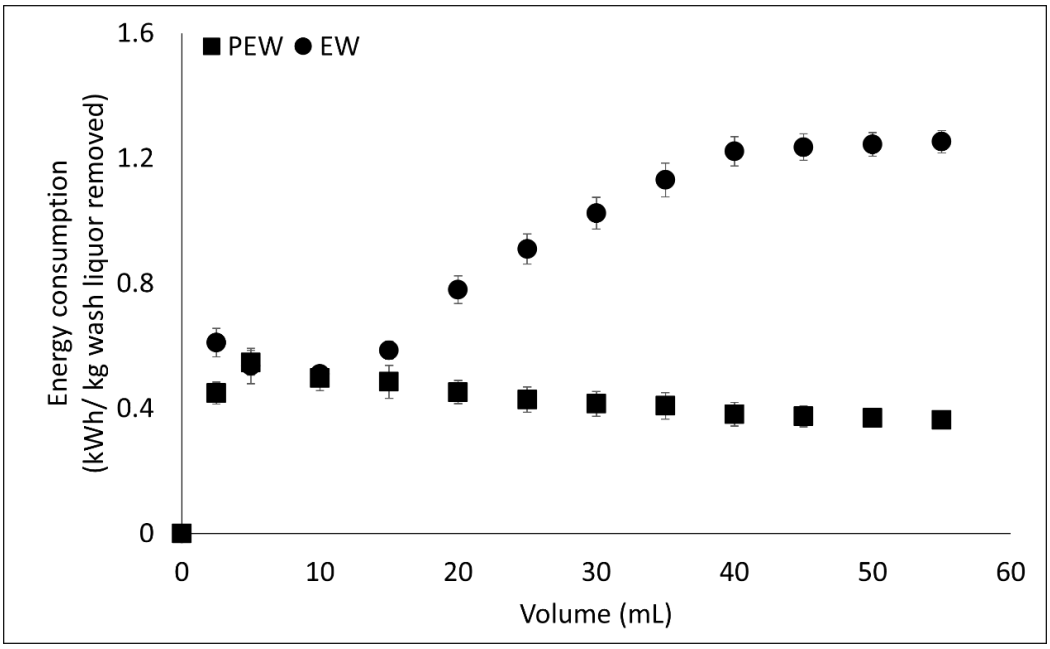

Figure 5.9. Energy consumption in function of the volume of wash liquor collected during PEW and EW

One must also take into account the added energy consumption of EW associated with the use of a peristaltic pump for the washing solution recirculation. Generally, the PEW process is less energy consuming than it was reported for electroosmotic mechanical dewatering [47,56,66,67].

4 Concluding Remarks

Washing and electrowashing were found to be promising methods to further extract microalgal biocompounds that are present in a formed microalgal filter cake. The application of an electric field was able to enhance the washing kinetics with the added benefit of using lower operating pressures. PEW seemed to be more promising than EW, especially in terms of energy consumption

and the recovery of proteins. PW was more effective for the extraction of CPC and APC which are temperature and pH sensitive pigments.

The process still needs to be improved and presents many aspects that should be explored for future work. Extraction yields of microalgae bio-compounds could be enhanced by optimizing the washing process. To minimize the negative effects of electrode reactions during electrowashing, the addition of chemical agents to the washing solution should be tested. Electric field strength and washing pressure can be optimized. The effect of the temperature and pH changes on the cake structure and functionality of the extracted bioactive compounds should be assessed for future work.

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Disclosure statement

The authors report there are no competing interests to declare.

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5.3 Conclusion

Cake washing was able to extract bioactive compounds trapped in the formed filter cake and electrowashing was able to enhance the filtration kinetics. Similarly to what was reported in Chapter 4, the pH changes caused by the application of an electric field deteriorated the bioactive compounds of interest. The use of buffer agents or other pH stabilizing methods should be explored in order to successfully recover bioactive compounds from the formed cake without compromising their quality. Moreover, the use of electrowashing also increased the cake dryness, thus serving as an additional dewatering technique.

Chapter 6: Optimizing the dewatering of Chlorella vulgaris by dead-end filtration and electrofiltration

6.1 Introduction

The use of electrofiltration for the concentration of *A. platensis* and the extraction of biocompounds was found to be promising in the previous chapters of this thesis especially when taking into account the filtration kinetics and energy consumption of the studied processes. Despite electrofiltration's ability to increase the cake dryness of *A. platensis* when compared to dead-end filtration without an electric field (F), the quality of the cake and filtrate was found to be degraded. This showed the need to perform more studies to improve the use of electrofiltration in terms of maintaining good filtration kinetics as well as improving the quality of the biocompounds present in both the filtrate and cake. Different methods have been suggested for the improvement of the electrofiltration process and the regulation of the pH of the filtrate streams, such as, the use of a recirculation unit for anode flushing [1–3], the recirculation of a cooled solution containing activated carbon that was mixed with the filtrate [4], and the shape of the membrane channels [5,6] to name a few.

This chapter explores the use of filtration and electrofiltration for the dewatering of a *C. vulgaris* suspension to verify that electrofiltration can improve the filtration kinetics for microalgae with different structures. Another aim of this chapter is to assess the effect of using a recirculation unit as a way to stabilize the pH of the filtrate streams. This was achieved by studying the overall filtration kinetics, cake properties (compressibility, specific cake resistance, dryness).

The data presented in this chapter has been accepted in the "18ème Congrès de la Société Française de Génie des Procédés" as an oral presentation (November 2022) accompanied by the opportunity to publish the conference proceedings as a peer reviewed article. The materials and methods used in this chapter can be found in Chapter 2.

6.2 Results and discussion

6.2.1 Effect of pressure and electric current density without recirculation

This section discusses all the results obtained without the use of a recirculation unit during the electrofiltration process.

6.2.1.1 Filtration kinetics

During filtration (F) and electrofiltration (EF) at 60 A/m^2 the effect of the hydraulic pressure on the filtration rate is shown in Figure 6.1.

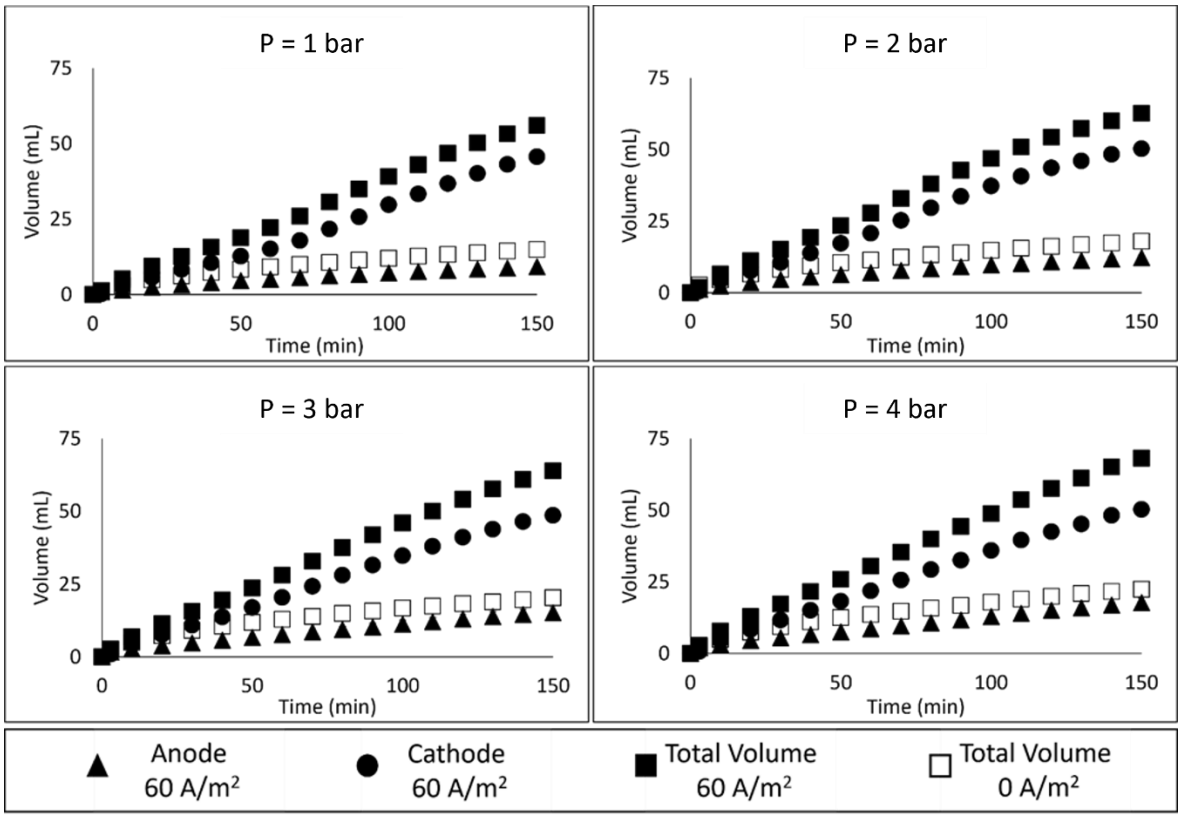


Figure 6.1. Filtration kinetics reported for different pressures for filtration (F) and electrofiltration (EF) at i = 60 A/m^2

For filtration (F), the total volume of filtrate recorded after 150 minutes of filtration was 15 ± 0.49 mL for a pressure of 1 bar and the total volume of filtrate was 22.4 ± 1.18 mL for a pressure of 4 bar (Figure 6.1). By increasing the pressure by 4 folds, the total volume of filtrate increased by 49.6% for *C. vulgaris*. Compared to the results that were reported with in Chapter 3, the increase in pressure from 1 to 4 bar was able to increase the total volume of filtrate by 9.8% for *A. platensis*, this shows that during filtration without an electric field, the pressure has a higher influence on the filtration kinetics with *C. vulgaris* than it does with *A. platensis.*

The effect of the pressure on the filtration kinetics can be justified by the microalgae cake's compressibility. The specific cake resistance α was calculated using the data from F and according to the transformed Ruth-Carman equation [7] as explained in Chapter 2. The values of the specific cake resistance α are presented in Table 6.1 for different pressures from 1 to 4 bar. These values increase with the increase in pressure, which shows that the cake is compressible.

Table 6.1. Specific resistance of filter cakes at different pressures for filtration (F)

Δp (bar)	α (m/kg)
1	1.09E+15
2	1.53E+15
3	1.87E+15
4	2.18E+15

The compressibility index *s* determined graphically by plotting ln (α) vs ln ($\Delta p/\Delta p_0$) is presented in Figure 6.2. When the value of $s > 0$ the filter cake is compressible, and if $s = 0.5$ the cake is moderately compressible [7,8]. Based on Figure 6.2, the obtained *C. vulgaris* filter cake is compressible with a compressibility index of 0.538. A similar compressibility index (0.439) has been reported in literature for *C. vulgaris*, where Babel and Takizawa [9] suggested that during the filtration process, water flows in between cells through a matrix of EOM that is being further compressed with an increase in pressure. Compared to the specific cake resistance reported for *A. platensis* at different pressures (Table 3.1, Chapter 3), *C. vulgaris* was found to have a higher cake resistance, but a lower cake compressibility (the *A. platensis* cake is highly compressible with s = 1.28). The difference in both the cake compressibility and the specific cake resistance for *A. platensis* and *C. vulgaris* further explains the observed differences in the filtration kinetics. The differences in the filtration behavior can be attributed to the differences in the physical properties of the two types of microalgae as shown in Chapter 2.

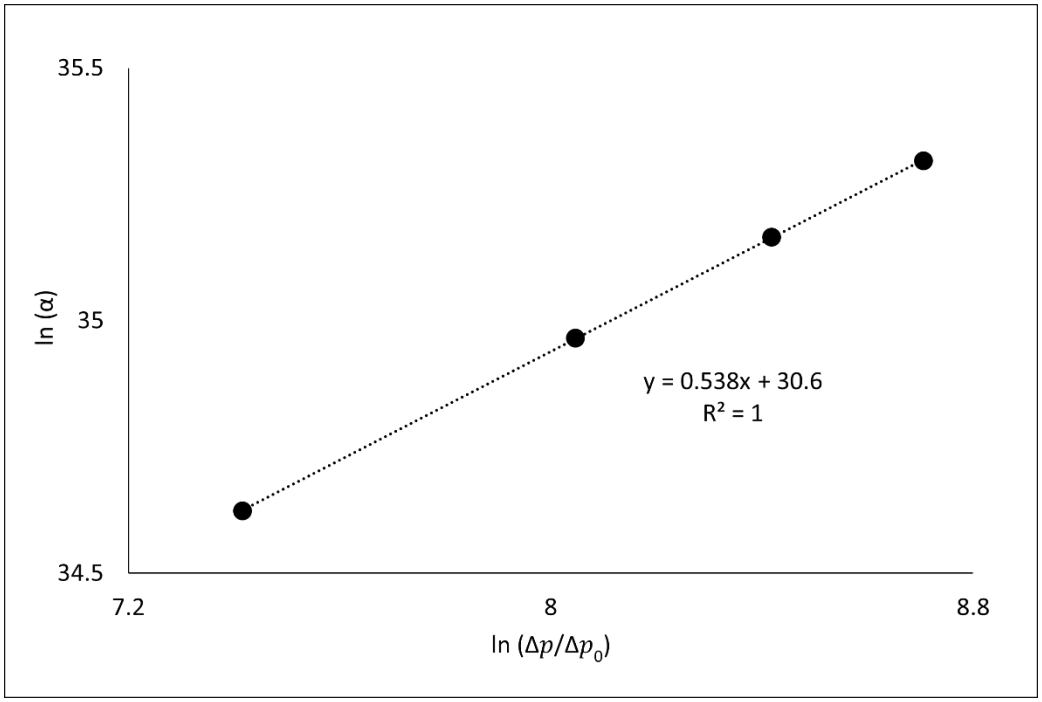


Figure 6.2. Dependence of ln *(α)* vs ln *($\Delta p/\Delta p_0$)* for determination of the cake compressibility index

For electrofiltration (EF), after 150 minutes, the total volume of filtrate increased by 17.7% with the increase in pressure from 1 bar (56.1 ± 0.27 mL) to 4 bar (68.1 ± 2.38 mL). Different volumes of filtrate were recuperated on the anode and cathode side for each pressure. On the anode side the final volume of filtrate was 9.21 ± 0.31 mL and 17.81 ± 1.53 mL respectively for a pressure of 1 and 4 bar. Whereas, on the cathode side, the final volume of filtrate for 1 and 4 bar respectively, was 45.7 ± 1.15 mL and 50.3 ± 2.76 mL. In other words, a larger portion of filtrate was obtained on the cathode side than the anode side. For example, during EF at 60 A/m^2 and 1 bar, approximately 81.5% of the filtrate was obtained on the cathode side.

Hence, the application of an electric current density of 60 A/m^2 was able to increase the filtration rate and the preferential path of filtrate flow was from the cathode side which is in accordance with the findings reported in literature [1,4,10–13]. These findings are similar to those reported in Chapter 3 with *A. platensis* and are also attributed to the electrophoretic movement of the negatively charged algal cells towards the anode, which is also in the same direction of the electroosmotic and hydraulic flows.

On the contrary, the flow rate of filtrate from the anode side should decrease due to the electrophoretic movement of the negative particles towards the positively charged anode, which is in the opposite direction of the electroosmotic and hydraulic flows. In other words, based on the concept of electrophoresis that takes place on the anode side of the filtration cell during electrofiltration processes, the algal cake gradually becomes thicker on the anode side due to the accumulation of negatively charged particles in the direction of the positively charged anode. This typically leads to the restriction of the flow of liquid towards the anode, eventually leading to the accumulation of less filtrate on the anode side when compared to F [1–3,10,14,15].

In this study, the majority of the filtrate was collected on the cathode side, this is in accordance with the findings reported in literature [1,4,10–13]. However, the volume of filtrate recuperated on the anode side by EF at 60 A/m^2 was found to be equal to or slightly higher than the volume of filtrate obtained on one side of the filtration cell by F, which is equivalent to half the total volume obtained by F (Table 6.2). This is not in line with the findings reported in both Chapter 3 and in literature [1,4,11,12], which indicate a decrease in the EF kinetics on the anode side when compared to F.

Table 6.2. Volume of filtrate for F and EF (at 60 A/m^2) after 150 min of filtration at different pressures

Pressure (bar)	Volume after EF (mL)		Half of the total volume after F (mL)
	Anode	Cathode	
1	9.21 ± 0.31	45.66 ± 1.15	7.47 ± 0.24
2	12.29 ± 0.91	50.26 ± 0.78	8.95 ± 0.33
3	15.22 ± 1.91	48.68 ± 1.2	10.13 ± 0.16
4	17.81 ± 1.53	50.32 ± 2.76	11.18 ± 0.59

Different factors may be responsible for such an anomalously increase in the filtrate quantity from the anode side. For instance, the structure of the filter cake formed during EF on the anode side of the filter chamber may be more friable and porous than that of the filter cake formed by F. These results need to be investigated in future work.

6.2.1.2 Filtrate and filter cake properties

Similarly to the findings reported in Chapter 3, the pH of the filtrates after F were found to be neutral (7.81 ± 0.02), and EF led to an alkaline pH on the cathode and an acidic pH on the anode. The conductivity of the filtrate after F for 150 min was (3.12 ± 0.06) mS/cm, whereas after 150 min of EF, the conductivity increased on both the anode and cathode sides and the value reported for the anode side was lower than that reported on the cathode side. This increasing trend in the conductivity was also reported in Chapter 3. For example, after EF for 150 min at a pressure of 1 bar, the conductivity on the anode side was (6.16 ± 0.26) mS/cm and the conductivity on the cathode side was (13.1 ± 0.6) mS/cm.

The cake dryness increased with the increase in pressure for the simple filtration and electrofiltration experiments (Figure 6.3). For each studied pressure, after 150 minutes, EF at 60 A/m^2 was able to double the cake dryness when compared to F.

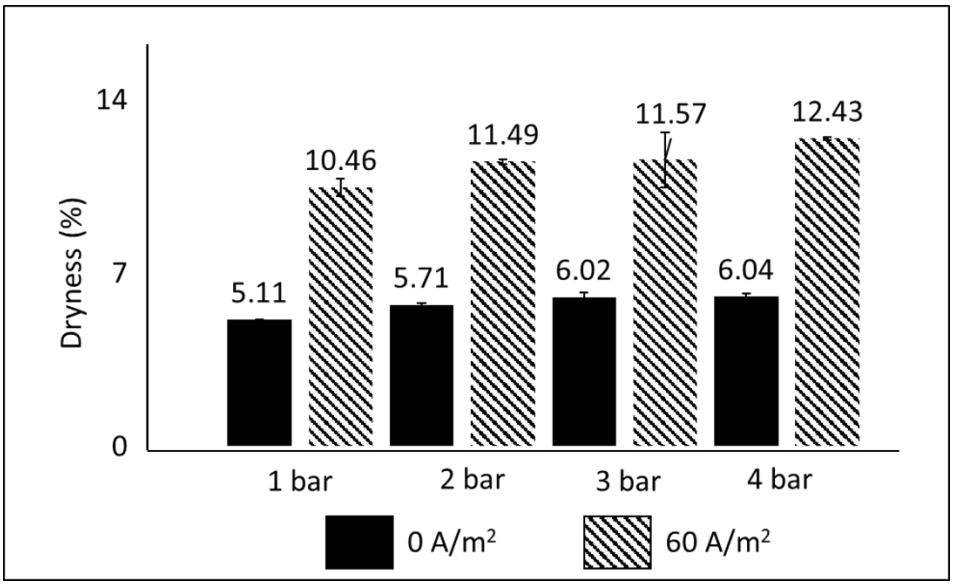


Figure 6.3. Effect of pressure and electric field on cake dryness

Under the same experimental conditions, the cake dryness reported in Chapter 3 for *A. platensis* was much higher than that observed for *C. vulgaris*. This is due to the difference in the cake properties (specific resistance and cake compressibility) between *A. platensis* and *C. vulgaris*, as mentioned earlier in this chapter.

6.2.1.3 Ohmic heating and energy consumption

EF caused ohmic heating in the filtration cell which increased the temperature near the electrodes, as observed by the temperature measurements made using flexible K-type thermocouples (Figures 6.4 A and 6.4 B).

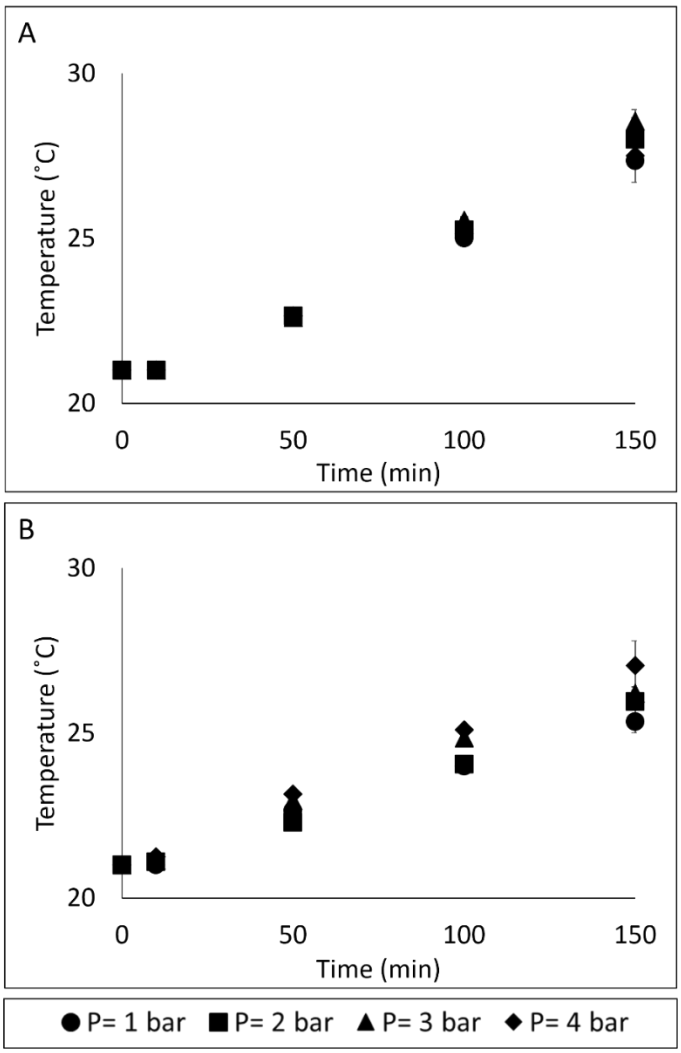


Figure 6.4. Increase of temperature over time during EF at 60 A/m^2 for 150 min at different pressures. Anode (A) and Cathode (B)

On the anode side (Figure 6.4 A), the temperature reached values of 27.4, 28.0, 28.6, and 27.5 °C respectively for a pressure of 1, 2, 3, and 4 bar. On the cathode side (Figure 6.4 B), the onset of ohmic heating was less important reaching a temperature of 25.4, 25.9, 26.2, and 27.1 °C respectively for a pressure of 1, 2, 3, and 4 bar. Higher extents of ohmic heating have been reported on the anode side when compared to the cathode side during EF [4,11,12], this was also reported in Chapter 3. The onset of ohmic heating can be eliminated or drastically reduced by the use of electrode flushing which is explored later on in this chapter [1].

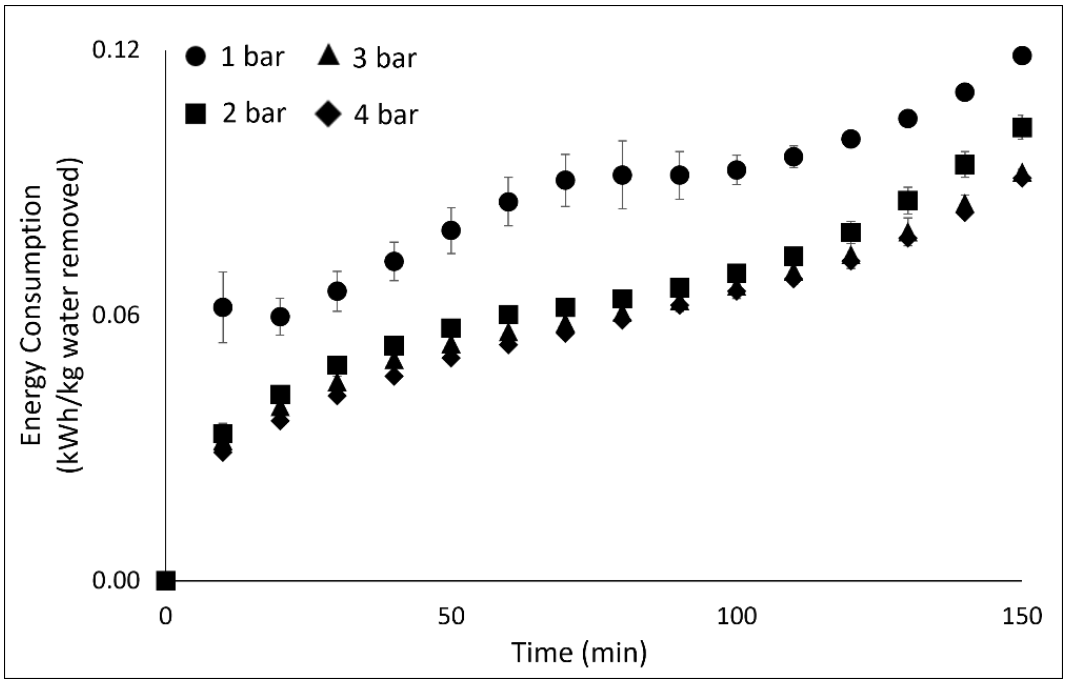


Figure 6.5. Specific energy consumption over time for EF at 60 A/m^2 and different pressures

Figure 6.5 presents the specific energy consumption during EF at 60 A/m^2 for a pressure of 1, 2, 3, and 4 bar. The specific energy consumption decreases with the increase of the operating pressure, due to the added effect of the hydraulic pressure, reaching values of 0.119, 0.103, 0.092 and 0.091 kWh/kg water removed respectively for a pressure of 1, 2, 3, and 4 bar after 150 min of EF. When comparing the energy consumption of EF at 60 A/m^2 and a pressure of 1 bar for *A. platensis* (0.067 kWh/kg water removed) with that of *C. vulgaris* (0.092 kWh/kg water removed), the latter consumed 1.37 times more energy than the former. Moreover, as mentioned earlier, a higher cake dryness was obtained for EF at 60 A/m^2 and a pressure of 1 bar for *A. platensis* (18.1 ± 0.16) % when compared with *C. vulgaris* (10.46 ± 0.37) %. These differences are related to the difference in the microalgae's properties, such as, their shape, size, and zeta potential, which in turn led to a difference in their filtration behavior, cake compressibility, and specific resistance of the filter cake.

Overall, when comparing EF of *C. vulgaris* with other drying techniques, EF is a less energy intensive option. For example, it has been reported that the specific energy required to dry *Chlorella sp.* by microwave drying was in the range of 26.2 to 34.9 kWh/kg water removed, whereas the use of a hot air drying technique consumed 51.7 to 55.1 kWh/ kg water removed [16].

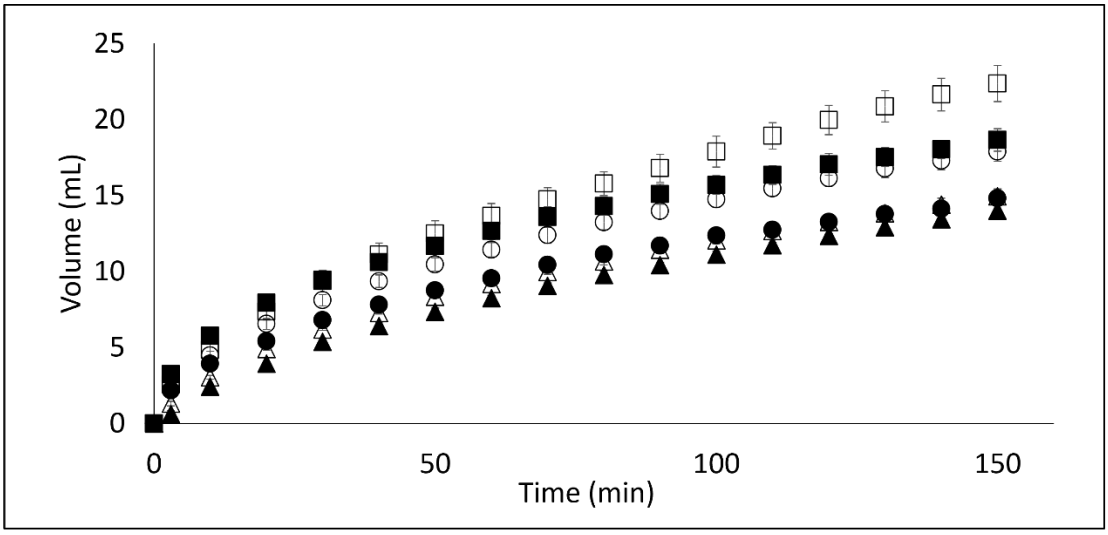
6.2.2 Effect of recirculation

The use of a recirculation unit during electrofiltration processes has been proven to be beneficial in multiple ways by controlling the increase of temperature caused by ohmic heating, flushing out salts and electrolysis products, extending electrode lifetime, and regulating the pH [1,4,10,11]. For

this reason, the effect of using different recirculation rates, of 20 and 160 mL/min, on the anode side was assessed, as illustrated in Figure 2.3 (Chapter 2). In this section, as stated in Chapter 2, the solution being recirculated consists of distilled water (207 mL) that is gradually being supplemented by the filtrate obtained from the anode side of the filter cell. The solution is then recirculated back into the filter chamber from the anode side of the filtration equipment.

6.2.2.1 Filtration kinetics

Figure 6.6 shows the filtration kinetics for the total filtrate volume obtained by F for 150 min with and without the use of a recirculation unit on the anode (for 0 and 20 mL/min). As previously discussed, increasing the filtration pressure helped increase the filtration kinetics. The use of recirculation on the anode (20 mL/min) did not have a large impact on the filtration kinetics at a pressure of 1 bar. However, the difference in the kinetics were more noticeable at the pressures of 2 and 4 bar, where in both cases, the use of recirculation on the anode side decreased the final filtrate volume by a factor of 1.2.



Pressure (bar)	1	2	4
Recirculation 0 mL/min	△	○	□
Recirculation 20 mL/min	▲	●	■

Figure 6.6. Filtration kinetics during F for recirculation on the anode at 0 mL/min and 20 mL/min

Figure 6.7 shows the filtration kinetics for EF of *C. vulgaris.* Recirculation at a rate of 20 mL/min barely affected the filtration kinetics regardless of the filtration pressure. The application of an electric field showed an increase in the volume collected; however, the most important difference was observed for P = 4 bar. Hence the analysis follows the same logic described in Section 6.2.1 in this chapter.

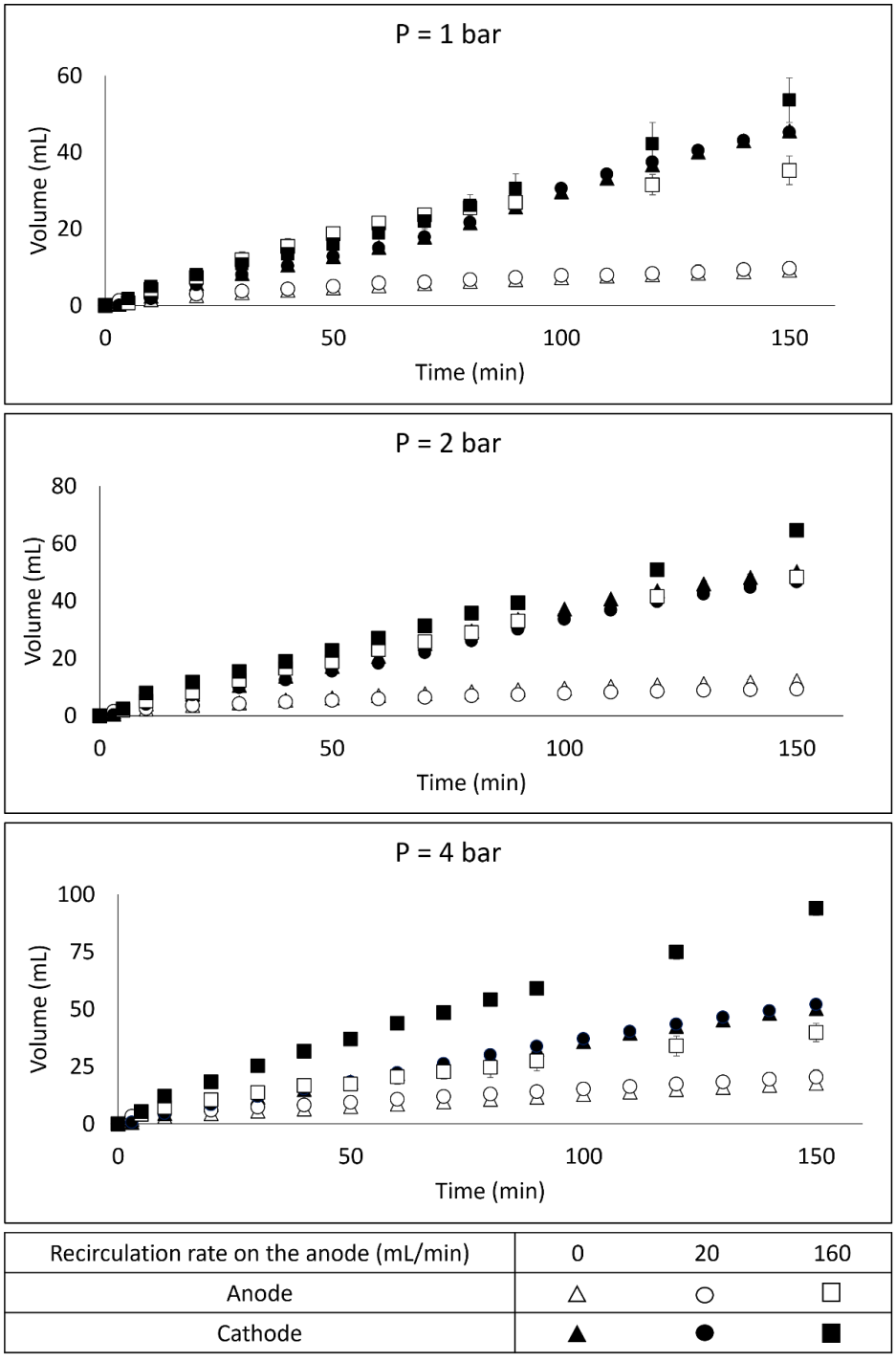


Figure 6.7. Effect of recirculation during electrofiltration at i = 60 A/m^2

Recirculation at a rate of 20 mL/min did not affect the filtration kinetics regardless of the filtration pressure. The application of an electric field showed an increase in the volume collected, however, the most important difference was observed for P = 4 bar. On the cathode side, the

application of the electric field resulted in a large increase in the volume collected when compared to experiments without an electric field. Whereas, on the anode side negligeable differences in filtrate were observed. Moreover, more volume was collected from the cathode than the anode.

For the filtration with a recirculation rate of 160 mL/min at a pressure of 1 bar, a total volume of (12.3 ± 0.32) mL was obtained after 150 minutes with F, whereas a total volume of (66.5 ± 3.17) mL was collected with EF at 60 A/m^2.

After EF at 60 A/m^2 for 150 minutes at 1 bar with a recirculation rate of 160 mL/min a volume of (20.2 ± 1.36) mL was obtained from the anode side and (46.3 ± 1.82) mL from the cathode side. Hence, the total volume of filtrate increased by 376% for electrofiltration at 60 A/m^2 with a recirculation rate of 160 mL/min on the anode, compared to the total volume of filtrate obtained by F without recirculation. When compared with electrofiltration at 1 bar and 60 A/m^2 without the use of recirculation, using a recirculation rate of 160 mL/min on the anode was able to increase the total volume obtained by 29.4% for a filtration time of 150 min.

6.2.2.2 Filtrate and cake properties

Table 6.3 shows the changes in the conductivity and pH of the filtrates caused by the presence of salts and ions produced by the electrolysis reactions during EF. After 150 min of F, regardless of the applied pressure, the filtrate was found to have a pH of 7.66 ± 0.44 and a conductivity of 3.13 ± 0.08 mS/cm on the side without recirculation and a pH of 7.49 ± 0.48 and a conductivity of 0.25 ± 0.01 mS/cm on the side with recirculation. The lower conductivity on the side with recirculation is expected since the filtrate becomes diluted when it is added to the beaker containing 207 mL of deionized water, the latter has a conductivity of 1.6 ± 0.05 µS/cm. In other words, the additional volume of filtrate gradually increases the conductivity of the recirculation fluid over time. The application of an electric field yielded a more acidic pH on the anode side and a more basic pH on the cathode side, and it increased the conductivity of the filtrates from both the anode and cathode side of the filter cell (Table 6.3).

Table 6.3. Electrical conductivity and pH of the filtrates at different pressures after EF at 60 A/m^2 for 150 min with recirculation on the anode

Recirculation rate (mL/min)	Pressure (bar)	Conductivity (mS/cm)		pH	
		Anode	Cathode	Anode	Cathode
0	1	6.16 ± 0.26	13.1 ± 0.6	2.45 ± 0.06	12.4 ± 0.07
20	1	1.43 ± 0.04	13.7 ± 0.1	3.21 ± 0.04	12.6 ± 0.02
	4	1.6 ± 0.04	13.5 ± 0.1	3.02 ± 0.02	12.7 ± 0.04
160	1	1.78 ± 0.03	14.05 ± 1.35	3.12 ± 0.06	12.53 ± 0.03
	4	1.87 ± 0.04	8.95 ± 0.25	3.12 ± 0.02	12.25 ± 0.07

The use of recirculation on the anode was able to noticeably decrease the filtrate's conductivity on the anode side. For example, at a pressure of 1 bar the conductivity on the anode side decreased from 6.16 ± 0.26 mS/cm (r = 0 mL/min) to respectively 1.43 ± 0.04 mS/cm and 1.78 ± 0.03 mS/cm for recirculation rates of 20 mL/min and 160 mL/min. The decrease in conductivity is due to the presence of the additional 207 mL of water that was added for recirculation, as explained earlier. The additional water dilutes the filtrate obtained from the anode side, which subsequently lowers the conductivity of the solution (for 20 and 160 mL/min) when compared to the more concentrated filtrate obtained from the anode without fluid recirculation (0 mL/min).

Table 6.4 shows the cake dryness obtained after 150 min of F and EF without and with recirculation on the anode side at a rate of 20 mL/min.

Table 6.4. Cake dryness for F and EF for different recirculation rates on the anode side

Recirculation rate (mL/min)	Electric current density (A/m^2)	Pressure (bar)	Cake dryness (%)
0	0	1	5.11 ± 0
		2	5.71 ± 0.05
		4	6.04 ± 0.11
	60	1	10.46 ± 0.37
		2	11.49 ± 0.09
		4	12.43 ± 0.06
20	0	1	5.02 ± 0.08
		2	5.61 ± 0.11
		4	5.98 ± 0.02
	60	1	11.07 ± 1.03
		2	11.62 ± 0.06
		4	12.43 ± 0.44

The use of a recirculation unit on the anode did not have a noteworthy impact on the cake dryness after both F and EF for 150 min at different pressures. In both cases, increasing the pressure slightly helped increase the cake dryness.

To help understand the effect of using a recirculation unit on the anode side during EF, the pH of different sections of the cake are reported in Table 6.5.

Table 6.5. pH distribution in the filter cake after EF at 60 A/m^2 with recirculation at 20 mL/min on the anode

Pressure (bar)	Anode	Middle	Cathode
1	2-3	4	12-14
2	2-3	4	14
4	3	4-5	14

The section of the cake that is closest to the anode has an acidic pH, which is expected as the filtrate that is being recirculated also has an acidic pH. Similarly, the section of the cake closest to the cathode has an alkaline pH.

6.2.2.3 Ohmic heating and energy consumption

EF led to ohmic heating within the filtration cell and caused an increase in the temperature near the electrodes as illustrated in Figure 6.8.

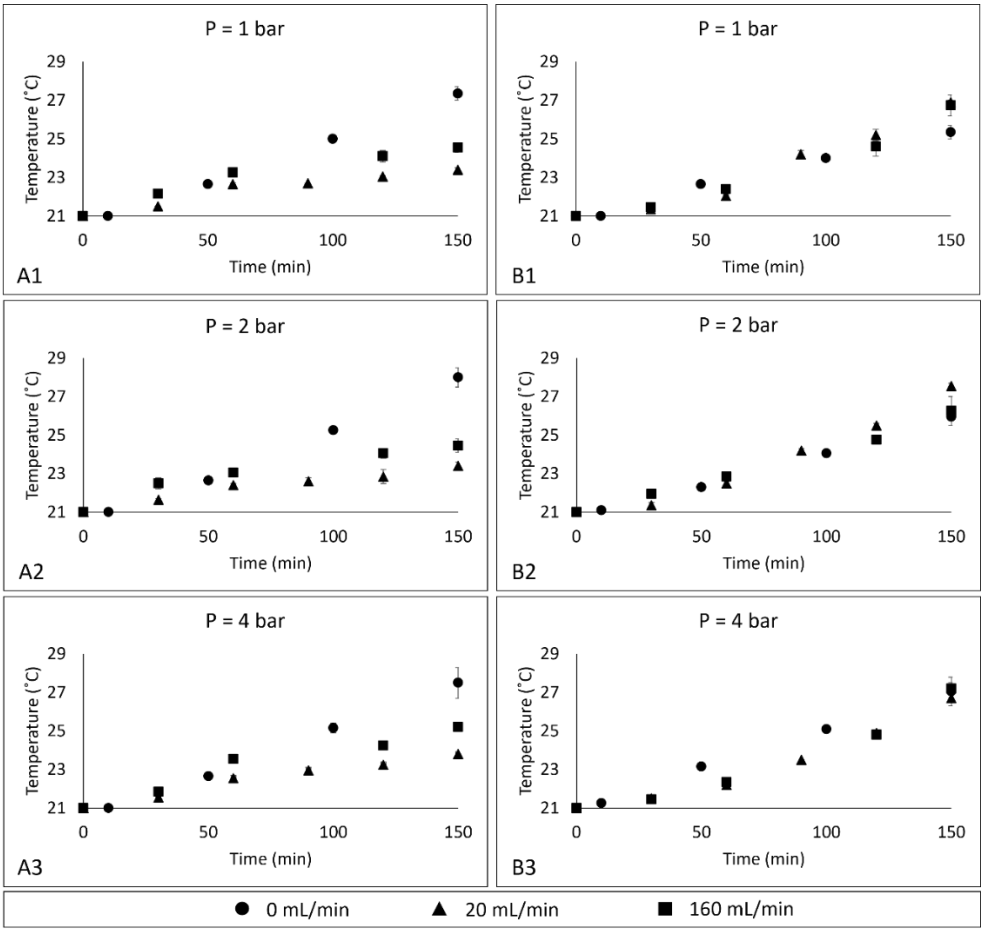


Figure 6.8. Increase in temperature in function of time on the Anode (A1, A2, A3) and Cathode (B1, B2, B3) sides during EF at 60 A/m^2 and pressures of 1, 2, and 4 bar

For instance, after 150 min of EF at 60 A/m^2 the temperature on the anode side reached 23.4, 23.4, 23.6, and 23.8 °C, respectively for a pressure of 1, 2, 3, and 4 bar. Ohmic heating was more important on the cathode side due to the absence of electrode flushing, where the temperature reached 26.9, 27.6, 27.4, and 26.7 °C respectively for a pressure of 1, 2, 3, and 4 bar after 150 min of EF at 60 A/m^2. Less important heating on the anode side compared to the cathode side was reported during EF when electrode flushing was used on the anode [1].

Figure 6.9 presents the specific energy consumption during EF at different pressures for an electric current density of 60 A/m^2 in function of the EF time.

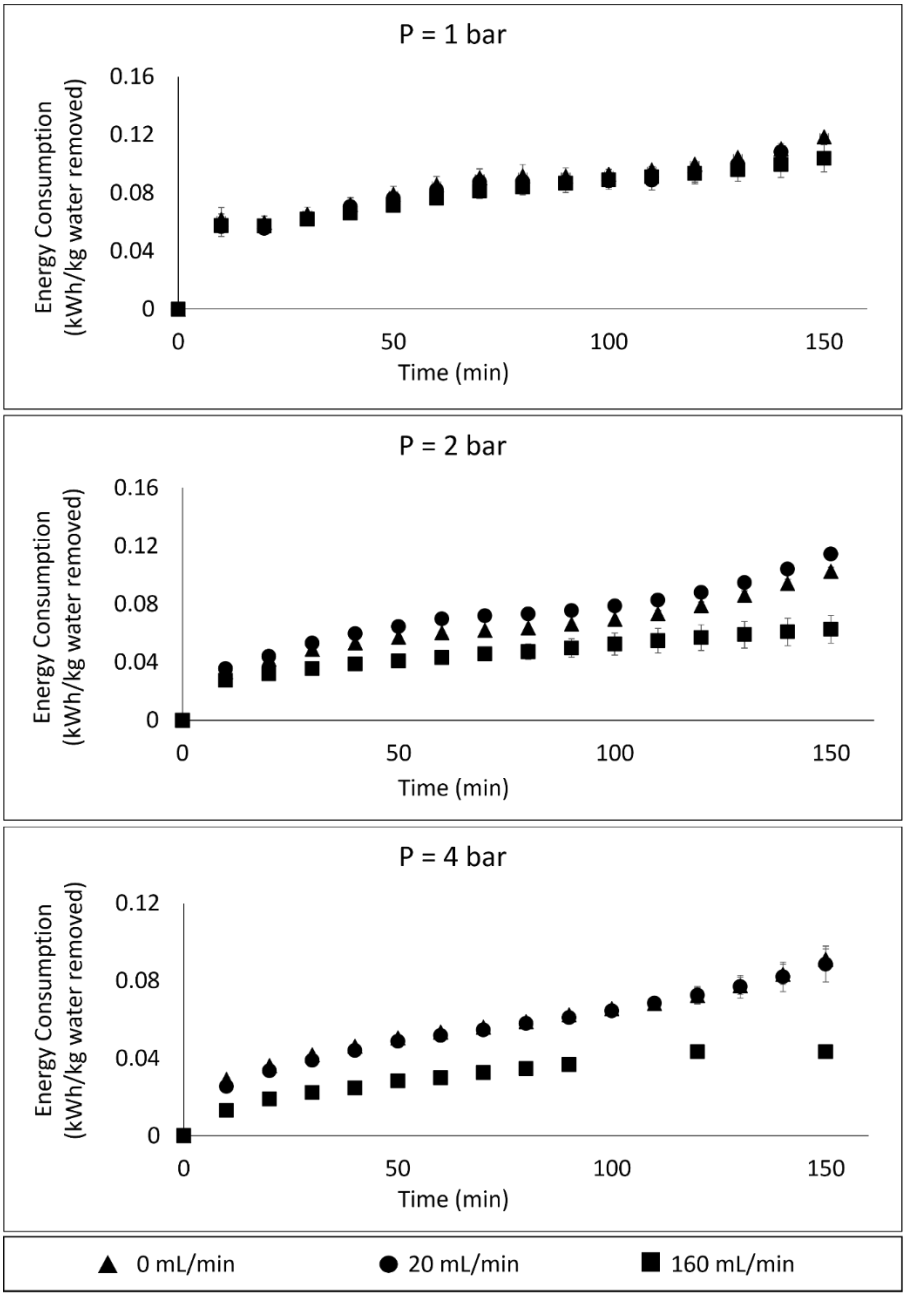


Figure 6.9. Effect of recirculation on the energy consumption during electrofiltration at 60 A/m^2

Increasing the pressure was found to be an easy method to decrease the energy consumption during the filtration process. The energy consumption related to the use of the pump is not considered in this analysis.

At a pressure of 1 bar, the recirculation rates of 0, 20, and 160 mL/min had comparable energy consumptions: recirculation at 0 and 20 mL/min during EF at 60 A/m^2 for 150 min consumed 0.119 kWh/kg water removed, whereas the recirculation rate of 160 mL/min slightly reduced the energy consumption to 0.104 kWh/kg water removed. At a pressure of 2 bar, the specific energy consumption for the recirculation rates of 0, 20, and 160 mL/min were respectively 0.103, 0.144, and 0.063 kWh/kg water removed. The specific energy consumption decreased even more at a pressure of 4 bar, respectively reaching 0.091, 0.089, and 0.043 kWh/kg water removed.

Thus, increasing the pressure from 1 to 4 bar decreased the energy consumption by a factor of 1.3, 1.33, and 2.42 respectively for the recirculation rates of 0, 20, and 160 mL/min.

6.2.3 Optimizing filtration with a recirculation rate of 160 mL/min

This section discusses the use of a recirculation rate of 160 mL/min during EF for 360 min. Filtration was carried out for a longer time in order to completely fill the filtration chamber and reach a higher cake dryness that is comparable to the cake dryness values reported in Chapter 3 with *A. platensis*. The effect of the electric field strength, pressure, and mixing the filtrate from the anode and cathode were assessed.

6.2.3.1 Effect of electric field strength

6.2.3.1.1 Filtration kinetics

In order to compare the effect of the electric field strength on the filtration kinetics with recirculation at a rate of 160 mL/min on the anode side, the total volume of filtrate in function of time is plotted in Figure 6.10.

Moreover, increasing the filtration time from 150 min to 360 min was able to drastically impact the final volume of total filtrate obtained. After 360 min of EF, final volumes of (82.2 ± 4.73), (122 ± 6.95), (159 ± 14.5), and (229 ± 10.3) mL were reported respectively for electric current densities of 30, 40, 60, and 80 A/m^2. Increasing the electric current density from 30 A/m^2 to 40, 60, and 80 A/m^2 respectively increased the volume of filtrate by 1.5, 1.9, and 2.8 folds. In other words, increasing the filtration time from 150 min to 360 min increased the yield respectively by 105%, 124%, 95%, and 105% for electric current densities of 30, 40, 60, and 80 A/m^2.

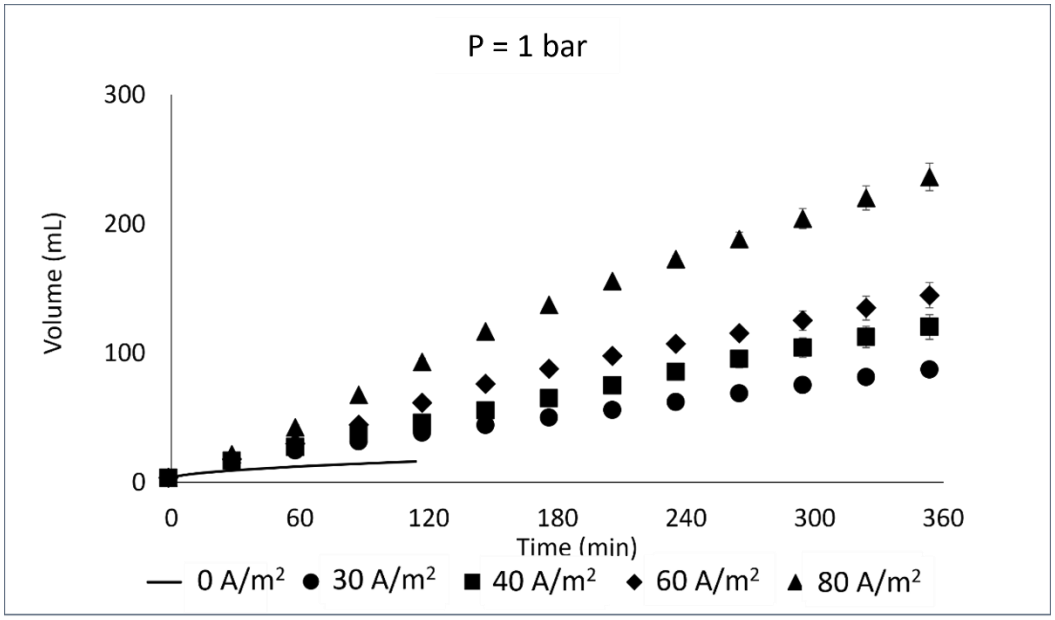


Figure 6.10. Total volume of filtrate obtained for different electric current densities

Generally, during electrofiltration, the voltage plays a role in setting the filtration rate; an increase in voltage has been linked to an increase in the volume of filtrate recovered [10].

It was also observed that, after EF for 360 min, more filtrate was recuperated from the cathode side than the anode side, where the percentage of filtrate obtained on the cathode was found to be 61.5%, 61.7%, 72.8 % and 69% respectively for 30, 40, 60 and 80 A/m^2 (Figure 6.11). For the cathode side, increasing the electric field strength from 30 A/m^2 to 40, 60, and 80 A/m^2 respectively increased the yield of filtrate by 41%, 99.9%, and 213%. As for the anode side, the same increase in electric field strength increased the volume of filtrate by 37.3%, 19.5%, and 124% for the respective electric field strengths of 40, 60, and 80 A/m^2.

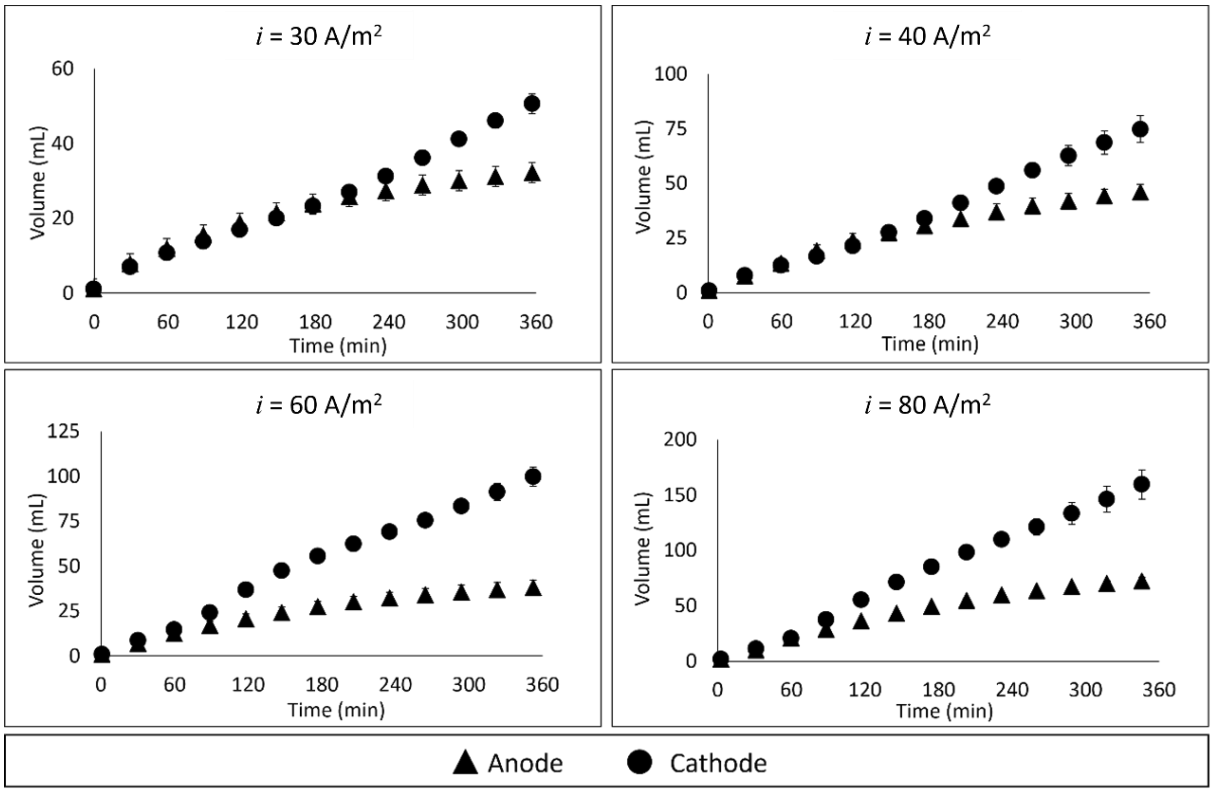


Figure 6.11. Filtration kinetics on the anode and cathode side at a pressure of 1 bar and different electric current densities

6.2.3.1.2 Filtrate and cake properties

Table 6.6 shows the characteristics of filtrate and filter cake after electrofiltration at different electric field strengths for 360 minutes. The pH on the anode side was acidic and within the same range for the different electric field strengths. Regardless of the value of the electric current density, the pH of the filtrate was acidic on the anode and alkaline on the cathode, which conforms with the general findings reported for the filtrate pH in this thesis. The pH values were almost identical for the different electric current densities, ranging from 2.73 to 2.81 for the anode side and from 12.6 to 12.7 on the cathode side. The filtrate obtained on the cathode side has a significantly higher value than that on the anode side, this can be explained by the presence of a higher concentration of salts (byproduct of the electrofiltration process) on the cathode side, compared to the anode side, noting that the filtrate on the anode side was being added to 207 mL of deionized water (1.6 ± 0.05 µS/cm).

Table 6.6. Filtrate characteristics and filter cake dryness after electrofiltration at different electric current densities for 360 minutes

Current density (A/m^2)		30	40	60	80
Filtrate pH	Anode	2.81 ± 0.05	2.89 ± 0.02	2.76 ± 0.01	2.73 ± 0.01
	Cathode	12.6 ± 0.07	12.7 ± 0.01	12.6 ± 0	12.6 ± 0.01
Filtrate Conductivity (mS/cm)	Anode	1.76 ± 0	2.06 ± 0.03	2.7 ± 0.05	3.11 ± 0.03
	Cathode	11.8 ± 0.03	12.2 ± 0.64	10.5 ± 0.34	10.2 ± 0.65
Filter cake dryness (%)		14.3 ± 0.21	15.3 ± 0.38	18.4 ± 0.68	19.7 ± 0.08

Besides enhancing the filtration kinetics, the application of an electric field led to the production of well-formed filter cakes (Figures 6.12 B to 6.12 E) when compared to F (Figure 6.12 A). The color of the microalgal cakes changed when the electric field strength was changed. This could be due to potential changes in the composition and/or concentration of the bioactive compounds present within the *C. vulgaris* cells, this hypothesis should be verified in future work.

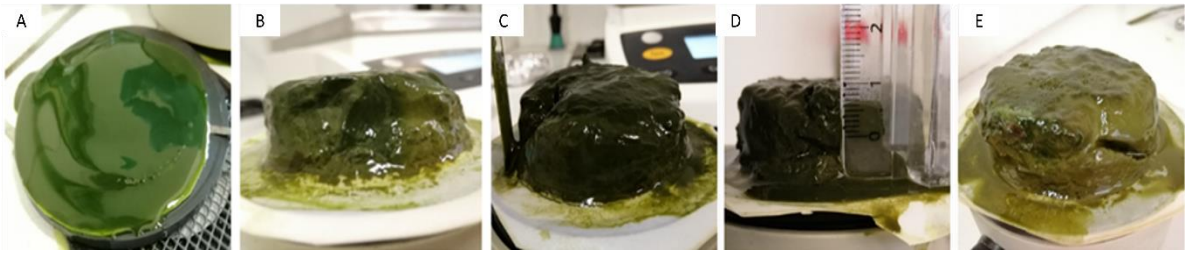


Figure 6.12. Images of filter cakes after 6 hours of filtration with a recirculation rate of 160 mL/min for F (A) and EF at electric current densities of 30, 40, 60, and 80 A/m^2 respectively for B, C, D, and E

The cake dryness (Table 6.6) increased on average by approximately 3 times for i = 30, 40, and 60 A/m^2 when compared with i = 0 A/m^2. The cake dryness increased by 4 times for i = 80 A/m^2 compared to i = 0 A/m^2. Despite obtaining the highest cake dryness of (19.7 ± 0.08) % for i = 80 A/m^2, the higher electric field strength led to a higher onset of ohmic heating, which in turn led to a higher temperature increase in the filter chamber.

6.2.3.1.3 Ohmic heating and energy consumption

EF led to ohmic heating within the filtration cell and increased the temperature near the electrodes, this was validated by the measurements made using flexible K-type thermocouples (Figure 6.13). Ohmic heating was more pronounced with higher electric current densities. For instance, the temperature on the anode side with the recirculation unit reached 23.3, 23.6, 26.7, and 26.8 °C after 360 min of EF with electric current densities of respectively 30, 40, 60, and 80 A/m^2. Ohmic heating was more important on the cathode side that was not equipped with a recirculation unit for electrode flushing, where the temperature reached 24.1, 24.7, 37.2, and 47.8 °C after 360 min of EF respectively for 30, 40, 60, and 80 A/m^2.

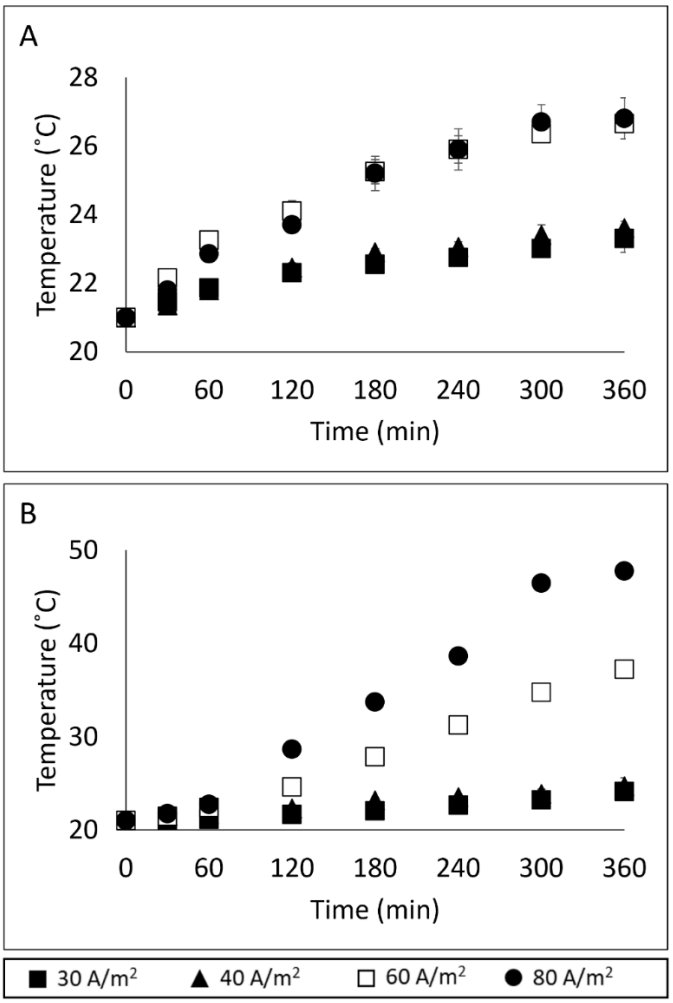


Figure 6.13. Increase in temperature over time for EF at a pressure of 1 bar at different electric current densities near the Anode (A) and Cathode (B)

The temperature increase on both the anode and cathode side could be considered acceptable, since it has been reported that an optimum drying temperature to avoid negative effects on the

appearance and composition of *C. vulgaris* is in the range of 60-80 ˚C [17]. However, this is not enough to assume that the quality of the *C. vulgaris* cells that are subjected to EF was not negatively affected, especially given the pH changes that take place during EF.

Figure 6.14 presents the specific energy consumption during EF at 1 bar for different electric current densities versus the EF time. As expected, the specific energy consumption increased with the increase of the electric current density, reaching values of 0.07, 0.09, 0.25 and 0.23 kWh/kg water removed respectively for the electric current densities of 30, 40, 60, and 80 A/m^2 after 360 min of EF.

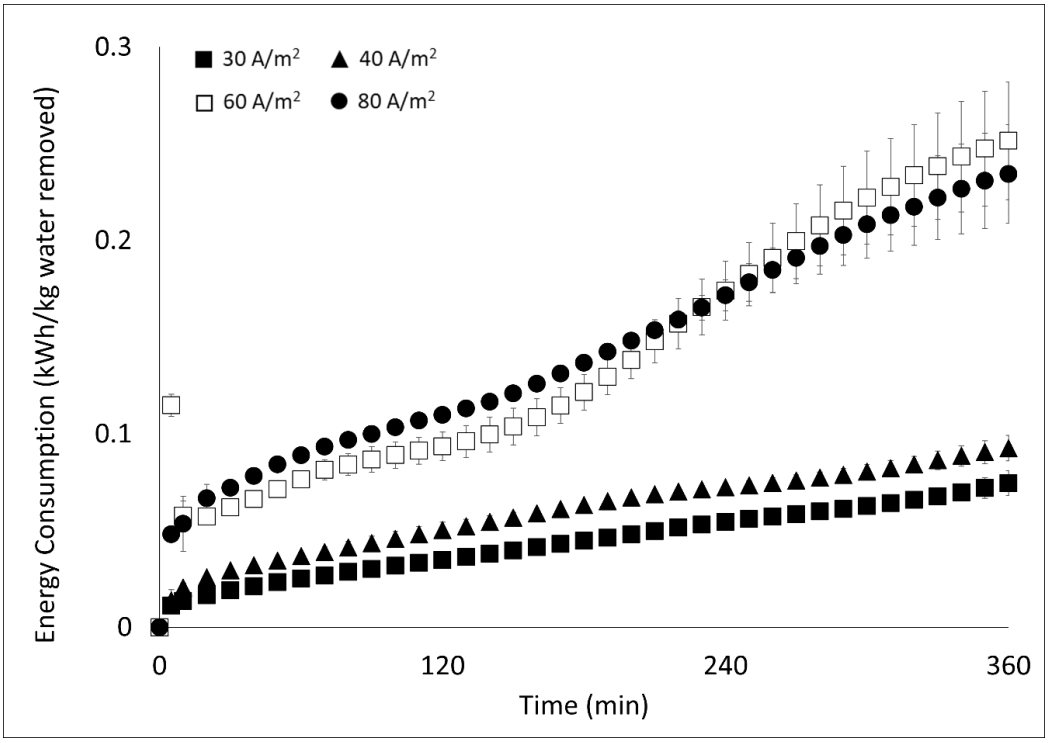


Figure 6.14. Specific energy consumption during EF at 1 bar and different electric current densities for 360 min with a recirculation rate of 160 mL/min on the anode

When observing the tendencies of the energy curves for 60 A/m^2 and 80 A/m^2, the use of an electric current density of 60 A/m^2 consumes more energy than 80 A/m^2 after EF for approximately 240 min. This shift in the energy consumption could be related to the observed ohmic heating on the cathode side, which was much higher for 80 A/m^2 as shown in Figure 6.12 B, and subsequently led to a further increase in the filtration rate alongside the effect of the electric current. Thus, by eliminating more water during the filtration process despite the higher electric current density, i = 80 A/m^2 consumed less energy than i = 60 A/m^2 after t = 240 min. Even though, i = 80 A/m^2 was associated with a relatively lower energy consumption and the highest cake dryness after EF for 360 min, this electric current density might not be the best choice due to the higher ohmic heating observed on the cathode side during EF. Some of the potential issues related to the higher

temperature observed for i = 80 A/m^2 are the possibility of shortening the cathode's lifetime, as well as possibility of degrading the quality of the biocompounds in the filter cake. Hence, more studies need to be conducted to optimize the process and reduce the ohmic heating on the cathode side.

6.2.3.2 Effect of pressure and mixing the filtrates

6.2.3.2.1 Filtration kinetics

In this section the effect of doubling the pressure combined with recirculating pure filtrate from the anode side or recirculating mixed filtrate from the anode and cathode side was assessed. For this reason, the studied pressures were 1, 2, and 4 bar. Based on the pH of the filtrate and cake obtained in sections 1.1 and 1.2 of this chapter, the concept of mixing the filtrate from the cathode and anode is used as an attempt to regulate the pH of the recirculation solution which in turn could potentially regulate the pH of the formed cake during EF. As shown in Figures 2.3 and 2.4 (Chapter 2), recirculation is conducted on the anode side of the filtration cell. Two configurations were studied: (1) a separate filtrate collection system where the filtrate from the cathode is collected in one beaker and that from the anode is collected in a different beaker containing 207 mL of distilled water, which is the solution that is recirculated towards the anode, and (2) a mixed filtrate collection system where the filtrate from the anode and cathode side are collected in a beaker containing 207 mL of distilled water, the content of this beaker is recirculated into the anode side of the filter cell.

Comparing the filtration performance of EF at 60 A/m^2 for the separate and mixed filtrate collection systems after 360 min (Figure 6.15) showed that the total volume of filtrate obtained during the separate collection system is slightly higher than the volume obtained in the mixed system. For the separate collection system, a total volume of (159 ± 14.5), (216 ± 3.91), and (352 ± 3.12) were respectively obtained for a pressure of 1, 2, and 4 bar. For the mixed collection system, a total volume of (125 ± 4.02), (185 ± 4.25), and (251 ± 0.58) were respectively obtained for a pressure of 1, 2, and 4 bar. Mixing the filtrate decreased the total volume by a factor of 1.27, 1.17, and 1.4, respectively for a pressure of 1, 2, and 4 bar.

Whereas increasing the pressure was found to increase the total volume of filtrate for both the mixed and separate configurations for filtrate collection. For the mixed collection system, increasing the pressure from 1 bar to 2 and 4 bar, respectively increased the volume of filtrate by a factor of 1.48 and 2.01, compared to an increase by a factor of 1.36 and 2.21 for the separate collection system when the pressure was respectively increased from 1 bar to 2 and 4 bar. This shows that the pressure has a slightly higher influence on the filtration kinetics with the use of a recirculation unit.

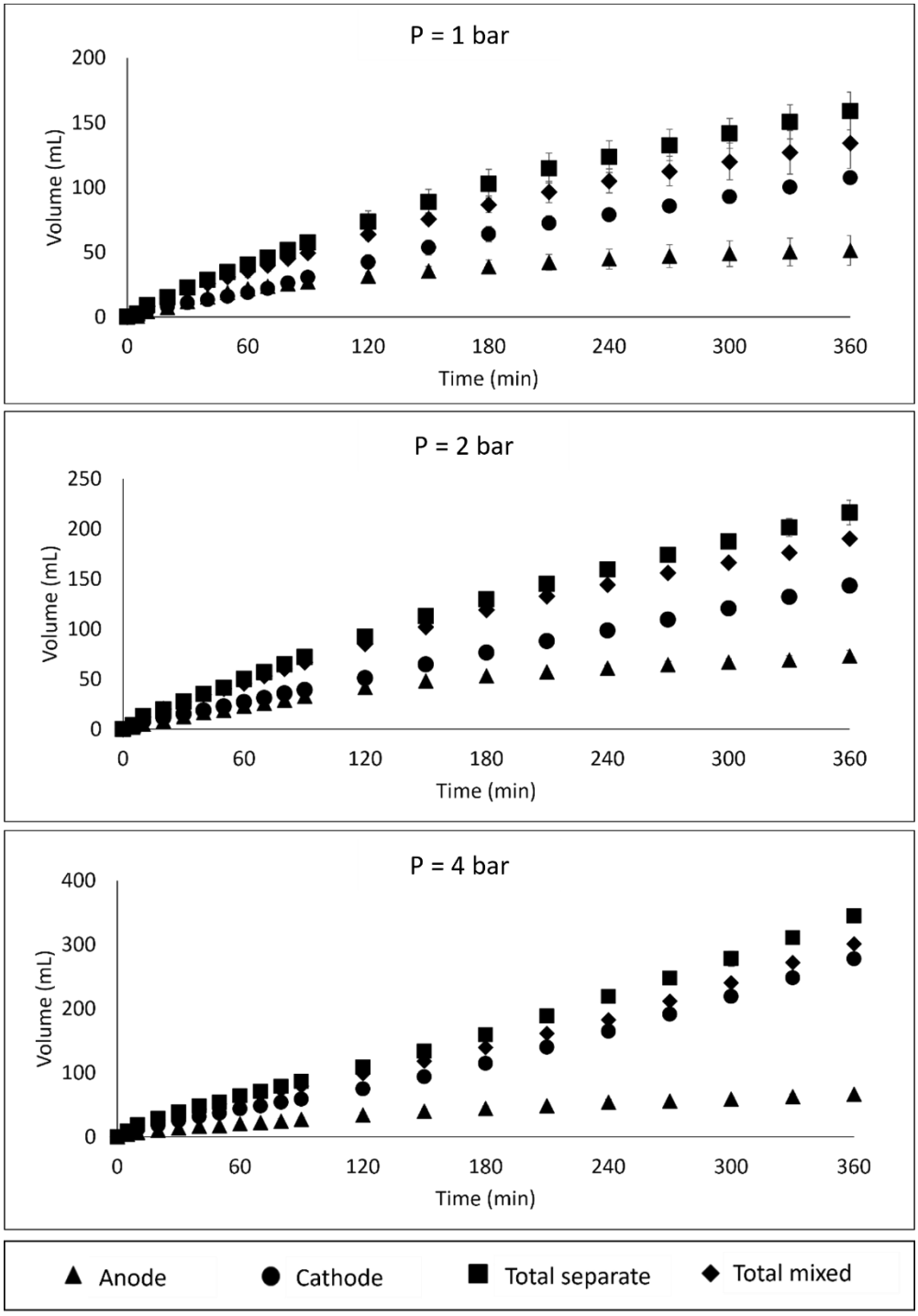


Figure 6.15. Filtration kinetics for separate and mixed collection of filtrates with recirculation on the anode at a rate of 160 mL//min for EF at 60 A/m^2

6.2.3.2.2 Filtrate and cake properties

Mixing the filtrate had an effect on both the pH and conductivity of the filtrate, as illustrated in Figures 6.16 and 6.17. The value of the pH was closest to 7 when the filtrate from the cathode and anode side were mixed, when collected separately, the filtrate from the anode side was acidic (with a value around 2) and the pH on the cathode side was alkaline (with a value around 12) as illustrated in Figure 6.16.

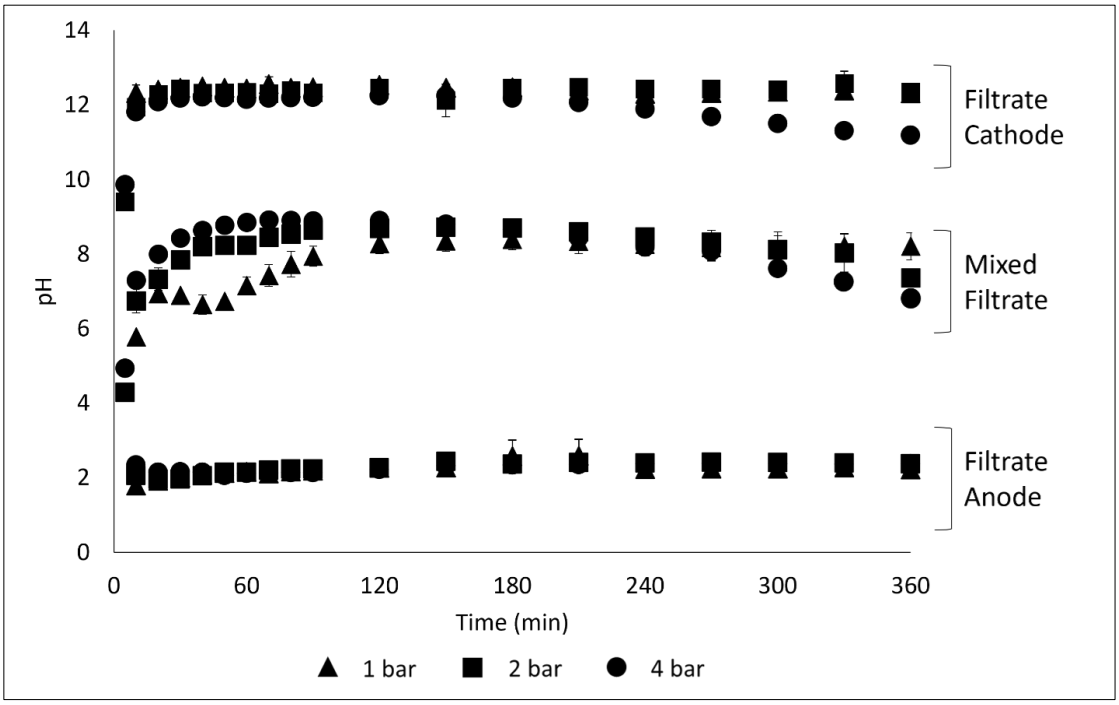


Figure 6.16. Effect of using a mixed collection system on the pH of the filtrate

Moreover, mixing the filtrate led to the decrease of the mixed filtrate's pH over time compared to the more stable pH profile that is observed for the collection of the filtrate from the cathode and anode side separately (Figure 6.16). This could be due to the reincorporation of the mixed filtrate in the filtration cell from the anode side, which exposes is to the electrochemical reactions that acidify the liquid over time.

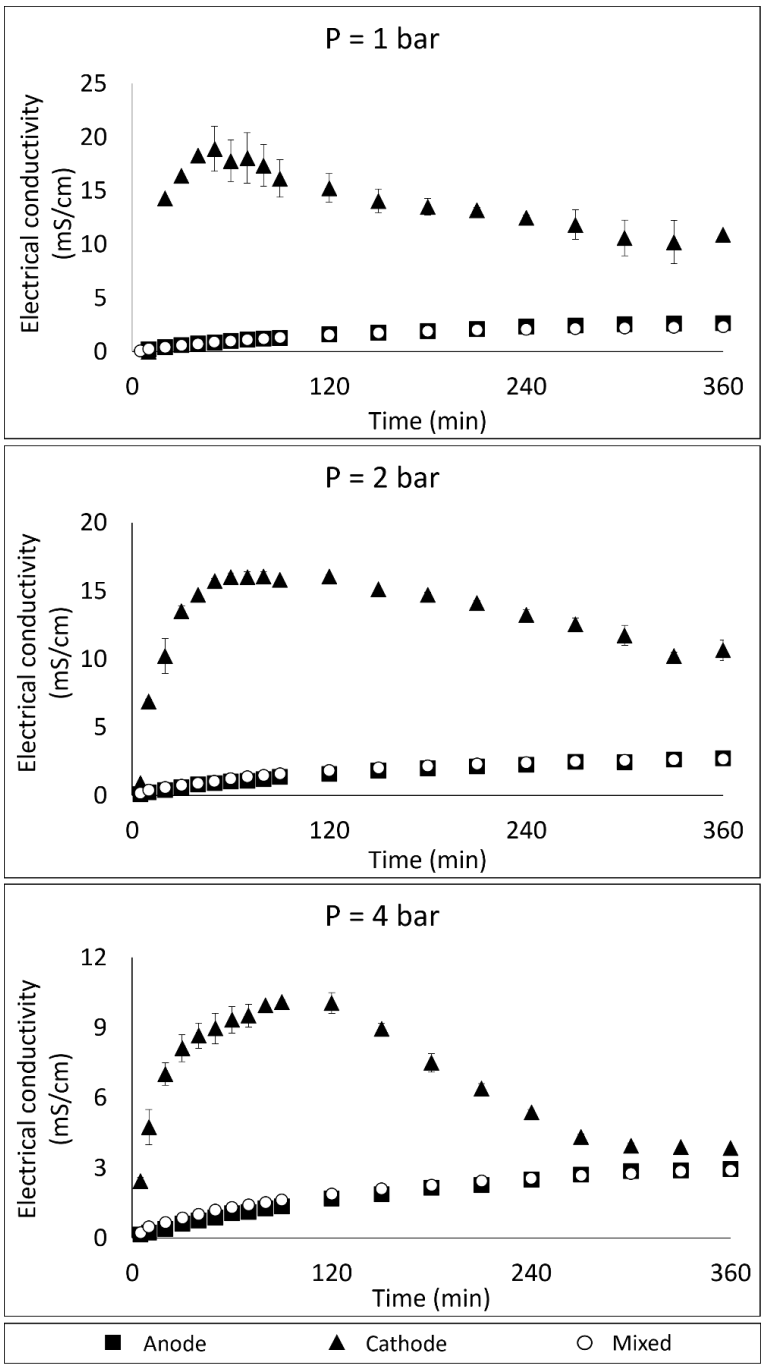


Figure 6.17. Change in the electrical conductivity of the filtrate during EF at different pressures, when collected separately and when mixed during collection

Based on the data illustrated in Figure 6.17, the conductivity of the mixed filtrate was almost the same as that of the filtrate obtained on the anode side (without mixing). This similarity in the conductivity values could be due to the dilution of the obtained filtrate in the 207 mL of deionized water that was used for the recirculation stream. After 360 min of EF, the conductivity of the

filtrate collected separately on the anode side was (2.66 ± 0.09), (2.72 ± 0.08), and (2.95 ± 0.06) mS/cm respectively for a pressure of 1, 2, and 4 bar and the conductivity of the mixed filtrate was (2.34 ± 0.04), (2.66 ± 0.15), and (2.9 ± 0.05) mS/cm respectively for a pressure of 1, 2, and 4 bar.

When the filtrate from the cathode was collected separately, its conductivity gradually increased and reached a maximum value of (18.9 ± 0.9), (16.05 ± 0.2), and (10.1 ± 0.1) mS/cm respectively for a pressure of 1, 2, and 4 bar. After 360 min of EF, the conductivity of the filtrate from the cathode side was (10.9 ± 2.01), (10.65 ± 0.75), and (3.85 ± 0.1) mS/cm respectively for a pressure of 1, 2, and 4 bar. The increasing and then decreasing tendency of the electrical conductivity on the cathode side might be due to the retention of the salts formed during EF in the filter cake and filter medium. This phenomenon requires more studies for future work.

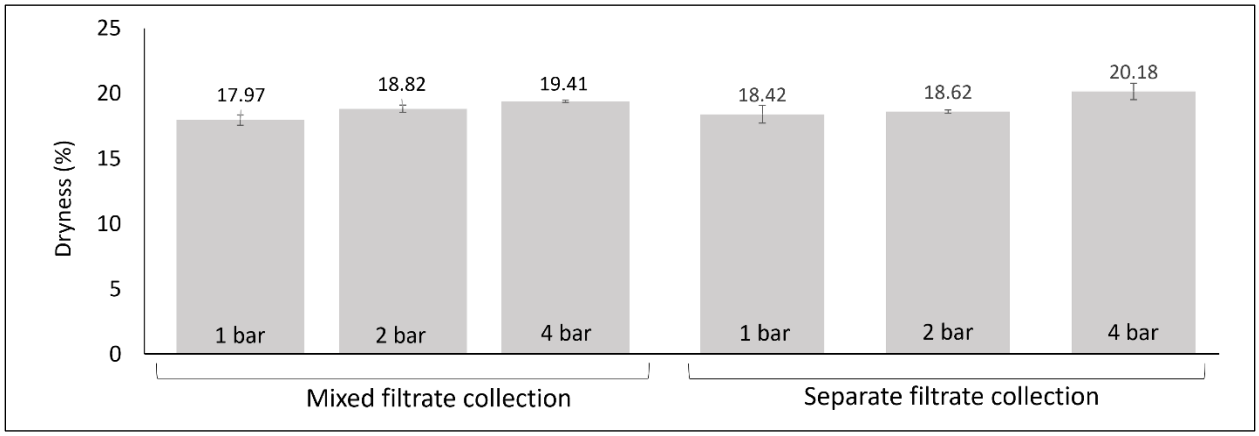


Figure 6.18. Cake dryness at different pressures for separate and mixed collection of filtrate

The pressure and the method of filtrate collection (mixed or separate) did not have a considerable effect on the cake dryness as shown in Figure 6.18, noting that the highest cake dryness was obtained for EF at 4 bar using the separate filtrate collection system (20.18 ± 0.63) % and the lowest was obtained for EF at 1 bar using the mixed filtrate collection system (17.97 ± 0.77) %.

Regardless of the operating pressure, the pH profile within the filter cake gradually transitioned from acidic on the anode side to alkaline on the cathode side, as shown in Table 6.7.

Table 6.7. pH values for different sections of the filter cake after EF at 60 A/m^2 for 360 min

Recirculation rate (mL/min)	Filtrate: Mixed or Separate	Cake pH profile		
		Anode side	Middle	Cathode side
0	Separate	1-2	3-5	12-14
160	Separate	2-3	4-5	12-14
160	Mixed	3	4-5	12-14

The use of a recirculation unit on the anode was able to decrease the acidity of the cake section that is formed near the anode (Table 6.7). The pH on the cathode side was not affected by the recirculation on the anode, this leads us to suspect that the use of a recirculation unit on the cathode side could help decrease the alkalinity of the cake and should be considered for future studies.

6.2.3.2.3 Ohmic heating and energy consumption

EF led to the onset of ohmic heating within the filtration cell which increased the temperature near the electrodes (Figure 6.19). The same extent of ohmic heating was obtained for the electric current density of 60 A/m^2 regardless of pressure.

For instance, for the separate collection of the filtrate from the anode and cathode side, the temperature on the anode side, with fluid recirculation, reached 26.7, 26.6, and 26.7 °C after 360 min of EF respectively for a pressure of 1, 2, and 4 bar. Ohmic heating was more important on the cathode side, where there was no recirculation, the temperature reached 37.2, 34.4, and 34.5 °C after 360 min of EF respectively for a pressure of 1, 2, and 4 bar.

For the mixed collection of the filtrate from the anode and cathode side, the temperature on the anode side, with fluid recirculation, reached 26.4, 36.5, and 26.5 °C after 360 min of EF respectively for a pressure of 1, 2, and 4 bar. Ohmic heating was more important on the cathode side, where there was no recirculation, the temperature reached 36.2, 35.8 and 36 °C after 360 min of EF respectively for a pressure of 1, 2, and 4 bar.

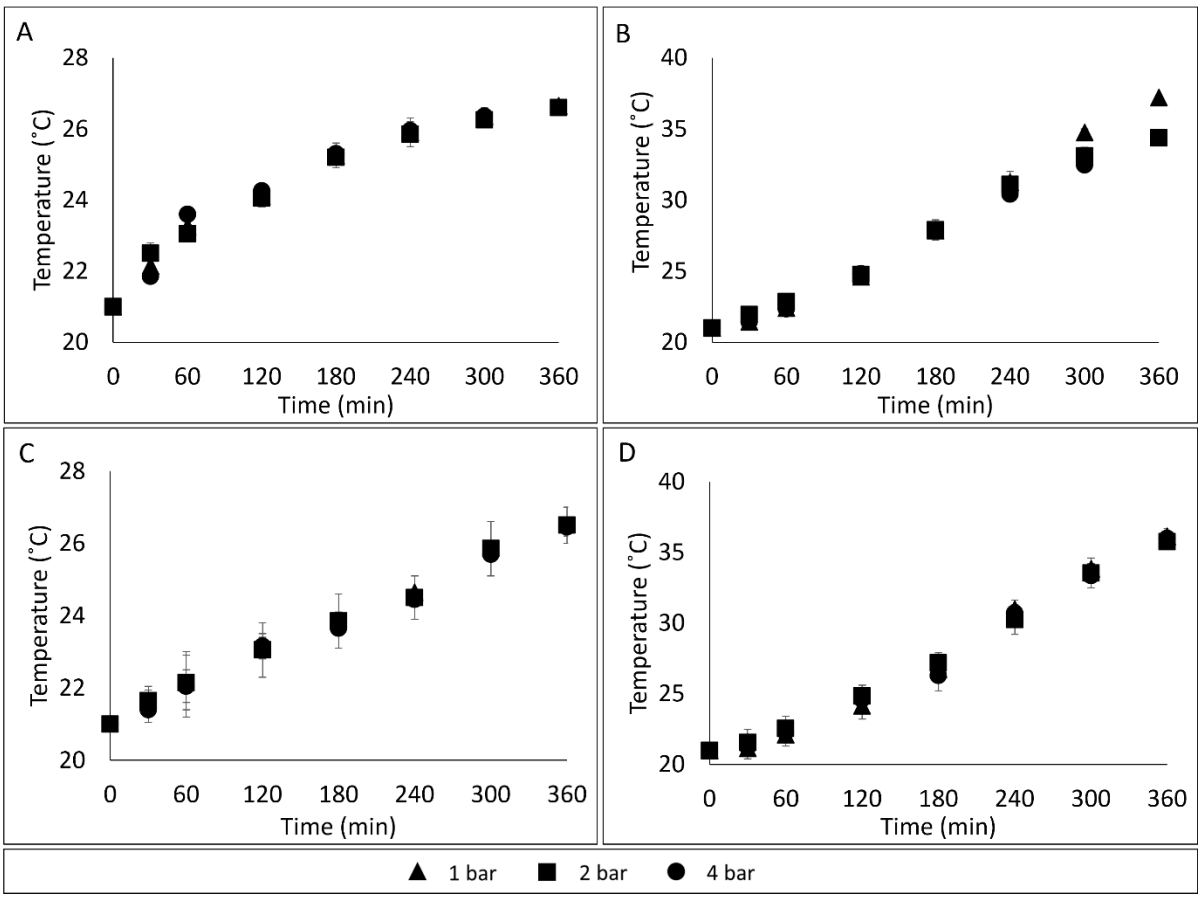


Figure 6.19. Increase in temperature over time for EF at 60 A/m^2 for different pressures. For the separate filtrate collection system near the Anode (A) and Cathode (B). For the mixed filtrate collection system near the Anode (C) and Cathode (D)

Without recirculation near the anode, more important heating on the anode side during EF has been reported compared to the cathode side [4,11,12] whereas a less important extent of ohmic heating has been reported near electrodes that are flushed by fluid recirculation [1]. This explains why the temperature on the anode side is lower than that on the cathode side in Figure 6.19.

Figure 6.20 presents the specific energy consumption during EF at 60 A/m^2 for a pressure of 1, 2, and 4 bar. The specific energy consumption decreased with the increase in pressure for both types of filtrate collection systems.

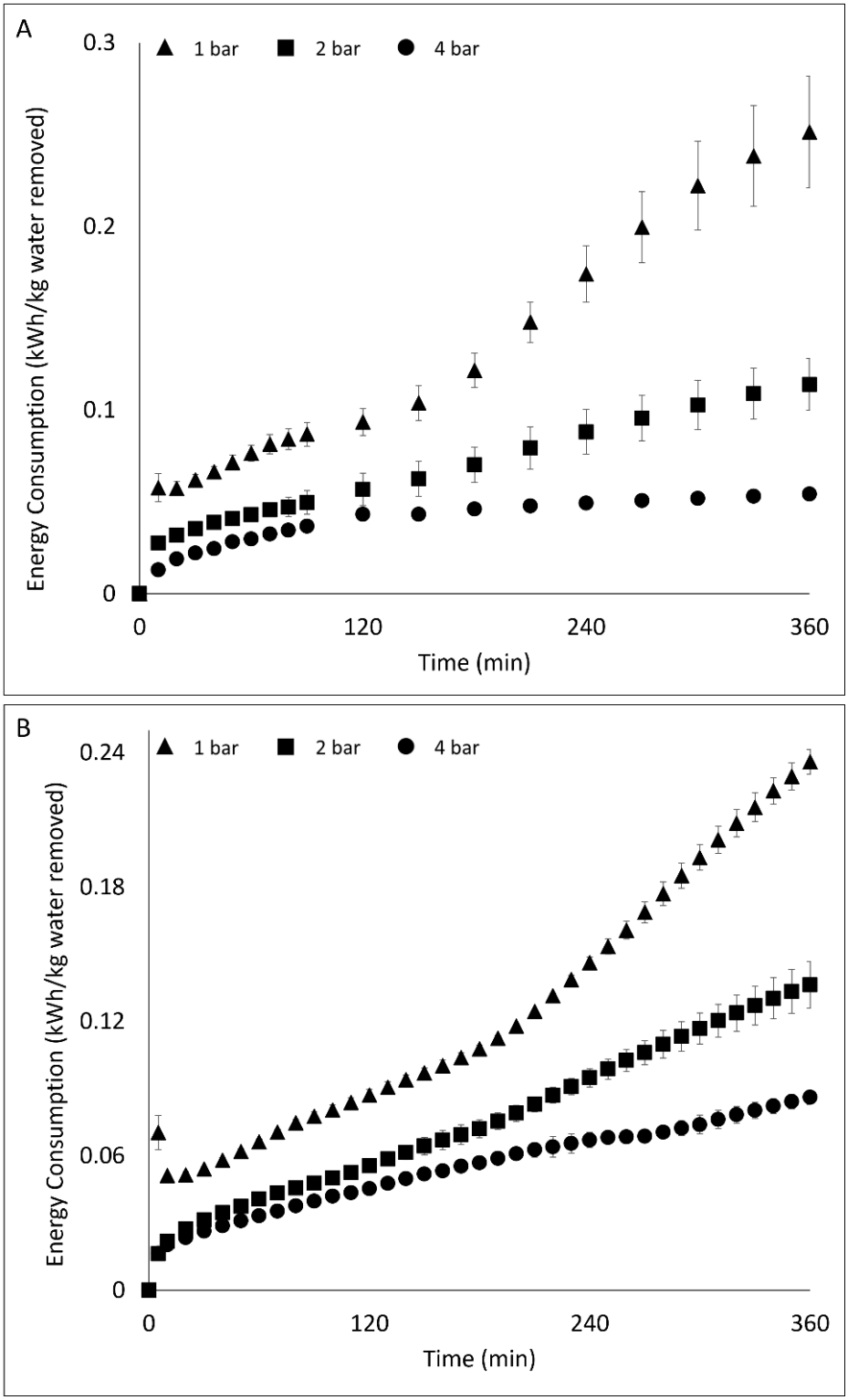


Figure 6.20. Energy consumption during EF at 60 A/m^2 and different pressures with a recirculation rate of 160 mL/min on the anode. A: separate filtrate collection. B mixed filtrate collection

For the separate filtrate collection system, after filtration for 360 minutes the energy consumption reached values of 0.25, 0.11, and 0.05 kWh/kg water removed respectively for a pressure of 1, 2, and 4 bar. For the mixed filtrate collection system, after filtration for 360 minutes the energy consumption reached values of 0.24, 0.14, and 0.09 kWh/kg water removed respectively for a pressure of 1, 2, and 4 bar. This shows that mixing the filtrate had a negligeable impact on the energy consumption for the operating pressure of 1 bar. However, mixing the filtrate from the anode and cathode sides increased the energy consumption by a factor of 1.27 and 1.8 respectively for a pressure of 2 and 4 bar.

6.3 Concluding remarks

Increasing the operating pressure during dead-end filtration does not lead to a better dehydration of *C. vulgaris* due to the compressible nature of the microalgal cake.

Electrofiltration can be an effective non-thermal drying method for *C. vulgaris* cells. The cake dryness can be increased by increasing the electric current density, but increasing the electric current density leads to a higher energy consumption. Nonetheless, compared to thermal dehydration methods used with *C. vulgaris*, electrofiltration is associated with a relatively lower energy consumption.

EF also modifies the filtrate and cake properties (changes in pH and conductivity) due to the electrolysis reactions that take place. This could affect the physical attributes as well as the composition of the *C. vulgaris* cells and the biocompounds that are potentially dissolved in the filtrate.

The use of a recirculation unit on the anode side for electrode reduces the extent of ohmic heating and modifies the pH and conductivity of the filtrate on the anode side. The cathode side remained unaffected by the recirculation on the anode. Mixing the filtrates was able to make the pH of the solution being recirculated more neutral.

Despite recirculating the mixed filtrate (neutral pH) back into the filtration cell during EF, the different sections of the filter cake still exhibit a pH ranging from acidic to alkaline. This shows the need for future work that attempts to regulate the pH of the cake and assess the effect of EF on the biocompounds present within the microalgal cells that are being concentrated. Some perspectives that can be considered for future work are the following:

- Studying the effect of EF and the use of recirculation on the biocompounds in the microalgal cake as well as the filtrate.
- The use of a recirculation unit on both the cathode and anode during electrofiltration, with the option of redirecting the filtrate obtained from the anode side towards the cathode of the filtration cell and redirecting the filtrate from the cathode side back to the anode side of the filtration cell as illustrated in Figure 6.21 A.

- The use of a polarity reversal strategy [18] to maintain a neutral pH, while attempting to improve or maintain good electrofiltration kinetics.
- The use of additives to neutralize the pH of the solution that is being recirculated back into the filtration cell and/ or to improve the electrofiltration kinetics (Figure 6.21 B). Some of the additives that could be considered are:
    - pH buffering agents to regulate the pH on the anode and cathode side.
    - Surfactants: they were found to increase the electroosmotic flow [18–20], but they were also removed with the fluid that is extracted under the effect of the electroosmotic flow. This shows the added benefit of using a recirculation unit that could reintroduce the surfactants into the electrofiltration cell. Some examples of surfactants are Triton X-100 (EK2) and Tween 80 (EK3).
    - Reducing and oxidizing agents (electro-Fenton method): These compounds can be added to the microalgal solution to change the particles' chemical composition and behavior under the influence of an electric field. This technique has been used to remove contaminants from soils and wastewater streams [21–24], as well as for the conditioning and dewatering of sludges [25,26].
    - Chelating agents (complexing agents): they have been found to improve the kinetics of electrofiltration and are capable of removing undesired compounds by forming reducible complexes [27,28].
- Cooling the recirculation fluid in order to decrease the conductivity of the filtrate and recirculation fluid [29], which subsequently makes it possible to use higher electric field strengths and obtain faster filtration kinetics.
- Combining some of the suggestions proposed in this list, such as, the use of chelating agents on one side of the recirculation stream and surfactants on the other (Figure 6.21 B), the use of surfactants with polarity reversal, etc…
- After optimizing the process on a laboratory scale, electrofiltration of microalgae should be scaled up to gain a better understanding of the performance on a pilot and eventually an industrial scale.

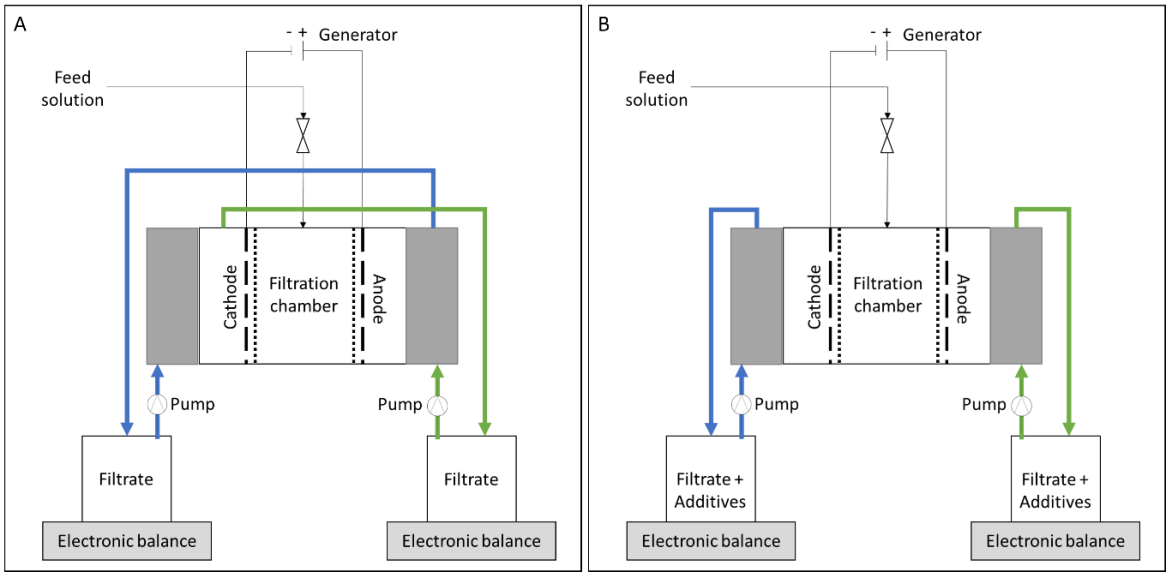


Figure 6.21. Proposed schematics for future work. (A) redirecting the filtrates to the opposite ends of the filtration cell, and (B) the use of additives with filtrate recirculation.

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General Conclusion

Microalgae are an important resource in a wide range of industries. However, the costs associated with concentrating and drying the microalgae suspensions are relatively high compared to the other steps involved in microalgae biorefineries. This is due to the high energy consumption of the available dewatering techniques.

This thesis focused on the use of dead-end electrofiltration as an enhanced microalgae dewatering technique with the main aim of reducing the energy consumption of the dewatering step.

When compared to dead-end filtration (F), electrofiltration (EF) was capable of enhancing the filtration kinetics regardless of the applied electric field strength. For example, the electrofiltration of *A. platensis* and *C. vulgaris* at a pressure of 1 bar and an electric current density of 60 A/m^2 for 150 min, increased the filtrate yield respectively by 1.27 and 3.67 folds compared to F. Increasing the electric current density increased the filtration rate, for example increasing the electric current density from 0 A/m^2 to 80 A/m^2 increased the filtrate yield by 50.6% for the EF of *A. platensis* at 1 bar for 150 min. However increasing the electric current density also increased the energy consumption of the process; i.e. during EF of *A. platensis* at 1 bar for 150 min, the specific energy consumption reached values of 0.019, 0.024, 0.067, and 0.105 kWh/kg water removed respectively for the electric current densities of 30, 40, 60, and 80 A/m^2. Electrofiltration is still less energy intensive than other conventional concentration techniques (reaching up to 2.35 kWh/kg water removed and 0.75 kWh/kg water removed respectively by solar and vacuum drying, see Chapters 1 and 3) and it presents a wider range of application in microalgae biorefineries with the better potential to be used on a larger scale. Electrowashing was capable of increasing the washing kinetics of a microalgae cake at lower operating pressures (1 bar, or no pressure) compared to the conventional high pressure washing techniques (pressure electrowashing took 187 minutes on average to recover 55 ml of wash liquor unlike pressure washing without an electric field which was 2.3 times slower to yield only 45 ml of wash liquor). Electrowashing also improved the dryness of the washed microalgae cake, with the potential of reaching a sectional cake dryness up to 60.5% as discussed in Chapter 5.

The use of filtrate recirculation was able to reduce ohmic heating on the electrode where recirculation is taking place. Recirculating the mixture of filtrates from the anode and cathode sides of the electrofiltration cell was capable of stabilizing their pH. However more studies need to be carried out to fully understand the effect of using a recirculation unit on the quality of the extracted bioactive compounds.

Despite the improvements in filtration kinetics and cake dryness that were associated with the application of an electric field, the deterioration of biocompounds of interest (proteins and pigments) was also reported in Chapters 3, 4, and 5. This was suspected to be a side effect of the electrokinetic phenomena that take place in the presence of an electric field. More studies are

needed to prevent the deterioration of biocompounds due to the application of an electric field during electrofiltration and electrowashing. As discussed earlier, the deterioration of biocompounds could be prevented by stabilizing the pH of the filtrate.

In addition, the results found in this work also showed the need to answer new research questions. Hence this work provides a foundation for future studies that are in alignment with the following perspectives:

- Optimizing dead-end electrofiltration and electrowashing to improve the quality and yield of the bioactive compounds present in the filtrate and the cake. This could be achieved by adding pH stabilizing compounds introduced into the system by a recirculation unit.
- Assessing the use of different methods involving filtrate recirculation (as discussed in the conclusion of Chapter 6) to improve the electrofiltration process.
- Assessing the effect of the state of the microalgae (dry, frozen, or fresh) as well as the cells' state of maturity and shape on the filtration and electrofiltration kinetics and the filter cake properties.
- Scaling up the electrofiltration and electrowashing processes while maintaining relatively low energy consumptions and relatively quick filtration kinetics, all while studying their effect on the cake and filtrate properties.
- Assessing the suitability of using electrofiltration on different types of microalgae and for different industrial applications.
- Further optimizing the electrowashing process by assessing the use of different electric current densities and washing pressures.
- Understanding the effect of the applied electric field on the flow of liquid through the cake pores during electrowashing, especially taking into account the effect of the electrokinetic phenomena.
- Studying the effect of the temperature and pH changes on the cake structure and functionality of the extracted bioactive compounds.
- Performing an economic study to fully assess the economic viability of using electrofiltration and electrowashing as dewatering techniques in microalgae biorefineries.