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**FEASIBILITY STUDY OF ELECTRODIALYSIS  
FOR VINASSE DESALTING AND POTASSIUM  
RECOVERY**

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**Belo Horizonte**

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Feasibility study of electrodialysis for vinasse desalting and potassium recovery

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## RESUMO

O Brasil é o maior produtor de cana-de-açúcar do mundo, configurando o setor sucroalcooleiro como uma das atividades de grande relevância para o país. Em muitas usinas se adota a fertirrigação em que o vinhoto retorna ao canavial, trazendo diversos resultados benéficos, entretanto, se aplicado em excesso, pode causar sérios impactos negativos. O potássio é o íon predominante no vinhoto, e por estar em concentrações elevadas, existem normas que limitam a aplicação do vinhoto em solo agrícola. O uso da eletrodialise, processo de separação por membrana em que há transporte iônico sob influência de um campo elétrico, permite que, com a redução do teor de potássio do vinhoto, o efluente já largamente usado para fertirrigação, possa ser aplicado em maior taxa sem prejudicar o solo, a cultura e a qualidade das águas. Ademais, por meio dessa tecnologia é possível concentrar os sais do vinhoto, dentre os quais o potássio, possibilitando sua utilização como adubo concentrado na agricultura. Aspectos como pré-tratamento, uso de diferentes membranas e configurações e soluções eletrolíticas com o enfoque de aplicação no solo foram avaliados. No que tange ao pré-tratamento, observou-se que a ultrafiltração, por remover parte considerável dos sólidos do vinhoto, minimiza a incrustação das membranas. Três configurações foram testadas: (1) membranas catiônicas e aniônicas seletivas monovalentes, (2) membranas catiônicas e aniônicas não monoseletivas e (3) configuração mista (uma membrana seletiva catiônica e as demais não seletivas). Os resultados revelaram que a configuração mista foi capaz de recuperar, após 8 horas, a 0,11 A, 72% de potássio com o menor consumo de energia (0,5 kWh.m<sup>-3</sup>) e a maior eficiência de corrente (54%). A remoção de potássio do vinhoto permite um aumento de 5 vezes na dose de aplicação do vinhoto no solo e consequentemente redução no custo de transporte do mesmo para aplicação no solo. Soluções de sulfato de sódio, sulfato de magnésio, nitrato de amônio e sulfato de potássio e água de torneira foram testadas. Soluções eletrolíticas de sulfato de magnésio e nitrato de amônio propiciaram melhores condições, no que tange à maior recuperação e remoção do potássio e maior potencial de aplicação do vinhoto como fertilizante. Foi avaliado ainda o potencial de recuperação do potássio do concentrado catódico na forma de K-estruvita e, por fim, uma avaliação primária de custos foi realizada. Desta forma, alinhado aos princípios da economia circular, o presente projeto de pesquisa propõe uma rota de tratamento para o vinhoto norteadada pela sua valoração por meio da recuperação de subprodutos e reúso agrícola da água.

Palavras-chave: Eletrodialise, Potássio, Membrana seletiva monovalente, Fertilizante.



## ABSTRACT

Brazil is the largest producer of sugarcane in the world, making the sugar and alcohol sector one of the activities of great relevance for the country. In many distilleries the fertigation is adopted, in which the vinasse returns to the crops, bringing beneficial results, however, if applied in excess, it can cause serious negative impacts. Potassium is the predominant ion in the vinasse, and because its high concentration, there are legislations that limit the application of vinasse in agricultural soil. The use of electrodialysis, a membrane separation process in which there is ionic transport under the influence of an electric field, enables, with the reduction of the potassium content of the vinasse, the increase of the rate of application of this effluent already widely used for fertigation, without compromising the soil, the crop and quality of water. In addition, by means of this technology it is possible to concentrate the salts of the vinasse, among which the potassium, enabling its usage as concentrated fertilizer in agriculture. Aspects such as pre-treatment, use of different membranes and configurations and study of different electrolyte solutions with the application focus in the soil were evaluated. Regarding pretreatment, it was observed that ultrafiltration, by removing much of the solids from the vinasse, minimized the inscrustation of the membranes. Three configurations were tested: (1) monovalent selective cationic and anionic membranes, (2) non-monoselective anionic and cationic membranes and (3) mixed configuration (one cationic selective membrane and the others nonselective membranes). The results revealed that the mixed configuration was able to recover, after 8 hours, with a current of 0.11A, 72% of potassium with the lowest energy consumption ( $0.5 \text{ kWh.m}^{-3}$ ) and the best current efficiency (54%). The removal of potassium from vinasse allows an increase of 5 times the dose of vinasse application and consequently reduction of the transport cost in the fields. Solutions of sodium sulfate, magnesium sulfate, ammonium nitrate and potassium sulfate and tap water were tested. Electrolyte solutions of magnesium sulphate and ammonium nitrate provided better conditions, considering greater recovery and removal of potassium and greater potential use of vinasse as fertilizer. The potassium recovery potential of cathodic concentrate in the form of K-struvite was also evaluated and, finally, a primary cost assessment was performed. In this way, in line with the principles of circular economy, the present research project proposes a treatment route for vinasse guided by its valuation through the recovery of by-products and agricultural reuse of water.

Keyword: Electrodialysis, Potassium, Monovalent selective membrane, Fertilizer.

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## LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

A	Area
ANA	National Water Agency
APHA	American Public Health Association
ASR	Apparent stack resistances
AOL	Applied Organic Load
BOD	Biochemical Oxygen Demand
CA	Compartment Concentrated Anodic
Can	Compartment Anodic
CC	Compartment Concentrated Cathodic
Ccat	Compartment Cathodic
CE	Current efficiency
C/N	Carbon/nitrogen ratio
CETESB	Environmental Technology and Sanitation Company
$C_i$	Concentration of ion
COD	Chemical Oxygen Demand
CONAMA	National Council for the Environment
COPAM	Environmental Policy Council
CEC	Cation Exchange Capacity
$C_f$	Feed conductivity
E	Energy
EC	Electrical conductivity
ED	Eletroctrodialysis
EDS	Energy dispersive X-ray spectrometer
F	Faraday constant
$h_f$	Length of feed channel
I	current
$J_i$	Flux of ion
MAP	$MgNH_4PO_4 \cdot 7H_2O$ (Struvite)
MPP	$MgKPO_4 \cdot 6H_2O$ (K-Struvite)
MS	Membrane surface
MSP	$MgNaPO_4 \cdot 7H_2O$ (Na-Struvite)

N	Number of membrane pairs
NF	Nanofiltration
PAR	Potassium absorption ratio
R	Recovery
$R_f$	Feed solution resistance
SAR	Sodium absorption ratio
SEC	Specific energy consumption
SEM	Scanning electron microscope
$S_B^A$	Selectivity
t	Time
$T_i$	Transport number of ion
UF	Ultrafiltration
V	Voltage
$VAR_{max}$	Maximum vinasse application rate
$V_e$	Effluent volume
Z	Valence
$\delta$	Thickness of boundary layer

# **CHAPTER 1**

---

## **INTRODUCTION**

## 1.1 BACKGROUND

Sugarcane is one of the world's major crops, grown in more than 100 countries, basis for sugar, ethanol, bioelectricity and other derivatives. Brazil is the largest producer of sugarcane, with an approximate production of 650 million tons per year (2016/2017 harvest) (UNICA, 2017), making the sugar and alcohol sector one of the activities of great relevance in the country's economy.

Regarding the sugar fabrication, Brazil is the largest producer in the world. In the 2016/2017 cycle, Brazil produced almost 39 million tons and exported 28 million tons of sugar - amounts equivalent to 20% of global production and 40% of all sugar exported in the world, respectively. In the case of ethanol, the country is the second largest producer, after the United States. In the 2016/2017 harvest, the volume produced reached 27 billion liters, with a decrease in this value among the last crops (UNICA, 2017).

The sugarcane industry, like any other industrial activity, causes environmental impacts arising from the generation of waste, whether gaseous, solid or liquid. With respect to liquid effluents, it is noted that the effluent with the greatest pollution power is vinasse, a byproduct of the ethanol production process obtained from the distillation of the fermented sugarcane juice. For each liter of ethanol produced, 10 to 15 liters of vinasse are generated (DECLoux et al., 2002). According to Freire and Cortez (2000), this effluent is characterized by a high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), the latter being in the range of 12,000 to 20,000 mg.L<sup>-1</sup>, besides being rich in potassium, sulfate, calcium and other minerals.

### 1.1.1 *Vinasse characterization*

The physical and chemical characteristics of vinasse are quite variable, due to a series of factors that range from the cane crop (soil, agricultural inputs, harvesting forms) to practically all the productive stages in the industry (type of must used, yield of fermentation, distillation efficiency, among others). The main constituent of vinasse is the organic matter, basically in the form of organic acids. In addition to organic matter, cations such as potassium, calcium and magnesium are present in relevant quantities. Although variations occur, the concentrations of sulfate and potassium are generally quite high, as opposed to concentrations of nitrogen and phosphorous, which may be present at relatively low to very high levels. The effluent also



presents high concentration of solids, characteristic strong smell, dark color and high turbidity (MACHADO and FREIRE, 2009).

The nutritional richness of vinasse is linked to the origin of the must. According to Barros et al. (2010), the molasses wort is richer in nutrients and presents nitrogen, phosphorus and potassium on average concentrations of: 0.57; 0.10; 3.95 kg.m<sup>-3</sup> in the vinasse, respectively. Mixed must, produced in distilleries, has levels of approximately 0.48 kg N.m<sup>-3</sup>; 0.09 kg P.m<sup>-3</sup> and 3.34 kg K.m<sup>-3</sup>. The broth wort shows average levels of N, P and K around 0.028; 0.09; 1.29 kg.m<sup>-3</sup> in the vinasse, respectively. Gemtos, Chouliaras and Marakis (1999) indicate that the concentration of sodium in sugarcane vinasse is lower than that of beet.

In general, vinasse is the distillery effluent of greater polluting potential and higher fertilizer value. Its polluting power, about one hundred times greater than that of domestic sewage, derives from its richness in organic matter, low pH, high corrosivity and temperature that can reach up to 90 °C (ROSSETTO, 1987), while its high fertilizer value, derived from its nutritional wealth, may allow its application in the agricultural soil.

### ***1.1.2 Typical application and treatment of vinasse***

With the advent of the Act of the Ministry of the Interior N°. 323 of November 29, 1978, the launching of vinasse in any water collection was prohibited, so that the industries looked for new alternatives of disposition. Therefore, the vinasse, previously released in the water course, started to be released in the soil, mostly by fertigation, meaning a low cost disposal method, as it does not require large investments and use of advanced technology and still use the potential of soil fertilization (CANELLAS et al., 2003).

Fertigation is a simple practice in which the vinasse is pumped or transported by channels and sprinkled on the cane fields. However, this practice is only economically feasible for short distances due to the cost of pumping. The great advantage of the use of vinasse in the fertigation is that this effluent can almost completely replace the nutrients provided in the mineral fertilization and still provide water for the crop in the periods of drought.

Considering the water recycling aspects, approximately 150 m<sup>3</sup> of fresh water are saved per hectare in each application, which corresponds to the average vinasse application rate (BNDES and CGEE, 2008; SILVA et al., 2014; ZOLIN et al., 2011). Regarding the nutrients presented

in vinasse, the reduction in the application in the crops, through mineral fertilization, of nitrogen is about 25% (SIVALOGANATHAN et al., 2013), while for potassium (as potash -  $K_2O$ ) and phosphorus (as  $P_2O_5$ ) the reduction may reach up to 50 and 80% (BNDES and CGEE, 2008), respectively. The presence of calcium and magnesium, also common in vinasse, enhances its fertilizing potential (ENSINAS et al., 2009). Furthermore, fertigation has low initial investment and maintenance cost and fast application (SANTANA and MACHADO, 2008; CRUZ, 2011). However, it is still unclear if the disposition of vinasse in the soil is indeed environmentally beneficial (RESENDE et al., 2006).

The lack of consensus about the polluting capacity of vinasse is exhibited by two main lines of thought in literature that indicate, on one side, beneficial effects and free environmental risk by rational use, and on the other side, deleterious effects on soil, ground and surface waters with non-rational application (PRADO, CAIONE and CAMPOS, 2013).

Properly used, vinasse contributes to improvements in soil properties and quality (NEVES, LIMA and DOBEREINER, 1983; SILVA et al., 2006; BEBE et al., 2009; BRITO, ROLIM and PEDROSA, 2009; ZOLIN et al., 2011; MENG et al., 2009; YOU et al., 2009; GEMTOS CHOULIARAS and MARAKIS, 1999; BUENO et al., 2009; MADEJON et al., 2001) and agricultural productivity and development of sugarcane (LI et al., 2008; MO et al., 2009; PAULINO et al., 2002; RESENDE et al., 2006; ZHOU et al., 2008; ZHOU et al., 2009; AO et al., 2009). Studies disposing vinasse in soils, conducted by Camargo, Valadares and Geraldi (1983), Glória and Orlando Filho (1983), Laime et al. (2011) and Jiang et al. (2012), have reported beneficial effects on crops and physico-chemical properties of the soils, as it increases moisture retention, porosity, potassium levels and electrical conductivity, in addition to biological activity. According to Fuess and Garcia (2014), there is an increase in the soil's potential in retaining water and increase in the soil's cation exchange capacity (CEC), which improves its capacity in retaining and releasing nutrients to the plants, especially potassium, calcium and magnesium. Some authors even suggest that their use is beneficial to soil physical attributes, such as stability and average weighted diameter of aggregates (VASCONCELOS et al., 2010)

On the opposite side, the direct application of vinasse in the soil, with higher dosages than the adequate, can cause salinization, leaching of metals present in the soil to groundwater, changes in soil quality due to unbalance of nutrients, mainly manganese (AGRAWAL and PANDEY,

1994), crop losses (KUMAR and VISWANATHAN, 1991), increase of phytotoxicity and unpleasant odor (NAVARRO, SEPÚLVEDA and RUBIO, 2000; SANTANA and MACHADO, 2008). Some studies have assessed the polluting potential of vinasse in the soil and water table (LYRA, ROLIM and SILVA, 2003; TENÓRIO et al., 2000) and a change in the physico-chemical characteristics of groundwater after intensive fertigation with vinasse has been noted in sandy soils and temperate climate by Hassuda (1989); Ludovice (1997) and Piacente (2005). According to Rodrigues and others (2017), excessive vinasse application in soil during tillering and in the initial growth phase causes nutrient leaching; this is in addition to salinization, due to salt concentrations that appear because of mineral excess, which can cause cationic imbalance. Moreover, successive applications in sandy soils can lead to an unbalance of bases and elements such as calcium, magnesium, potassium, and sodium, which are used to evaluate soil fertility (SILVA, GRIEBELER and BORGES, 2007).

High rates of K fertilization can increase soil erosion, (AUERSWALD et al., 1996) can cause clay swelling and dispersion as well as increasing overall soil salt levels and hence degrade soil quality and land productivity (MARCHUK and RENGASAMY, 2010). Some researchers (SMILES and SMITH, 2004a,b; KRUGER, TAYLOR and FERRIER, 1995; ARIENZO et al., 2009; RENGASAMY and MARCHUK, 2011) have reported a reduction in saturated hydraulic conductivity from the accumulation of exchangeable K. Auerswald et al. (1996) also reported high concentrations of sediments ( $15 \text{ g.L}^{-1}$ ) in water, which evidenced the disruption of the soil structure due to the high inputs of potassium. Mariano et al. (2009) and Rolim et al. (2013) have reported significant rises in groundwater potassium concentrations after stillage land application ( $\sim 10\text{-}380 \text{ mg.L}^{-1}$ ), which could indicate the soil saturation with  $\text{K}^+$  ions. Thus, elevated potassium concentrations in wastewaters could limit their disposal onto land (ARIENZO et al., 2012).

Organic matter has a direct influence on the chemical properties, physical and biological properties of the soil and it is considered an extremely important element in agricultural productivity. When the organic matter contained in the vinasse is incorporated into the soil, it is colonized by fungi, which in humus, neutralizing the acidity of the medium, providing the proliferation bacterial. Therefore, vinasse also favors the development of these microorganisms, which act in the biological fixation of nitrogen (SILVA, GRIEBELER and BORGES, 2007). But, any source of organic matter, macro or micronutrients used in soil can be considered as potential sources of pollution when not well managed (SILVEIRA, 2016).

The introduction of vinasse through the fertigation of sugarcane crops is a widespread practice in Brazil, being carried out in almost all the distilleries (CORTEZ, MAGALHAES and HAPPI, 1992, CORAZZA, 2006). In order to avoid soil saturation and guarantee its natural characteristics, legislation was proposed both in Minas Gerais and São Paulo in order to limit the amount of vinasse to be applied in the soil. The Normative Resolution COPAM nº 164 of March 30, 2011 discusses the application of vinasse in agricultural soil and mentions that when there are no adequate application criteria or when applied at high rates, vinasse may lead to the alteration of the natural conditions of the soil fertility and salinization problems, also creating anaerobic conditions and risk of contamination of surface and groundwater (MINAS GERAIS, 2011). In this way, in its Article 8º, it is prohibited the application of vinasse at rates higher than the nutritional requirements of the crop. In sugarcane cultivation it must be adopted the equation recommended by the Soil Fertility Commission of the State of Minas Gerais, as Equation 1.1.

$$D = \frac{[(CEC_{\text{potential}} \times 94) + 185]}{TK} \quad (1.1)$$

Where:

D = Vinasse dose (in  $\text{m}^3 \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ );

$CEC_{\text{potential}}$  = cation exchange capacity, obtained by soil analysis; soil potential at pH 7 ( $\text{cmol}_c \cdot \text{dm}^{-3}$ );

94 = factor obtained considering 5% of the  $CEC_{\text{potential}}$  and a soil depth of 40 cm;

185 = sugarcane extraction capacity ( $\text{K}_2\text{O}$ , in  $\text{kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ ), obtained by considering the average productivity of ratoon's cutting (about  $80 \text{ t} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ ) and an average  $\text{K}_2\text{O}$  extraction of  $2.33 \text{ kg} \cdot \text{t}^{-1}$  cane sugar per year;

TK =  $\text{K}_2\text{O}$  content of vinasse ( $\text{kg} \cdot \text{m}^{-3}$ ); considering that for high  $CEC_{\text{potential}}$  soils at pH 7 ( $> 15 \text{ cmol}_c \cdot \text{dm}^{-3}$ ), use up to a maximum of  $700 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$  of  $\text{K}_2\text{O}$ .

With this restriction to the application of vinasse in the soil and high water demand in the production processes of the distilleries, many studies are looking for treatment alternatives for this effluent. There are several treatment processes for the vinasse that are being researched:

physico-chemical treatments such as coagulation, flocculation and sedimentation, stabilization ponds, biological filters, anaerobic and aerobic reactors, treatments using fungi and algae, membrane separation processes and advanced oxidative processes (SANTOS, 2013).

Another important aspect, which aims at greater sustainability in the sector prioritizing by-product recovery, is the energetic use of vinasse, through anaerobic biodigestion and biogas production. This technology has been increasingly studied, since it represents an alternative of supplying of sustainable energy and contributes to reduce the polluting potential of vinasse. There are some challenges for anaerobic digestion that include, among others, temperature (CHEUNBARN and PAGILLA, 2000), pH (FORESTI, 1999), C/N ratio (SGORLON et al., 2011) and salinity that modifies the characteristics of the sludge and the microbial community (REID, LIU and JUDD, 2006; YOGALAKSHMI and JOSEPH, 2010). In relation to salinity, the vinasse has high concentrations of ions, especially of potassium, that leads to the reduction of the biodegradation efficiency.

The high salt levels present in many biorefinery waste streams can severely inhibit efficient bio-methanation (SATYAWALI and BALAKRISHNAN, 2008; LIM, 2013; KHANDEGAR and SAROHA, 2012) with methane production being severely reduced when concentrations of particular species (for example, potassium  $> 2.5 \text{ g L}^{-1}$ , sodium  $> 5 \text{ g.L}^{-1}$ , sulfide  $> 0.2 \text{ g.L}^{-1}$ , or ammonium  $> 1 \text{ g.L}^{-1}$ ) were excessive (CHEN, CHENG and CREAMER, 2008; FANG, BOE, and ANGELIDAKI, 2011; ELFERINK et al., 1994; KHAN and TROTTIER, 1978; KUGELMAN and MCCARTY, 1965)

Identification of a suitable technology to separate salts from organics in biorefinery wastewaters could potentially lead to a substantial improvement in anaerobic digester performance and hence the energy recovery possible through biogas production. Desalting might not be viewed simply as a treatment cost, as it may be possible to valorize the concentrated salt streams in a range of ways. For example, streams rich in potassium and/or ammonium could potentially be further concentrated (e.g. using reverse osmosis) and incorporated into saleable fertilizers (CALCINO, 2017; WILMAR, 2017). Similarly, effluent streams rich in sulfate ions (resulting from cellulose hydrolysis) could be used to produce sulfuric acid which could be recycled back into the process, thereby reducing the amount of fresh acid needed (GOLDSTEIN et al., 1989). In order to address this aim, it is clearly necessary to identify a suitable technology which can reliably and cost-effectively separate salts from organic species (LUIZ et al., 2017).

The high concentration of K limits, therefore, both the application in the soil and the methanization of the vinasse, by making the biological medium saline, reducing the diversity of microorganisms in the reactor. Thus, the prospect of recovery of potassium of vinasse envisions the improvement of the sustainability of the sector, allowing the optimization of the energy utilization of this effluent, besides increasing the rate of application in the soil, enlarging the prism of fertigation, contributing with the financial and environmental aspects.

Also, Brazil is one of the most important agricultural powers in the world, with growing export targets. However, fertilizers are extremely demanded by agriculture to meet its internal needs, so the goal is to reduce the import of nitrogen, phosphate and potassium, in order to guarantee greater profitability for agribusiness. Brazil's biggest deficiency in fertilizers is owing to potassium, responsible for the import of million tons of  $K_2O$ . Due to that, new sources of potassium, rather than the mineral fertilizer, must be scrutinized and the recovery of potassium from wastewaters, reusing nutrients present in materials initially considered as waste, which impact the environment less, is of great interest (SILVA et al., 2017; VERSTRAETE, CLAUWAERT and VLAEMINCK, 2016).

There are some viable technologies for potassium recovery as precipitation, ion exchange, and membrane separation processes, such as reverse osmosis and electrodialysis (ED). ED stands out for giving greater selectivity, giving the by-product a greater degree of purity.

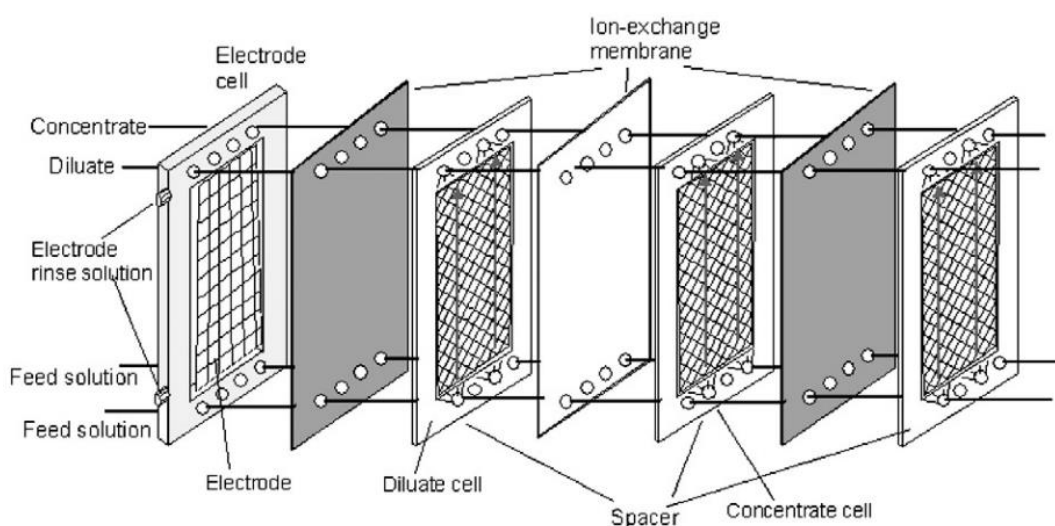
By means of ED, therefore, it is possible to concentrate the salts of vinasse, among those the potassium, in which the value-added solution can be sold or used in sugarcane crops as fertilizer. Concurrently, the generation of a desalinated stream, the treated vinasse with much lower concentration of ions, can be applied in the fertigation with higher rate, without compromising the needs of the crop, the health of the soil and the environment.

### **1.1.3 Electrodialysis**

Electrodialysis has been used for over 50 years for the production of drinking water from brackish water sources. Since then, with the improvement of the membranes and their characteristics and improved properties, several processes related to electrodialysis have been developed, enabling a series of new applications in water and wastewater treatment, as well as application in industrial effluents (STRATHMANN, 2010; KARIDURAGANAVAR, KITTUR and KULKARNI, 2012).

Electrodialysis is a membrane separation process in which ionic ions are transported under the influence of an electric field, and in this transport two solutions are generated, one more concentrated and the other more diluted than the original (JAMALUDDIN et al. , 1995, ROWE and ABDEL-MAGID, 1995, SOLT, 1971, BIRKETT, 1978, GENDERS and WEINBERG, 1992).

The ED system consists of cationic and anionic membranes arranged alternately between a cathode and an anode. Between the membranes are placed spacers, made of polymeric material, used to separate the membranes and improve the mass transfer conditions. The saline solution is pumped into the cell and an electrical potential difference is applied between the electrodes, which causes the cations to migrate towards the cathode and the anions towards the anode. The cations will pass easily through the cationic membranes, but will be retained by the anionic membranes. The same will occur with the anions, which will be retained by the cationic membranes, but will pass easily through the anionic membranes. This phenomenon results in an increase in the concentration of ions in alternating compartments, while the other compartments are desalinated. The solution most concentrated in ions is referred to as the concentrate, while the less concentrated solution is named diluted. (BAKER et al., 2004). Each set cationic membrane, spacer through which the diluted solution circulates, anionic membrane and spacer through which the concentrate solution circulates forms a pair of cells. Figure 1.1 shows the scheme of an electrodialysis cell.



**Figure 1. 1 - Components of a ED unit.**

STRATHMANN (2010)

The ionic transport through the ED membranes is governed by three types of mechanisms: convection, diffusion and electrodifusion (migration). The convection is mainly caused by the difference in hydrostatic pressure and, although it is negligible inside the membranes, it acts significantly inside the solution, and the more turbulent the flow of the solution, the better the convective transport. Diffusion, in turn, occurs due to the chemical potential gradient caused by the difference in concentration of the species, which migrate from one compartment to another diffusively. Finally, electromigration results from the difference of electric potential applied to the system and is the main transport mechanism in the membranes, responsible for the ionic movement (SCARAZZATO, 2013; GALUCHI, 2010).

The movement of cations and anions through the membranes promotes the circulation of electric current in the ED unit according to the transport number of the ions (T, dimensionless). The transport number indicates the charge carried by the ions and is defined by the relationship between the valence (z, dimensionless), the flow of the species (J, mol.s<sup>-1</sup>.m<sup>-1</sup>) and the applied current density (i, A.m<sup>-2</sup>), according to equation 1.2 (BAKER, 2004; SCARAZZATO, 2013; GALUCHI, 2010).

$$T = \frac{z.F.J}{i} \quad (1.2)$$

Where F is the constant of Faraday (96.500, C.mol<sup>-1</sup>).

The ion transport number is influenced by the charge, ion size and concentration, ion conductivity, pH and medium temperature and current density applied. Since there is a direct relationship between the charge and the size of the ion and its mobility, ionic species of the same size will be differentiated by their charge; similarly, ions of the same charge will be differentiated by their atomic radius. Higher charged or smaller sized species are more mobile (SCARAZZATO, 2013).

As can be observed from Table 1.1, the mobility of the different ions in aqueous solution does not vary much, except for the H<sup>+</sup> and OH<sup>-</sup> ions, since their mobility is higher due to their different transport mechanism.



**Table 1. 1** - Ionic mobility in water in the limit case of infinitely diluted solutions.

Cations	$u$ ( $10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ )	Anions	$u$ ( $10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ )
$\text{Li}^+$	4.01	$\text{F}^-$	5.7
$\text{Na}^+$	5.19	$\text{Cl}^-$	7.91
$\text{K}^+$	7.62	$\text{Br}^-$	8.09
$\text{NH}_4^+$	7.63	$\text{NO}_3^-$	7.4
$\text{Ca}^{2+}$	6.17	$\text{SO}_4^{2-}$	8.29
$\text{Cu}^{2+}$	5.56	$\text{CO}_3^{2-}$	7.46
$\text{H}^+$	36.23	$\text{OH}^-$	20.64

ATKINS (1990) apud STRATHMANN (2004), p.77.

Thus, the ionic separation promoted by electrodialysis is based on the difference between the transport numbers of the ions in the solution and in the membranes. As the ions present in the membrane are fixed in their polymer matrices, the transport of electric current in the membranes is carried out only by the mobile cations referred to as counter-ions (STRATHMANN, 2004). Thus, the equation 1.3 describes the transport of ions across membranes, according to Baker (2004).

$$i = \frac{F}{1-T} * \frac{D}{\delta} * (c - c_{(0)}) \quad (1.3)$$

Where  $i$  is the applied electric current density ( $\text{A.m}^{-2}$ ),  $F$  is the Faraday constant ( $96,500 \text{ C.mol}^{-1}$ ),  $T$  is the ion transport number (dimensionless),  $D$  is the ion diffusion coefficient in water ( $\text{m}^2 \text{ s}^{-1}$ ),  $\delta$  is the thickness of the boundary layer ( $\text{m}$ ),  $c$  is the concentration of the ion in the solution and  $c_{(0)}$  is the concentration of the ion at the interface of the membrane ( $\text{mol.m}^{-3}$ ).

In addition to the ionic movement, reactions of reduction (cathode) and oxidation (anode), promoting the formation of  $\text{H}_2$  and  $\text{O}_2$ , respectively, according to the reactions are observed in the compartments that are in contact with the electrodes (BENVENUTI, 2012):



Hydrogen has a lower atomic radius than the other ions, consequently presenting greater mobility and becoming a preferential species in the transport of ions. This preferential transport of hydrogen can cause changes in pH and increase the electrical resistivity of the solution, interfering negatively on the performance of ED. Thus, in order to avoid this effect, the anodic and cathodic compartments must be filled with saline solution, which maintains the conductivity of the system without interfering in the process (SCARAZZATO, 2013).

In any practical electrodialysis process, the current flowing through the stack cannot be utilized entirely for desalting the feed solution. Several factors may contribute to incomplete current utilization in an electrodialysis stack since the membranes are not perfectly selective, due to water transfer across the membranes, due to osmosis and electroosmosis, etc. Thus, the total current efficiency is defined as the current required in practice to obtain a certain amount of product water of a given quality divided by the theoretically required current (STRATHMANN, 2004).

One phenomenon that occurs in all membrane separation processes is concentration polarization. In ED occurs as a result of the difference between the transport numbers of the ions in the solution and in the membranes, and the number of transport is a function of the ion concentration. As the concentration of the ionic species is continuously changed during the ED process, the mobility of the ions in the membranes and in the solution is also altered (STRATHMANN, 2010).

On the surface of a membrane in contact with the diluted solution, the transport number of the ions in solution is much lower than the transport number of the ions in the membrane, causing a smaller number of ions to be transported from the solution to the surface of the membrane than the number of ions that are removed by the membrane. This effect causes a reduction in the number of ions at the interface of the membrane and generates a concentration gradient, promoting diffusive transport. Similar effect occurs on the other surface of the membrane, facing the concentrated solution. The accumulation of charges at the interface of the membrane is the result of the higher amount of ions transferred by the membrane than the solution is able to transport, generating a new concentration gradient and causing diffusion ions transport (SCARAZZATO, 2013; GALUCHI, 2010).

Thus, a reduction in the electrolyte concentration in the solution present in a thin layer near the surface of the membrane (boundary layer) occurs and a concentration gradient is formed

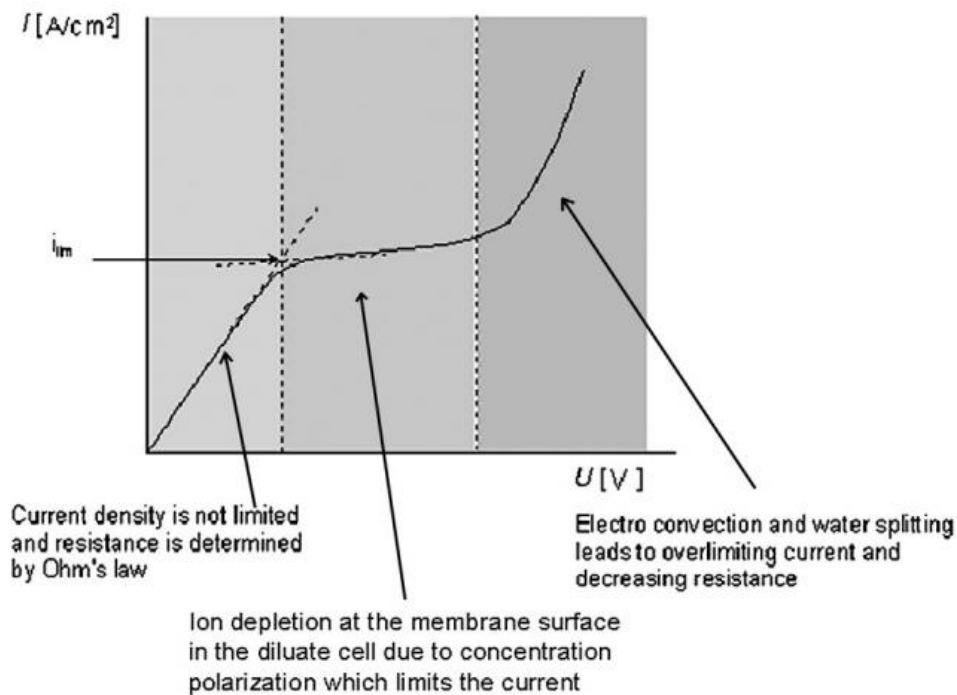
between the membrane surface and the solution core. This phenomenon in which the number of ions in one of the membrane interfaces tends to zero, while in the other interface there is accumulation of charges due to the difference in the migration speed of the ions through the membrane and in the solution is the concentration polarization.

At a certain point, the number of ions that cross one of the membrane interfaces will tend to zero, indicating the maximum current that can pass through the membrane, that is, the limiting current (BAKER, 2004; STRATMANN, 2004; ROCZANSKI, 2006 ).

The limiting current density of a given system depends on the concentration of the feed, the type of membrane used, the concentration of salts in the diluted and the flowrate of the solution in the cell (ZHENG et al., 2015; BUZZI et al., 2014 ). Once the limiting current is reached, any increase in the potential difference across the membrane will not increase the ion transport or the current through the membrane. If the potential difference exceeds the limit value, secondary reactions will occur, such as the dissociation of water at the interface membrane/solution with the generation of  $H^+$  and  $OH^-$  (BAKER, 2004; STRATHMANN, 2010).

The consequences of water dissociation are loss of current utilization and a drastic change in pH value: with an increase in the surface of the anionic membrane in the concentrate compartment and a decrease in the surface of the cationic membrane. Increasing the pH can lead to the precipitation of polyvalent ions on the surface of the membranes and lowering the pH can damage them (STRATHMANN, 2004).

According to Benvenuti (2012), current density should be kept below 80% of the limiting current density, since values higher than this would cause excessive energy expenditure. The current limit value can be determined by different methodologies, according to Baker (2004), being the most usual the one based on the construction of a voltage (V) versus applied current density ( $mA.cm^{-2}$ ) curve, called polarization curve, shown in Figure 1.2.



**Figure 1. 2** - Current density versus voltage curve.

STRATHMANN (2010)

This type of curve has three well-defined regions. In the first, the ohmic region, the resistance in the ED cell is constant and the current density increases linearly with the voltage according to Ohm's law ( $V = R \cdot i$ ). The second region, is characterized by the occurrence of a *plateau* that begins with the value of the limiting current density. The stability of the current value, even with the increase of the potential difference, is due to the zero concentration of salts on the surface of the membrane, which makes it impossible to carry electric current. The resistance increases dramatically until a point where the resistance of the cell decreases with the increase of voltage (third region: region of over-limiting current), that is, the current increases linearly again with the applied voltage, caused by the decoupling of the molecules of water which begin to conduct electric current (MARDER, 2002).

The occurrence of the concentration polarization causes the electrical resistance of the compartments between membranes to become higher than the resistance of the membranes. In an ideal system, electric potential drops should only occur through the membranes (BAKER, 2004). Thus, the dissipation of electric potential becomes greater during the transport of ions through the boundary layer than during the passage of ions by the membranes themselves, causing the energy consumption of the process to increase significantly (NOBLE and TERRY,

2004). In addition, there may be accumulation of ions on the surface of the membrane towards the concentrate, which may lead to salt precipitation when the concentration exceeds the solubility limit of these salts (STRATHMANN, 2010).

As in the solution the flow is turbulent, the concentration polarization does not occur within the solution, only in the boundary layer. Thus, the reduction of the laminar layer and the increase of the turbulence within the solution (for example, through the use of spacers) are ways of minimizing the effects of concentration polarization (ROCZANSKI, 2006; SCARAZZATO, 2013).

Ion exchange membranes can be considered as ion exchange resins in film form (STRATHMANN, 2004). The two types of ion exchange membranes used in electrodialysis are (VALERO-CERVERA, BARCELÓ and ARBÓS-SANS, 2011):

- Polymer structures carrying negatively charged groups and enabling the permeation of cations are referred to as cation exchange membranes. Commercial cation membranes generally consist of crosslinked polystyrene that has been sulfonated to produce  $-\text{SO}_3\text{H}$  groups attached to the polymer, in water this group ionizes, producing a mobile counter-ion ( $\text{H}^+$ ) and a fixed charge ( $-\text{SO}_3^-$ ).
- Polymer structures carrying positively charged groups and enabling the permeation of anions are referred to as anion exchange membranes. Usually, the membrane matrix has fixed positive charges from quaternary ammonium groups ( $-\text{NR}_3^+$ ), which repel positive ions.

The properties of ion exchange membranes are determined by the base polymer and the type and concentration of the fixed charges. The base polymer determines the mechanical, chemical and thermal stability of the membrane. The type and concentration of the fixed ions determine the permselectivity and the electrical resistance (STRATHMANN, 2000). The most desirable properties for ion exchange membranes are high permselectivity, low electric resistance, good mechanical and form stability and high chemical stability.

The electrodialysis membranes can be deteriorated by fouling and scaling (LINDSTRAND JONSSON and SUNDSTROM, 2000a,b; AYALA, POURCELLY and BAZINET, 2006). The deposition of suspended matter on the membrane surfaces forming films causes the surface

fouling and scaling. Usually, small particles suspended are removed from a feed solution by using sand filtration, membrane filtration, such as microfiltration or ultrafiltration, coagulation sedimentation filtration, and others. Nevertheless, smaller particles may pass through the filter, enter into an electrodialysis system and deposit on the membranes (TANAKA, 2007). Organic ions, polyelectrolytes, suspended and colloidal matter and multivalent salts near the saturation level can cause severe problems in electrodialysis due to partial penetration into the membranes or by precipitation on the membrane surfaces. This precipitation also causes an electrical resistance increment of the stack and may lead to physical damage of the membranes (STRATHMANN, 2004; BERNARDES et al., 2013).

Organic fouling of an ion exchange membrane is caused by the precipitation of colloids on the membranes and is one of the major problems in electrodialysis. Since most of the colloids present in natural water are negatively charged, the anion exchange membranes are the most affected. Organic anions such as humates, for instance, can precipitate as humic acid and cause a drastic increase in the electric resistance. In general, mechanical and/or chemical cleaning can restore the original properties of the membranes, however a severe problem is the poisoning of membranes by organic anions that can penetrate the membranes due to small size, but whose electromobility is so low that these ions remain inside the membrane, provoking a sharp increase in the membrane resistance. (STRATHMANN, 2004; BAKER, 2004; BERNARDES et al., 2013).

#### **1.1.4 Use of ED for potassium recovery**

There are few articles that report the use of ED to reduce the level of potassium in distillery effluents and since the 1980s some works have shown good results. Wilde (1987) applied ED to molasses after pretreatment, obtaining 60% removal of potassium from the effluent with a current efficiency of about 50 to 55% and energy consumption of 0.75 to 0.85 kWh per kilogram of potassium removed. Milewski and Lewicki (1988) concluded that electrodialysis with cation and anion-exchange membranes remove 70-85% of ash from vinasse at a current density in the range of 5-15 mA.cm<sup>-2</sup> at 35 °C and at a vinasse concentration of 6-20 °Brix. The efficiency was assessed considering variation of temperature, current density and vinasse concentration. El Khattabi et al. (1996) studied nine pairs of multiple ion exchange membranes for ED for sugar cane juice and for one selected pair of membranes they observed 85% removal of ions (K and Na) from sugarcane juice at a current density of 27.77 mA.cm<sup>-2</sup>, also emphasizing that

pretreatment is interesting to avoid the fouling of the membranes with organic substances. Tako and Brahim (1993) tested ED for molasses obtained up to 89% of salt removal with 40 to 57% of organic loss. Thampy and others (1999) achieved from 50 to 90% of salt removal from sugar cane juice with only 0.4% organic loss and energy consumption of 2-2.5 kWh.m<sup>-3</sup>.

Decloux et al. (2002) tested the electrodialysis for ultrafiltrated vinasse (beet molasses), vinasse after sedimentation (sample collected directly from the top of a 200 liter tank) and raw vinasse (collected after shaking the tank). It was concluded that there were no significant differences in the efficiency of removal of potassium with raw and ultrafiltrated vinasse. Expressed in equivalents, the potassium concentration decrease was 0.5 equivalent with 0.2 m<sup>2</sup> membrane area in nearly 30 min, reaching a reduction of potassium in the effluent of 75% to 95%. Elmidaoui et al. (2006) applied ED to three solutions of sugar beet and obtained high removals of ions such as potassium, sodium and calcium. Finally, Luiz et al. (2017) studied biorefinery effluents including sugarcane juice and concluded that the salt removal rate for both potassium and total cations increased with the effluent concentration, reaching 6.8 mol L<sup>-1</sup> h<sup>-1</sup> m<sup>-2</sup> A<sup>-1</sup>. ED was capable to remove up to 63% ions from molasses effluent with minimal transfer (6.3%) of soluble organic matter through the ED membrane in the salt stream.

In these articles the saline solution used were usually sodium chloride, but also potassium chloride and potassium nitrate. The study of different electrolyte solutions were not considered, nor the potential use as fertilizer of the concentrated compartment.

## **1.2 JUSTIFICATION**

According to ANA (2009), the sugarcane sector has undergone a new cycle of growth since 1995, with the growing of sugar export and the resumption of ethanol consumption in 2001. Consequently, with the increasing production of the distillery products, vinasse is being more and more generated, aggravating the environmental problem of disposal of this effluent.

Fertigation is a very widespread practice among brazilian distilleries. Penatti et al. (1988) point out that the use of vinasse produces beneficial results in sugarcane productivity, besides generating savings with the acquisition of fertilizers. However, according to Freire and Cortez (2000), if applied in excess, it can cause serious changes in the quality of the raw material for the industry, such as the reduction of broth quality, as well as contaminate soil and ground and surface water bodies.

The potassium is the predominant and of greater importance ion in the vinasse (RODELLA and FERRARI, 1977; FREIRE and CORTEZ, 2000). On one hand its deficiency can cause serious problems to the plant, on the other hand the excess of this element may induce the lack of magnesium (MALAVOLTA, VITTI and OLIVEIRA, 1989) and increase the ash content in the broth (CASAGRANDE, 1991), besides conferring problems of salinization and risk of contamination of surface and groundwater. Therefore, Normative Resolution COPAM N°. 164 of march 30, 2011 limits the application of vinasse in soil. The maximum permitted application rate is a function of the potential CEC of the soil and the potassium content in the effluent.

Considering the above, potassium removal and recuperation of vinasse can bring several benefits. Firstly, the reduction of salts of vinasse contributes to biogas production in anaerobic reactors when the energetic use of vinasse is aimed. Also, when the fertigation is considered the best destination for vinasse, the reduction of potassium content would permit higher application rates. Finally, the stream concentrated in potassium, originally in vinasse, would compose a fertilizer by-product that could be sold and generate profit.

Potassium is the second nutrient most absorbed by plants and therefore with high demand in agriculture. The country has few deposits of potassium ore and is still deeply dependent on imports to meet domestic demand, with potassium chloride being responsible for a considerable amount of brazilian imports (DNPM, 2009).

According to Jiang and others (2012) after application of hight amount of vinasse in sugarcane fields, there is no need to apply K fertilizer, which generate economic benefits due to the panorama of importation of the mineral fertilizer.

Finally, this dissertation proposes to bring scientific advances, not only for ratifying the use of ED for the recovery of ions such as potassium, but also to contribute to aspects little addressed in the literature, such as the comparison between monovalent and non-monoselective membranes in different configurations and the study about electrolyte solutions for better soil applicability.



## **1.3 OBJECTIVE**

### **1.3.1 General objective**

The aim of this master thesis is to evaluate the efficiency of electrodialysis to remove and concentrate the potassium present in the vinasse in order to recover it as fertilizer, as well as obtaining a higher quality effluent for more intensive application in agricultural soils.

### **1.3.2 Specific objectives**

- Compare the potassium recovery efficiencies of raw and ultrafiltrated vinasse, analyzing the importance of ultrafiltration as a pretreatment;
- Evaluate the performance of three different configurations, using two distinct membranes, one selective to monovalent ions and the other non-monoselective, in the recovery of potassium; and
- Compare different electrolyte solutions regarding potassium recovery efficiency and potential use as fertilizer.

## **1.4 DOCUMENT STRUCTURE**

This master thesis is divided into 3 chapters: Chapter 1 is an introduction and contains a compiled revision of the literature, objectives and the document structure; Chapter 2 focuses on vinasse desalting, addressing the importance of ultrafiltration as a pretreatment for the ED process and the evaluation of the different membranes used by selecting the best configuration in terms of potassium recovery and energy consumption. Chapter 3 is the study of electrolyte solutions under the prism of agricultural application, considering the reference element and the use of both desalted vinasse, in higher dose in the soil, and the concentrated stream rich in potassium that can be used as fertilizer.

## **CHAPTER 2**

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# **INVESTIGATION OF ELECTRODIALYSIS CONFIGURATIONS FOR VINASSE DESALTING**

## 2.1 INTRODUCTION

Vinasse, a byproduct of the ethanol production process obtained from the distillation of the fermented sugarcane juice, is the effluent with the greatest pollution potential of distillery industries, and the production of this effluent is expected to increase with the ethanol production which is expected to keep growing for the next decade, reaching 134 billion liters in 2024 (OECD, 2015).

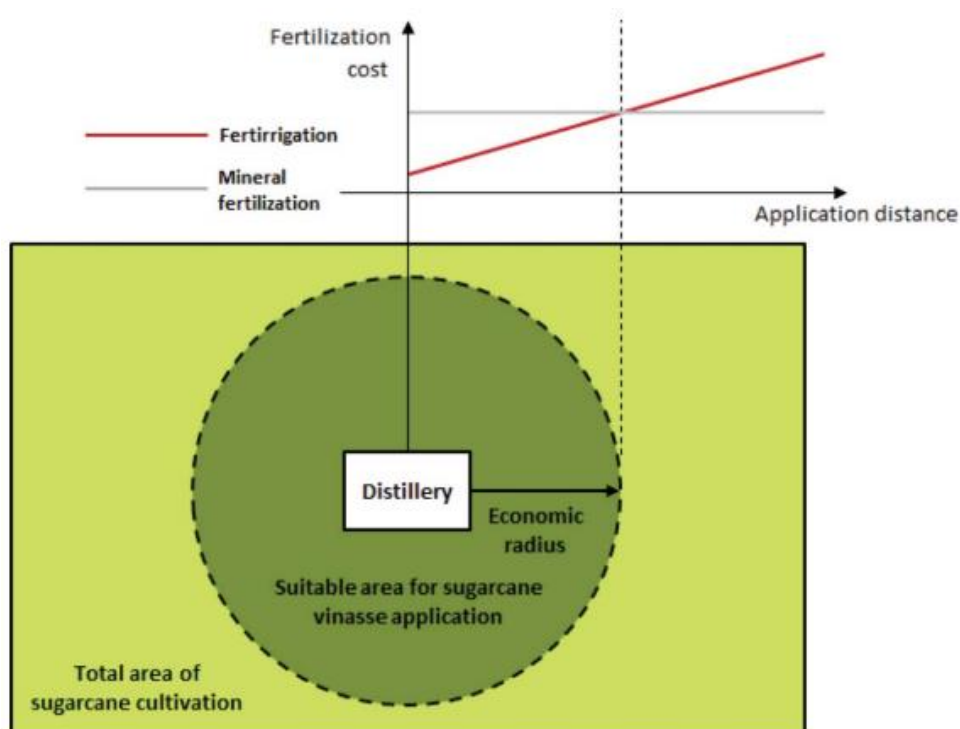
Due to its chemical composition, vinasse applications in soil are an effective economic alternative for sugar cane irrigation and fertilization, becoming a common practice in sugarcane refineries beginning in the 1980s (CORAZZA, 1996). Fertigation consists of the application of vinasse in the soil of sugarcane crops (CAMARGO et al., 2009). When applied in natura to the soil, sugarcane vinasse presents attractive possibilities, such as nutrient and water recycling, mitigating severe water shortages and lowering cost with synthetic fertilizers. (LAIME et al., 2011).

Several studies were developed on the positive and negative effects of the use of vinasse in the soil. The vinasse as fertilizer in sugarcane promotes changes in the physical, chemical and biological properties of the soil, which, when beneficial, increases the availability of some ions, improving soil CEC (cation exchange capacity), generates fertility, porosity and retention of water, collaborating for better development and productivity of cane (GLÓRIA and ORLANDO FILHO, 1983). However, application of high doses of vinasse can lead to soil acidification and salinization, loss of soil fertility, insect proliferation and contamination of groundwater (PANT and ADHOLEYA, 2007).

The continuous application of the vinasse in the same soils can cause cation saturation, mainly of potassium, causing problems of leaching of its constituents to the groundwater. High concentrations of K favor the formation of chemical complexes with neutral charge that are easily leached. The complex formed between  $K^+$  and  $NO_3^-$  is environmentally disturbing because nitrate is a major pollutant in waters (MUTTON, ROSSETO and MUTTON, 2007).

The fact is that the appropriate application of vinasse must take into consideration the characteristics of each soil, climatic conditions, the proximity of water collections, besides aspects like the history of vinasse application and the intensity of cultivation in the agricultural

area (PRADO, CAIONE and CAMPOS, 2013). Furthermore, it should be taken into account that the transportation of vinasse to the agricultural field depends on the radius of economic distribution (SILVA, 2012), detailed in Figure 2.1, which compares the application distance and the mineral fertilization cost, determining the limit distance in which the transportation of the effluent is economically feasible. As the vinasse generated in a distillery will be applied within a certain area of sugarcane cultivation, there will be concentration of a wide variety of organic and inorganic compounds in the soil. (FUESS, RODRIGUES and GARCIA, 2017)



**Figure 2. 1** - Economic radius for the transportation of sugarcane vinasse.

FUESS, RODRIGUES and GARCIA (2017).

With respect to fertigation in Brazil, the concentration of potassium defines the application rate into the sugarcane fields and higher rates may be used only if the value of K in relation to soil CEC is below 5% (CETESB, 2015). Traditionally, application of K to soils has been perceived as a benefit due to a large body of published research demonstrating the positive effects of K on soil fertility and crop yield (ARIENZO et al., 2008). However, in practical terms, the inputs of K (and other compounds) into the soils are much higher than the values calculated from the normative instruction, suggesting that the agricultural areas closer to the biorefineries are more susceptible to the negative impacts from fertigation (FUESS, RODRIGUES and GARCIA, 2017).

Concerning the exposed above, the environmental risks due to excessive inputs of potassium in soil and high cost of synthetic fertilizers, it is of great importance study technologies that can enable a more efficient and safety application of vinasse in the soil, considering the recycling of the large quantities of organic and inorganic residues produced as byproducts of the sugar and alcohol industries, in agriculture.

Anaerobic digestion is another attractive alternative for vinasse disposal. This process consists of the biodegradation of the vinasse organic load to produce biogas, enhancing the profitability of distillery through the generation of surplus electricity, and biodigested vinasse, reducing the polluting organic load of vinasse. Furthermore, the removal of nutrients in anaerobic digestion reactors is negligible, which means that the fertilizing potential of in natura vinasse is maintained in the treated effluents (MORAES, ZAIAT and BONOMI, 2015; SALOMON et al., 2011). Nevertheless, moderate to high vinasse salinities present a challenge to biological treatment, altering sludge characteristics and microbial community (YOGALAKSHMI and JOSEPH, 2010; REID, LIU and JUDD, 2006). Therefore, the reduction of salinity of vinasse also contributes to the prospect of its energy use, since it improves the efficiency of biodegradation and conversion of organic matter into biogas through bioreactors.

Electrodialysis is a membrane separation process in which ion transport is carried through ionic membranes (cation and anion membranes alternately positioned between a cathode and an anode) under the influence of electric field, and in this transport two solutions are generated, a more concentrated and a more diluted than the original (ROWE and ABDEL-MAGID, 1995; SOLT, 1971; JAMALUDDIN, 1995; GENDERS and WEINBERG, 1992). Therefore, the use of electrodialysis for vinasse treatment could generate two streams, a diluted stream that could be used for optimized biogas production or higher rate soil application, and a concentrated stream, rich in potassium and other ions, such as calcium and magnesium, that could be profitably commercialized as fertilizer.

ED is a mature technology, in which improvements in the manufacture of ion-exchange membranes have led to an increase in the number of new applications in water, waste water treatment and in various industry effluents (STRATHMANN, 2010). Conventional ED has limitations to separate ions of the same charge but different valence. Selective anion or cation exchange membranes have significantly different transport properties for monovalent and multivalent ions and consequently have capability to separate ions on the basis of their valence.

For a selective ED membrane, a very thin layer on the surface of conventional membranes allows the passage of only monovalent anions while restricting the passage of multivalent ions.

Regarding the distilleries, the reduction of potassium content of many sugar industry byproducts has been studied (WILDE, 1987; MILEWSKI and LEWICKI, 1988; TAKO and BRAHIM, 1993; EL KHATTABI et al., 1996; THAMPY et al., 1999; DECLoux et al., 2002; ELMIDAoui et al., 2006; YOGALAKSHMI and JOSEPH, 2010; LIM, 2013; LUIZ et al., 2017). In the preliminary experiments carried out by Decloux et al (2002), the beet vinasse potassium concentration decrease from 10 to 0.5 g.L<sup>-1</sup> by using electrodialysis. However the high vinasse organic load can contribute to membrane fouling and thus compromise process performance.

According to Buzzi and others (2014), a simple pretreatment, as centrifugation, might avoid contamination of membranes by organic matter, consequently minimizing membrane fouling. However, simple processes, as centrifugation, can have instabilities and low efficiency, then to ensure a good quality feed in ED it is important to use robust pretreatment processes such as ultrafiltration. In a previous article the authors evaluated ultrafiltration applied to vinasse treatment. By operating with a permeate recovery rate of 93%, the ultrafiltration showed complete retention of suspended solids and 55% of COD retention, evidencing its potential to be used as pretreatment of electrodialysis (MAGALHÃES et al., 2012).

In this context, this chapter aims to propose a selective ED system for vinasse processing and valuation by recovering potassium and producing a treated effluent (desalted vinasse) with attractive characteristic for fertigation or biogas production (anaerobic digestion). For that, the effect of three different configurations using two distinct membranes, a monovalent ion selective membrane and a non-monoselective heterogeneous membrane on key performance parameters (desalination rate/potassium recovery rate, current efficiencies of different ions, specific electrical energy consumption and membrane fouling) were investigated. The ultrafiltration (UF) was also evaluated as pretreatment stage for ED. Although substantial researches have been published involving electrodialysis over the last years, little information is available about the application of ED in potassium removal from high organic and inorganic concentration wastewaters sugarcane vinasse. Furthermore, only in 1996 it was evaluated different exchange membranes, including the selective membranes, for potassium recovery (El Khattabi et al., 1996), the other articles focused in other aspects, lacking more study on the

applicability of selective membranes in vinasse treatment by ED. At last, it was assessed the effect of desalination of vinasse in irrigation criteria and the feasibility of enlargement of vinasse application in soil with an environmental free risk way.

## 2.2 MATERIALS AND METHODS

### 2.2.1 *Vinasse and pretreated vinasse*

The vinasse used in this study was supplied by a distillery plant located in the state of Minas Gerais, Brazil, which produces ethanol from sugarcane juice. The plant has a production capacity of 1,100 m<sup>3</sup> day<sup>-1</sup> of ethanol, milling up to 2,500,000 tons of sugarcane per harvest. The samples were stored in a refrigerator at 4 °C until experimental trials. Electrodialysis experiments were conducted with raw and ultrafiltrated effluent and Table 2.1 exhibits values from a historical data series. The concentrate of the UF process can be used both in soil and biodigestion. Vinasse ultrafiltration were carried out in a bench-scale membrane filtration set-up which consists of two tanks (10 L - membrane and permeate storage tank), a diaphragm with a motor velocity controller, needle valves for flow adjustment, rotameter for permeate flow measurements and a manovacuumeter. The submerged UF membrane module (PVDF hollow fiber membrane, average pore size of 0.04 µm, total surface area of 0.9 m<sup>2</sup>, ZeeWeed 500D - GE) was operated at a pressure of 0.7 bar and a permeate recovery rate of 80%.

**Table 2. 1** - Values of physicochemical parameters of raw and ultrafiltrated vinasse.

Parameters	Unit	Raw vinasse	UF permeate
COD	mg L <sup>-1</sup>	30,468 ± 3,246	15,687 ± 1,398
Electrical Conductivity	mS cm <sup>-1</sup>	11,5 ± 1.2	9.5 ± 0.1
pH	-	4.5 ± 0.2	4.4 ± 0.1
Total suspended solids	g L <sup>-1</sup>	5.4 ± 0.1	-
Volatile Suspended Solids	g L <sup>-1</sup>	4,3 ± 0.1	-
Sodium	mg L <sup>-1</sup>	23 ± 6	15±4
Ammonium	mg L <sup>-1</sup>	131 ± 18	128 ± 6
Potassium	mg L <sup>-1</sup>	2693 ± 936	2699 ± 74
Magnesium	mg L <sup>-1</sup>	183 ± 17	159 ± 1
Calcium	mg L <sup>-1</sup>	653 ± 12	640 ± 9
Sulfate	mg L <sup>-1</sup>	1356 ± 225	1235 ± 38
Total phosphorus	mg L <sup>-1</sup>	44 ± 9	38 ± 2

## 2.2.2 Electrodialysis membranes

Two types of membrane were tested. The NEOSEPTA® CIMS selective monovalent cation exchange membrane and the NEOSEPTA® ACS selective monovalent anion exchange membrane - both from ASTOM Co., Japan - were compared to the non-monoselective heterogeneous HDX membranes provided by Hidrodex® (Table 2.2).

**Table 2. 2** - Properties of membranes.

<i>Parameter</i>	<i>HDX 100 (Cationic)</i>	<i>HDX 200 (Anionic)</i>	<i>Neosepta CMS</i>	<i>Neosepta ACS</i>	<i>Unit</i>
Functional group	-SO <sub>3</sub> <sup>-</sup>	-NR <sub>3</sub> <sup>+</sup>	-SO <sub>3</sub> <sup>-</sup>	-NH <sub>4</sub> <sup>+</sup>	-
Capacity of ion exchange	≥ 2.0	≥ 1.8	1.5-1.8	1.4-2.0	mol.kg <sup>-1</sup>
Resistance (0,1 mol NaCl)	≤ 20	≤ 20	1.8	3.8	Ω.cm <sup>2</sup>

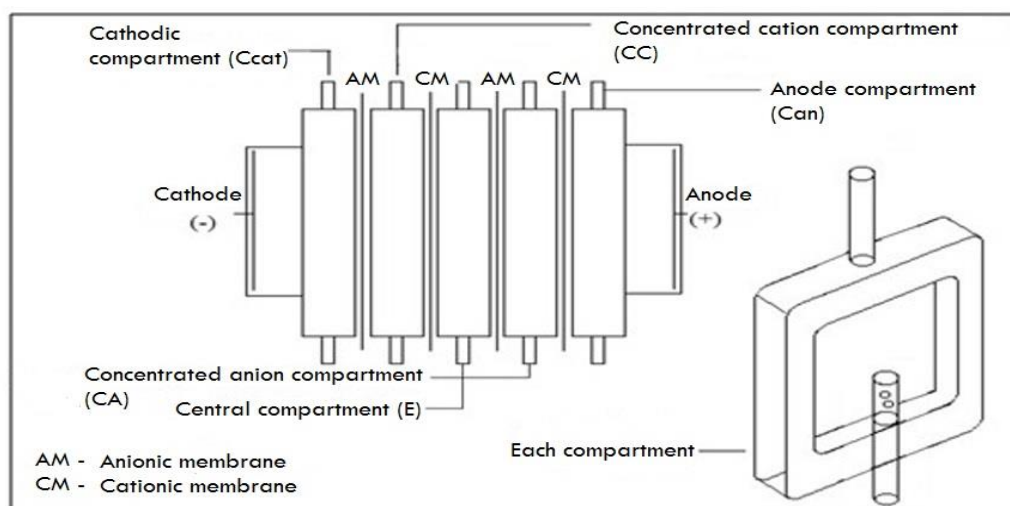
Adapted from SCARAZZATO et al. (2015); ZHANG et al. (2017).

## 2.2.3 Experimental apparatus

The bench-scale ED system was constructed (Figure 2.2) and the ED membrane cell was fabricated using acrylic sheet and comprises five compartments: central compartment, where the vinasse is introduced and the diluted solution is obtained at the end of the process; concentrated anion compartment; concentrated cation compartment; and anodic and cathodic compartments. The inner dimension of each compartment was 16 cm<sup>3</sup>. The compartments are separated by cation and anion membranes arranged in an alternating pattern, each membrane with an effective area of 16 cm<sup>2</sup>. The vinasse and concentrate compartment and electrode solutions were circulated through the ED rig using a centrifugal pump at a flow rate 10 L h<sup>-1</sup> (cross-flow velocity of 2.5 m.h<sup>-1</sup>; Reynolds number of 11 and a retention time of 5.76 s). 16 cm<sup>2</sup> of titanium plates coated with titanium oxide and ruthenium (70TiO<sub>2</sub>/30RuO<sub>2</sub>) and stainless steel plates were used as anode and cathode respectively which placed in respective compartments in the ED cell. The power supply used was an ICEL PS-5000 providing data of potential and current of the system. In addition, two multimeters (Minipa ET-1639) monitor these two control parameters separately.



Each compartment was connected to a 1L-reservoir. The effluent was inserted in the central compartment (E), and the electrolyte solution in each of the other compartments: Cathodic compartment (Ccat), compartment concentrated in cations (CC), compartment concentrated in anions (CA) and anodic compartment (Can). A 0.03 M  $\text{Na}_2\text{SO}_4$  (conductivity of approximately  $5.5 \text{ mS.cm}^{-1}$  and pH around 8) was used as electrolyte solution.  $\text{Na}_2\text{SO}_4$  is a salt widely used in laboratory and industrial scale ED.



**Figure 2. 2** - Illustration of the electrodialysis cell.

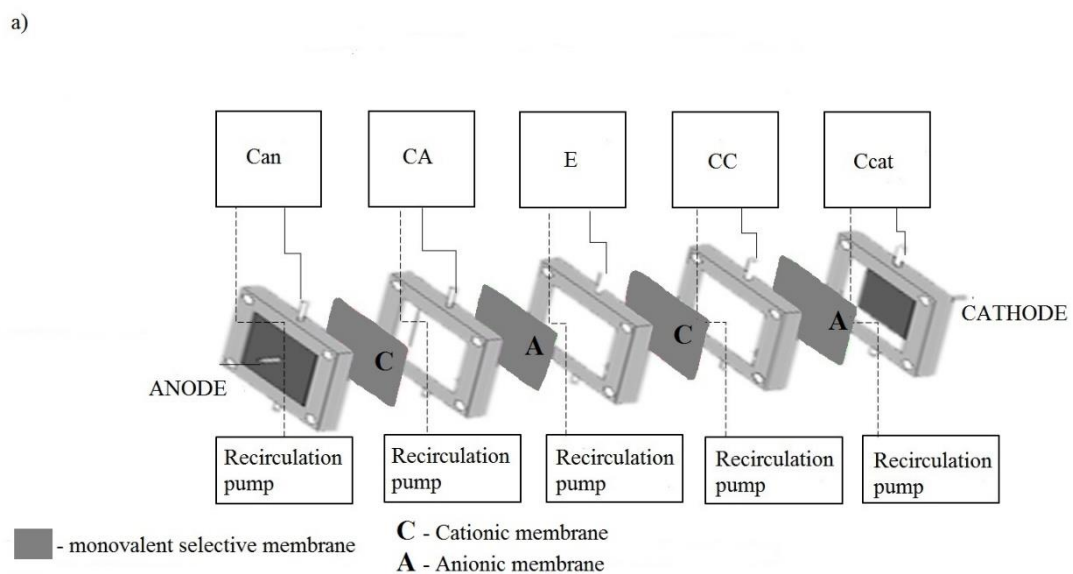
Adapted from BENVENUTI (2012)

#### **2.2.4 Experimental procedure**

During the experiments, the ED was operated in a recirculating batch mode. Firstly, ED performance with raw and ultrafiltrated vinasse was compared using the monovalent selective membrane. Values of the limiting current density were obtained graphically using the method of Cowan and Brown (1959). A polarization curve was constructed and the inflection point, observed when it leaves the ohmic region and reaches the plateau region, was identified. Polarization curves were constructed by gradually increasing the applied current at 2 mA every 5 minutes and measuring the corresponding voltage between the faces of the cationic membrane by a platinum wire. Only cationic membrane was analyzed, since it is expected a lower limiting current due to the greater mobility and consequently removal of potassium in the system, being, therefore, responsible for defining the global system limiting current.

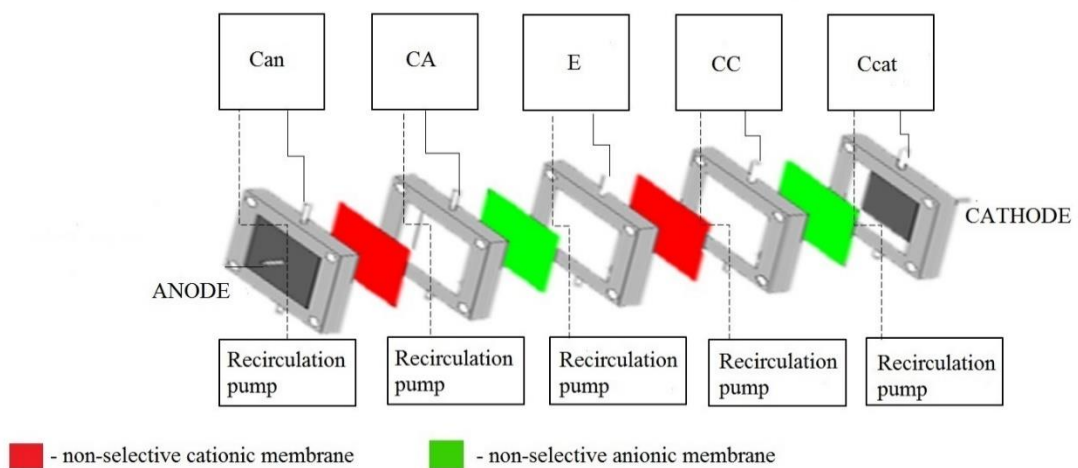
Also, quality of diluted and concentrated streams were assessed and membrane fouling was investigated by scanning electron microscope (SEM) analysis. Tests were performed in triplicate. The same membranes were used in the experiments of a triplicate test and no chemical cleaning was done, only mechanical cleaning under running tap water. From one triplicate test to another, new membranes were placed in the ED unit.

After pretreatment evaluation, different configurations of membranes were tested: (1) Selective configuration (all membranes used were monovalent selective (Figure 2.3 a)); (2) Non-monoselective configuration (all membranes used were non-monoselective (Figure 2.3 b)); and (3) Mixed configuration - one cationic membrane (between compartments E and CC) was monovalent selective and the others were non-monoselective (Figure 2.3 c)).



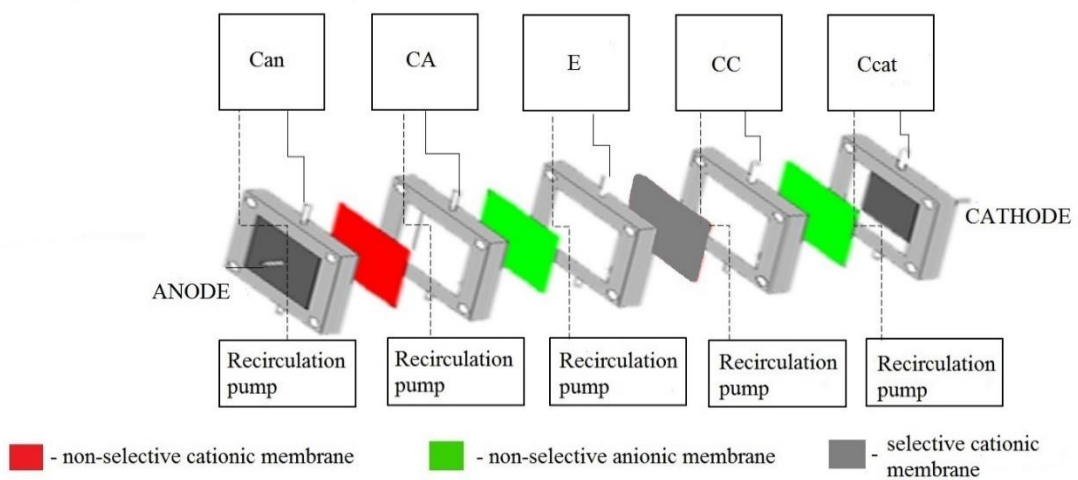
(a)

b)



(b)

c)



(c)

**Figure 2. 3** - a) Selective configuration. b) Non-monoselective configuration. c) Mixed configuration.

Adapted from SANTOS (2016).

For each configuration, the limiting current was determined. Then, 8-hour tests were performed for each configuration at 80% of the measured limiting current. Concentrations of ions on diluted and concentrated streams were analyzed and the best configuration was selected.

Since composition of vinasse varies significantly, it was analyzed and compared two different vinasses (Vinasse A and Vinasse B), one more concentrated than the other, in terms of performance in the ED system and also the consistency with irrigation criteria for desalted vinasse.

### **2.2.5 Calculation**

Percentage of recovery (R) were calculated according to Equation 2.1.

$$R = \frac{(C_f - C_i)}{C_e} * 100 \quad (2.1)$$

Where  $c_i$  and  $c_f$  are the concentration of the ion in the compartment concentrated in cations at the beginning and at the end of experiments, in  $\text{mg.L}^{-1}$ , respectively, and  $c_e$  is the concentration of the ion in the effluent in the beginning of experiments, in  $\text{mg.L}^{-1}$ .

The current efficiency (CE, dimensionless) relates the applied current, the energy consumption and the ionic transport along the ED process. This parameter expresses the fraction of the total electric current that circulates through the ED unit that in fact carries ions of interest from the feed solution to the adjacent compartments (ZHENG et al., 2015). The current efficiency can be calculated by Equation 2.2.

$$CE = \frac{F * z * V_e * \Delta c}{i * \Delta t} \quad (2.2)$$

Where F is the Faraday constant ( $\text{C.mol}^{-1}$ ), z is the ion valence (dimensionless),  $V_e$  is the circulated effluent volume (L),  $\Delta C$  is the variation of the ion concentration in the effluent ( $\text{mol.L}^{-1}$ ), i is the applied current (A) and  $\Delta t$  (s) is the time interval analyzed.

Moreover, the specific energy consumption ( $\text{kWh.m}^{-3}$ ) is given by Equation 2.3 (ZHENG et al., 2015):

$$E = \int_0^t \frac{V \cdot i}{V_e} dt \quad (2.3)$$

where V is the electric voltage (V), i is the applied current (A), Ve is the effluent volume (L) and t is the operating time (s).

Also, the energy per quantity of potassium recovered (kWh.g<sup>-1</sup> K<sup>+</sup>) is calculated dividing the Equation 2.3 by the concentration of potassium (c<sub>k+</sub>, in mg.L<sup>-1</sup>) in the concentrated stream, at the end of experiment (Equation 2.4).

$$\frac{E}{K^+} = \frac{\int_0^t \frac{V \cdot i}{V_e} dt}{C_{K^+}} \quad (2.4)$$

The quantity of potassium recovered per each unit of current (mgK<sup>+</sup>.L<sup>-1</sup>.mA<sup>-1</sup>) can be calculated by dividing the concentration of potassium (c<sub>k+</sub>) by the current applied (i) in A (Equation 2.5).

$$\frac{K^+}{i} = \frac{C_{K^+}}{i \cdot 1000} \quad (2.5)$$

The selectivity of membranes between ion A and B ( $S_B^A$ ) was calculated as shown in Equation 2.6 (LIU et al., 2017):

$$S_B^A = \frac{T_A}{T_B} \times \frac{C_B}{C_A} = \frac{J_A}{J_B} \times \frac{C_B}{C_A} \quad (2.6)$$

$$T_A = \frac{J_A}{\sum J_i}$$

Where C<sub>i</sub> is the concentration of the ion i on the dilute side of membrane, T<sub>i</sub> is the transport number of the ion i through the membrane, J<sub>i</sub> is the flux of ion i through the membrane.

Apparent stack resistance (Ω) was calculated according Equation 2.7:

$$ASR = \frac{V}{i} \quad (2.7)$$

Where V is the voltage (V) and i is the current (A).

The feed solution resistance  $R_f$  ( $\Omega$ ) can be calculated using equation 2.8 (MCGOVERN, ZUBAIR and LIENHARD, 2014):

$$R_f = N \frac{h_f}{C_f A} \quad (2.8)$$

where  $N$  is the number of membrane pairs,  $h_f$  is the length of the feed channel (m),  $C_f$  is the feed conductivity ( $S.m^{-1}$ ) and  $A$  is the membrane surface area ( $m^2$ ).

After checking the efficiency of ED and selecting the ideal configuration for ED stack, the focus became the impacts that the treated effluent would bring to the soil through an initial analysis. For this, the risk of loss of the structure of the medium was evaluated with the calculation of the sodium adsorption ratio (SAR) and potassium adsorption ratio (PAR), presented in Equation 2.9 (SEVERINO et al., 2014) and 2.10 (SMITH, OSTER, SPOSITO, 2015).

$$RAS = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \quad (2.9)$$

$$PAR = \frac{[K^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \quad (2.10)$$

All concentration units for SAR and PAR calculation are  $(meq.L^{-1})^{0.5}$ .

### 2.2.6 Analytical methods

Samples from all five compartments were analyzed by the following physico-chemical parameters according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2012) regarding the following physicochemical parameters: sulfate (turbidimetric method -  $4500 SO_4^{2-}$ ), ammoniacal nitrogen (titration method -  $4500-N-NH_3C$ ), chemical oxygen demand (COD) (colorimetric method - 5220 D Closed Reflux), potassium, calcium, magnesium, and sodium. The potassium and sodium were determined by flame photometer (Micronal model B462), calcium and magnesium by means of the atomic absorption spectrophotometer (Shimadzu model AA-7000).

The membranes were air-dried and their surface morphology was analyzed by a FEI Quanta 200 SEM with an additional energy dispersive X-ray spectrometer (EDS) analysis. Prior to analysis, membrane samples were coated with carbon layer by a sputter coating machine (Leica EM SCD 500 with a pressure of  $10^{-2}$ - $10^{-3}$  mbar and a 2.5 A current).

## 2.3 RESULTS AND DISCUSSION

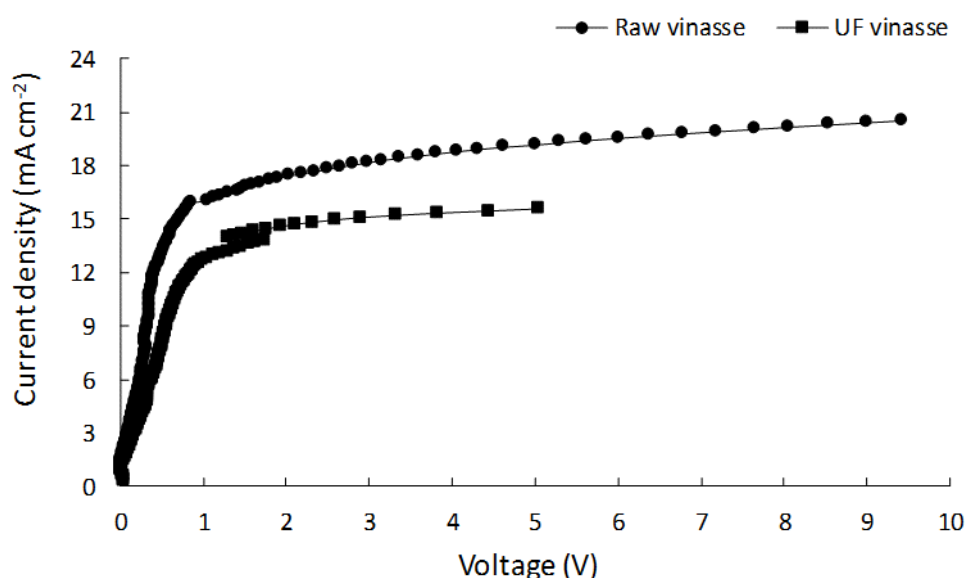
### 2.3.1 Effect of feed pretreatment using UF in the ED performance

Table 2.3 presents the physicochemical parameters of ultrafiltrated vinasse and the UF efficiency. UF was highly efficient for suspended solids removal. Conductivity was also partially reduced. It may have been caused by retention of dissolved cations and anions by electrostatic interactions between the solutes and the membrane surface and pores (ALVENTOSA-DELARA et al., 2014) or ion adsorption on membrane or cake (TANHAEI et al., 2014). However, since inorganics ions retention was smaller than organic matters (except for sulfate), it is believed that the major portion of conductivity removal was due to the retention of charged organic compounds. Vinasse organic matter varies both in terms of charge (typically majority uncharged and some negatively charged) and molecular weight. Since high molecular weight organics is generally retained by UF (SCOTT, 1995), the results suggest that the conductivity removed by UF was associated with vinasse high molecular weight charged organic compounds.

**Table 2. 3** - Values of physico-chemical parameters for ultrafiltrated vinasse and UF efficiency.

Parameter	Unit	Uf Vinasse	UF Efficiency
Potassium	mg.L <sup>-1</sup>	906.5 ± 96.3	9%
Calcium	mg.L <sup>-1</sup>	287.1 ± 44.3	3%
Magnesium	mg.L <sup>-1</sup>	91.3 ± 39.2	26%
Sodium	mg.L <sup>-1</sup>	51.6 ± 9.9	25%
Ammoniacal nitrogen	mg.L <sup>-1</sup>	10.3 ± 2.1	20%
Sulfate	mg.L <sup>-1</sup>	220.8 ± 75.5	63%
Total phosphorus	mg.L <sup>-1</sup>	38 ± 2	17%
COD	mg.L <sup>-1</sup>	8875.6 ± 2878.8	41%
pH	-	4.3 ± 0.4	-
Electrical conductivity	mS.cm <sup>-1</sup>	3.4 ± 0.3	-
Total suspended solids	g.L <sup>-1</sup>	-	-

Figure 2.4 presents the I–V curves of the monovalent selective membranes in raw and ultrafiltrated vinasse (UF vinasse). A higher voltage needs to be applied to result in the same current density when treating the UF vinasse compared to raw vinasse. Limiting current density was 15.7 and 13.0 mA.cm<sup>-2</sup> for raw and UF vinasse respectively.



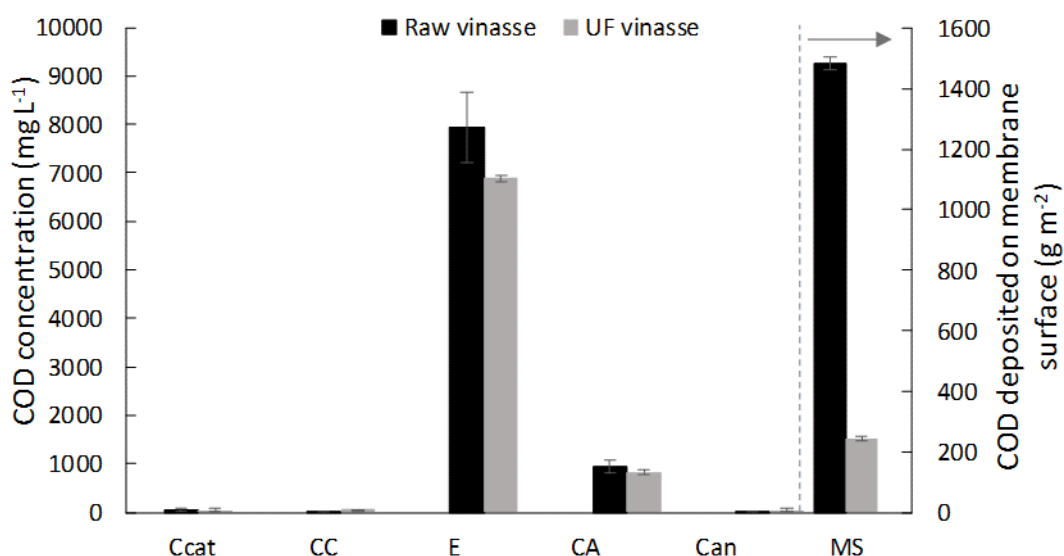
**Figure 2. 4** - Polarization curves for tests with raw and ultrafiltrated vinasse.

The apparent stack resistances (ASR) for the limiting current density was 3.19 and 3.56  $\Omega$  for raw and UF vinasse respectively. The apparent stack resistances involve contributions of anion and cation exchange membrane resistances; feed, concentrate and electrode solution resistances; overall Nernst potential created at the membrane-solution junction; and thermodynamic potential and overpotential of the electrodes. Since the same membranes and electrode solution were used and the raw effluent had higher conductivities (5.6 mS.cm<sup>-1</sup>) than UF vinasse (3.6 mS.cm<sup>-1</sup>), the solution resistance would be higher for the UF vinasse compared to raw effluent.

The calculated feed resistances for raw and UF vinasse was 1.11 and 1.74  $\Omega$  respectively, which correspond to 35 and 49% of apparent stack resistances, showing that important contribution to the apparent stack resistance comes from the solution resistance.



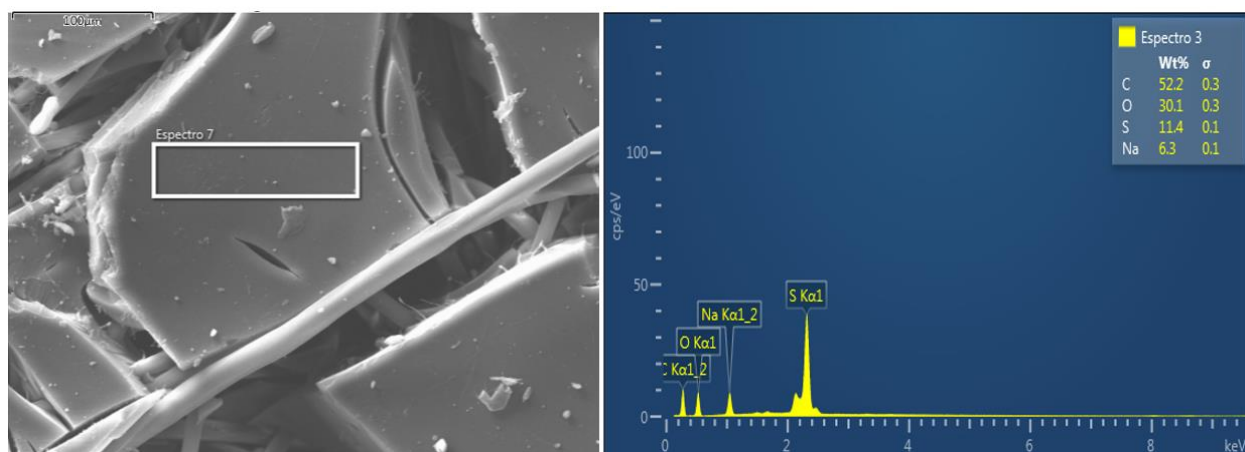
The COD concentration in the diluted and concentrated streams after ED process are shown in the Figure 2.5.



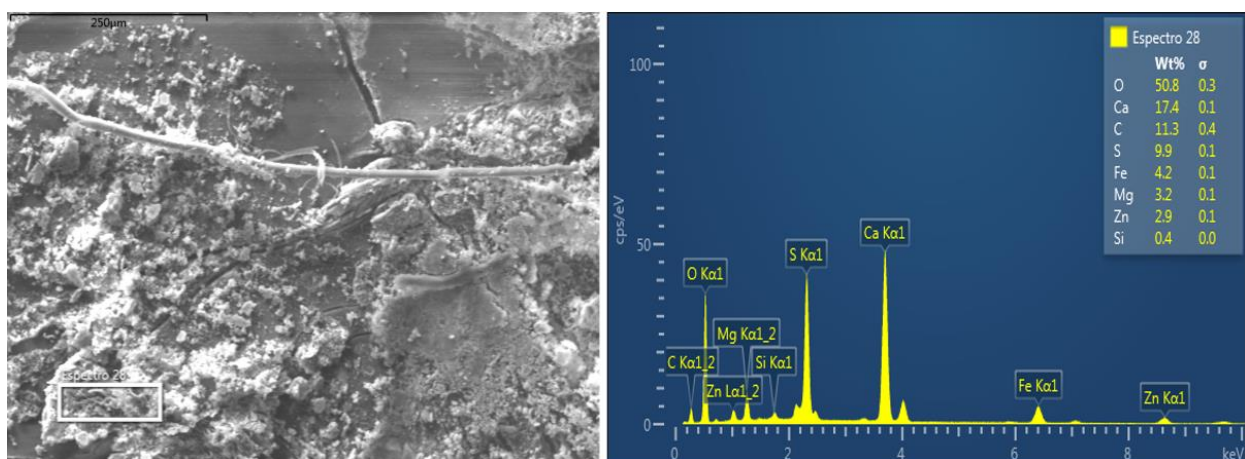
Ccat – Cathodic compartment; CC – Compartment concentrated in cations; E – Central compartment; CA – Compartment concentrated in anions; Can – Anodic compartment; MS – Membrane surface.

**Figure 2. 5** - COD concentration after ED process in all compartments and in the membrane surface.

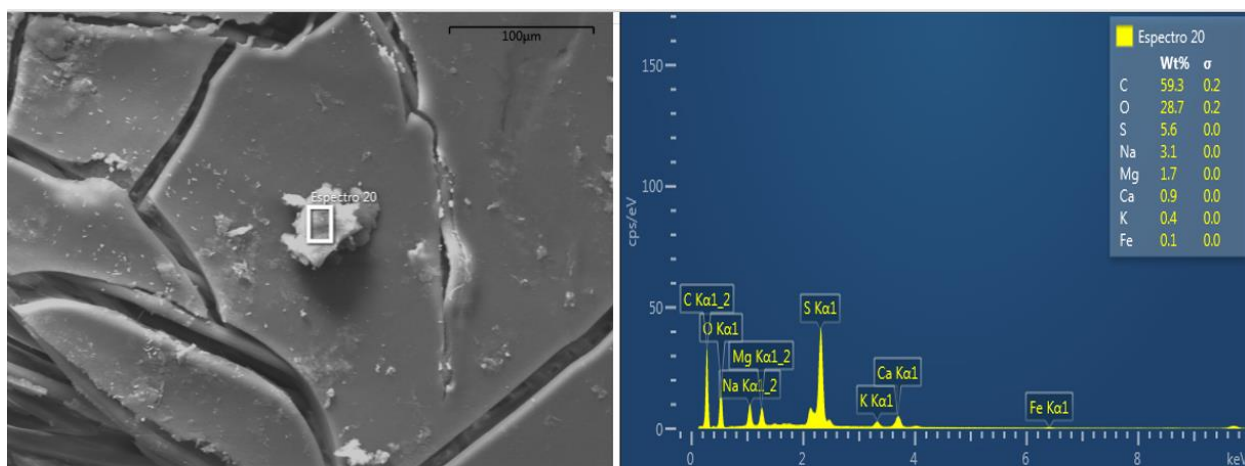
The charged low molecular weight compounds cross the membrane to anodic compartment with a flux of  $7.3 \times 10^{-2}$  and  $5.5 \times 10^{-2} \text{ kg m}^{-2}\text{h}^{-1}$  for raw and UF vinasse respectively. The COD mass transferred to concentrated compartments was lower than mass depleted in the feed compartment, indicating that some portion of COD had deposited over membrane. The mass balance of COD indicated that  $1.4 \pm 0.1$  and  $0.25 \pm 0.08 \text{ kg}$  of COD deposited per  $\text{m}^2$  of membrane surface when fed with raw and UF vinasse. The materials deposited on membrane surface can be seen in the SEM images (Figure 2.6), where the more pronounced fouling layer on the surface of membrane fed with raw vinasse is evident.



(a)



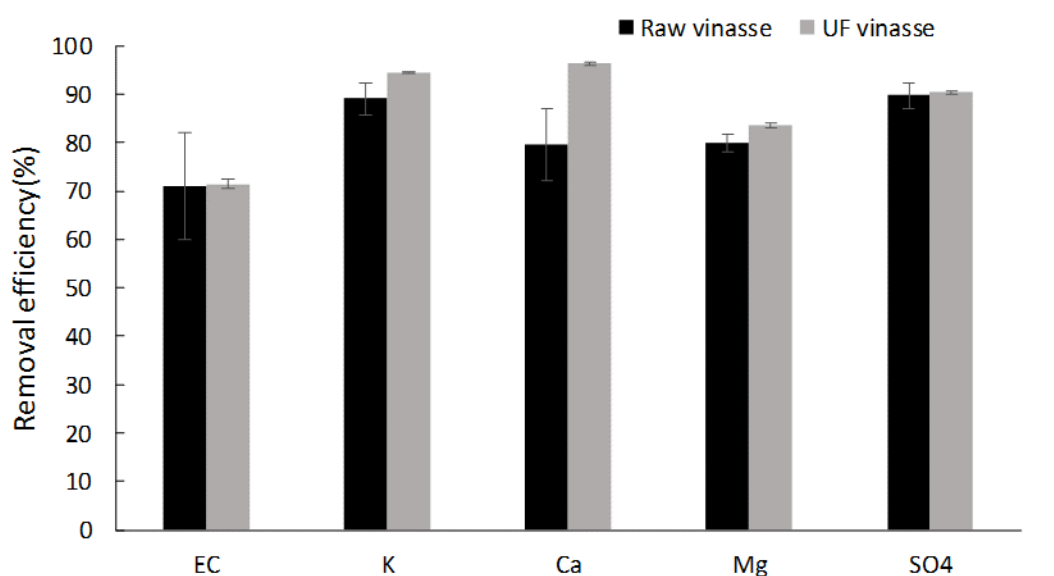
(b)



(c)

**Figure 2. 6** - SEM and EDS analysis of cationic (a) Piristin membrane, (b) Membrane (between compartments CC and E) from the concentrated side fed with raw vinasse test and (c) Membrane (between compartments CC and E) from the concentrated side fed with ultrafiltrated vinasse test.

It should be highlighted that the piristin membrane already presents a fissured web, that is maintained in all tests and the difference noticed in the Figure 2.6 is the amount of material deposited on the membrane surface. The ED process fed with UF vinasse shows more stable performance in terms of ions rejection since the coefficient of variation of ions removal was on average six times lower than that observed for ED fed with raw vinasse (Figure 2.7). In this way, although UF reduce ion content on the effluent and thus increase solution resistance, its use as a pretreatment is important to prevent membrane fouling and improve ions separation.

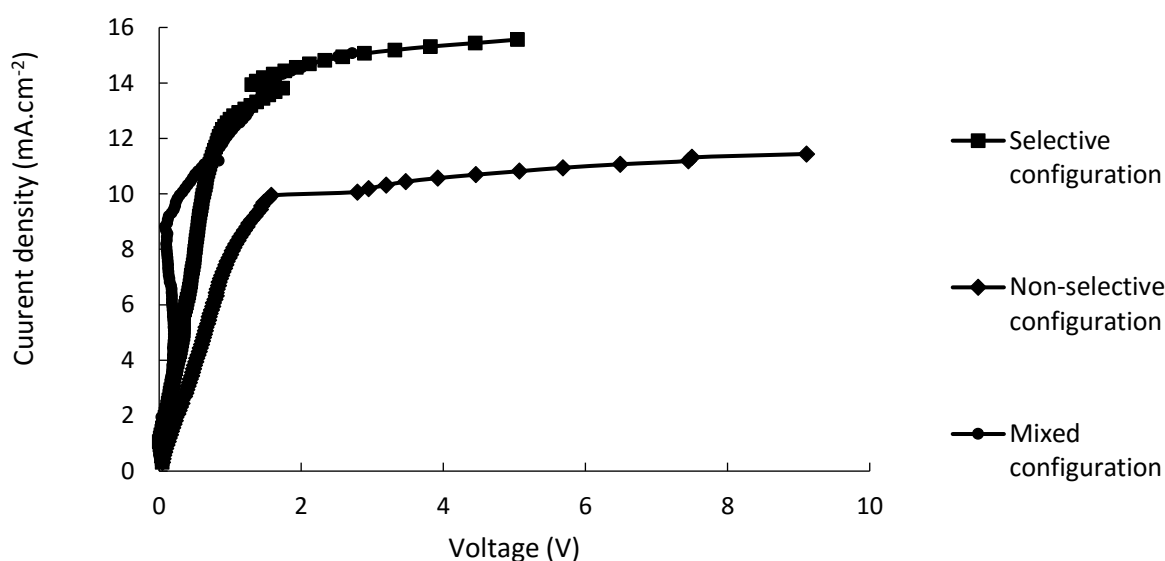


**Figure 2. 7** - Comparative of removal of ions after ED process for raw and ultrafiltrated vinasse.

### **2.3.2 Comparison of three distinct configurations of membranes**

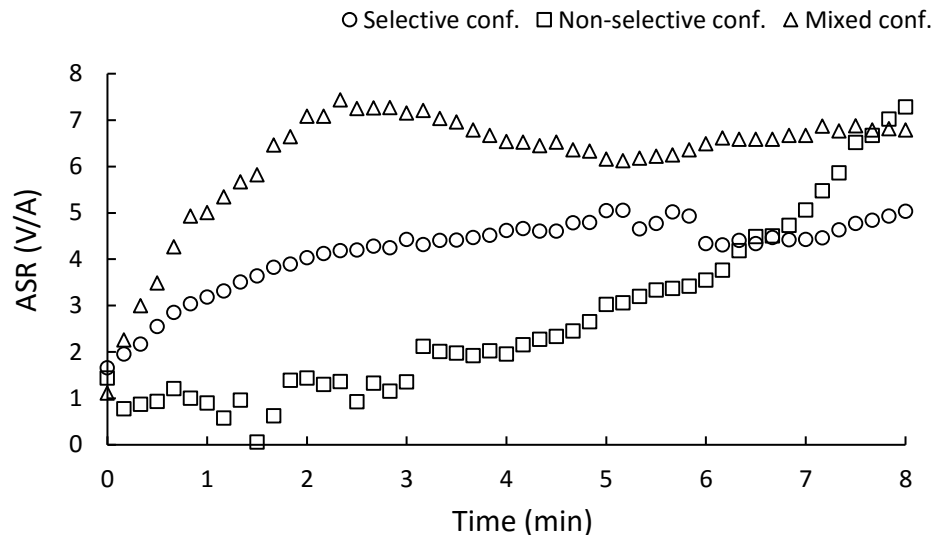
In this research, ED was applied to remove potassium from vinasse to achieve the relatively pure salt recovery and a dessalting vinasse with better quality for fertigation or anaerobic digestion application. Non-monoselective ED could not separate ions of the same charge but different valence. On the other hand, this selective separation can be achieved by using selective membranes. When potassium recovery is intended, the use of monovalent selective cationic membrane can be employed to improve the ED selectivity to potassium.

In this way three ED configurations were evaluated in this study by using (I) selective membranes; (II) non-monoselective membranes and (III) mixed configuration (monovalent cationic membrane integrated to a non-monoselective membrane) considering permeability, membrane resistance, and selectivity with respect to both inorganic and organic ions and energy consumption. The experiments were carried out at constant current density equivalent to 80% of limiting current density. The limiting current density was experimentally determined with correspondent values of  $11.3 \text{ mA.cm}^{-2}$ ,  $8.0 \text{ mA.cm}^{-2}$  and  $6.9 \text{ mA.cm}^{-2}$  for the selective, non-monoselective and mixed configuration, respectively. The I–V curves of the membranes used to determine the limiting current are provided in Figure 2.8.



**Figure 2. 8** - Polarization curves for the three configurations.

As shown in Figure 2.9, the initial ASR for the non-monoselective configuration was lower than selective configuration, that are consistent with the electrical resistance data shown in Table 2.2 where the non-monoselective membrane has the lower electrical resistance. Furthermore, for the non-monoselective membrane, the ASR were approximately constant during the first 3 hours and then began to increase. For selective and mixed configuration, the ASR increased in the begin of experiment and remained constant after 2 hours of operation.



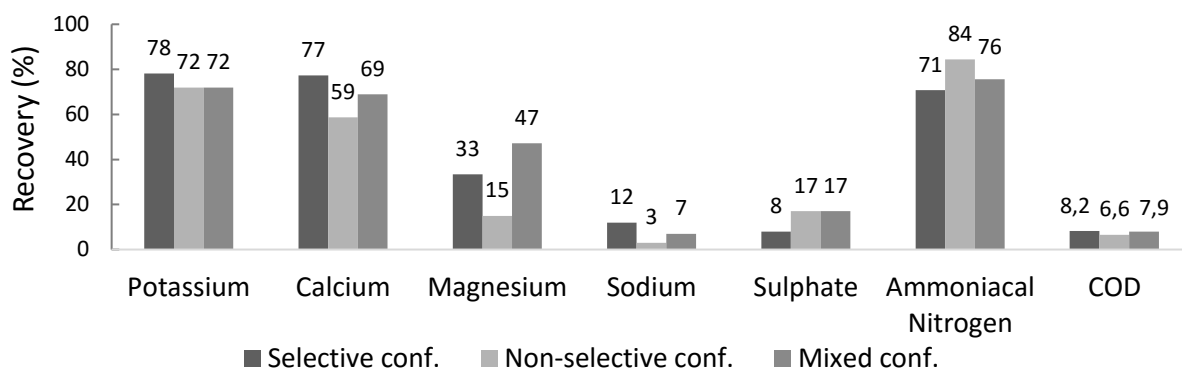
**Figure 2. 9** - Apparent stack resistances (ASR) for all configurations.

The observed increase in the ASR could be associated to fouling and/or depletion of the ions most easily transported by the membrane from the feed to the concentrated stream. Once such ions are depleted, the current must be transported by other ions that have a lower membrane permeability resulting in an increased total resistance.

ASR profile observed for the different configurations can be explained by composition of vinasse. In the vinasse, the anionic constituents are most likely to be divalent species (sulfate) and/or organics, while the cationic constituents are mainly monovalent (potassium) and to a lesser extent divalent (calcium and magnesium). The transport of potassium, the ion in higher concentration and with higher permeability, is limited by the opposite anion transport across the membrane, since the charge in the feed solution needs to be conserved. As shown in Figure 2.10 the transport of cation potassium, magnesium and calcium was higher in the selective configuration than in the non-monoselective configuration, showing that anion transport was facilitated across cationic selective membrane.

Since sulfate transport across monovalent selective membrane is hindered, the negative charge movement was based on negatively charged COD transport. Accordingly, the flux of COD transferred to anionic compartment was 74 and 46  $\text{g.m}^{-2}.\text{h}^{-1}$  for selective and non-monoselective configuration respectively. Therefore, the transport of lesser permeable anions (charged COD) resulted in the greater ASR for the selective membrane.

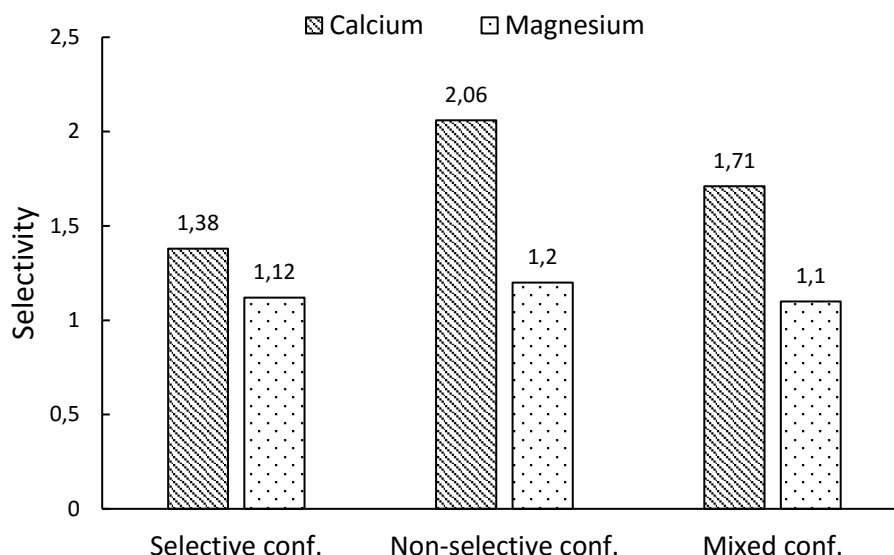
When the selective cationic membrane was integrated to non-monoselective configuration (mixed configuration), the transport of cation to the concentrated compartment was less hampered by COD transport; since the flux of COD transferred was increased to  $69 \text{ g.m}^{-2}.\text{h}^{-1}$ . Sulfate fluxes for selective, non-monoselective and mixed configurations were 21, 43 and  $43 \text{ g.m}^{-2}.\text{h}^{-1}$ , respectively. Luiz et al. (2017) investigated the different membranes for conventional ED applied to vinasse treatment and also observed that the membrane with the most COD being transported across the membrane had the lowest ASR. However, the high COD flux crossing the membrane also contributed to membrane fouling. The COD deposited on the membrane surface was 342, 249 and  $325 \text{ g m}^{-2}$  for selective, non-monoselective and mixed configuration respectively.



**Figure 2. 10** - Recovery of ions and COD for the three configurations.

As expected, the cations removal efficiencies ( $\text{K} > \text{Ca} > \text{Mg}$ ) follow their hydration energy ( $295, 1592$  and  $1904 \text{ kJ mol}^{-1}$ , respectively, (BINDER and ZSCHORNIG, 2002)). The cations  $\text{K}^+$  and  $\text{Ca}^{2+}$  must be completely or partly shed from their hydration shell to cross the membrane (VAN DER BRUGGEN, KONINCKX and VANDECASTEELE, 2004). However, given its extremely small ionic radius ( $0.074 \text{ nm}$ ),  $\text{Mg}^{2+}$  requires the hydration shell to attenuate the electric field that would otherwise hold it irreversibly to the fixed negative charges, and therefore it crosses as the larger hydrated ion ( $0.429 \text{ nm}$ ).

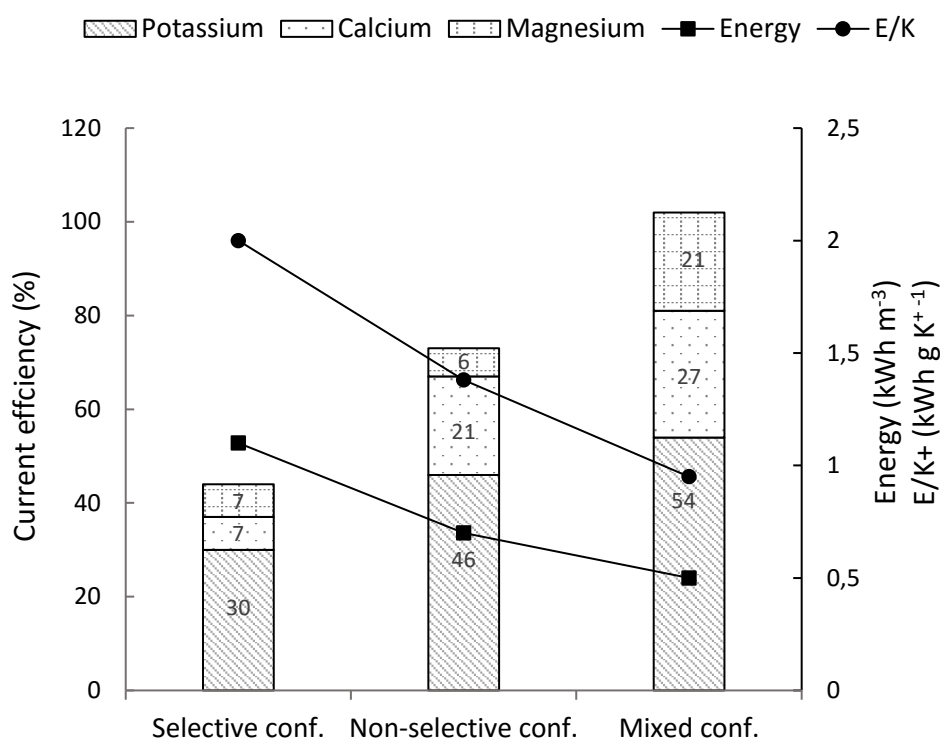
The permselectivities between calcium and magnesium and potassium ions ( $S_{Ca}^K$  and  $S_{Mg}^K$ ) of the membrane in the different configurations are presented in Figure 2.11.



**Figure 2. 11** - Selectivity for the three configurations.

All membranes show a higher selectivity in separating monovalent from divalent anions ( $S_{Ca}^K$  and  $S_{Mg}^K$ )  $> 1$ ). Although the ions flux was higher in the selective and mixed configuration, the non-monoselective membrane had the highest monoselectivity. There are inconsistent findings related to monoselectivity of CMS membranes (ABDU et al., 2014, FIRDAOUS et al., 2007, SATA, SATA and YANG, 2002) in the literature. The lack of agreement between CMS monovalent cation selectivity can be explained by the difference in the initial conductivities of the studied effluents, as lower initial ionic strength interferes with cation monovalent permselectivity. At low EC, the screening of the cation polyelectrolyte layer is less effective so that the monovalent ion is as retarded as the divalent ion. On the other hand, at high EC, the monovalent ion is less rejected because of the high ionic strength successfully screening the field of the polycation coating with respect to the monovalent charge much better than it screens the coating from the divalent charge (COHEN, LAZAROVITCHA and GILRON, 2017). Therefore, the lower extent of monoselectivity of the selective and mixed configuration can be associated to the low electrical conductivity of the vinasse studied. Furthermore, the higher monoselectivity of the non-monoselective membrane was achieved by the low flux of calcium and magnesium, since the removal of potassium by this configuration was similar to others (Figure 2.10). The lower flux of calcium and magnesium can be associated to greater electrical resistance of the non-monoselective membrane compared to selective membrane (Table 2.2). Independently of the membrane, the number of transport of potassium is the highest.

The current efficiencies of  $K^+$  were higher than  $Ca^{+2}$  and  $Mg^{+2}$  for all configurations (Figure 2.12) reinforcing the monoselectivity character of the three configurations. The voltage drop across the membranes was also measured and was then used to calculate the specific energy consumption of the membrane system per mole of transported  $K^+$  ions (Figure 2.12). Selective, non-monoselective and mixed configuration requires specific energy of 2.0, 1.38 and 0.95 kWh.kg<sup>-1</sup>  $K^+$  respectively. This striking difference in the energy consumption could be due to the fact that the selective membrane possesses a dense membrane matrix. These values are greater than observed in the literature for vinasse, except for mixed configuration, which range from 0.75 to 0.96 kWh.kg<sup>-1</sup>  $K^+$  for potassium removal between 50 and 64% (WILDE, 1987, LUIZ et al., 2017), which could be associated to the low concentration of ions in the vinasse used in this study.



**Figure 2. 12** - Calculations of current efficiency, energy and E/K+ for all configurations.

Although the higher potassium and calcium recovery for the selective configuration test, the current efficiency for the same cations and the energy consumption are the worst. The best configuration in terms of recovery of ions with better current efficiencies, lower energy consumption and lowest energy demanded per gram of potassium recovered, besides higher amount of potassium carried by each unit of current is the mixed configuration.



With the best configuration determined, a 10-hour test were done to be compared with the 8-hour test for mixed configuration. Table 2.4 compare the performance of both tests in terms of conductivity for compartments “E” and “CC” and the recovery in compartment “CC” of potassium, calcium and magnesium, respectively.

**Table 2. 4** - Comparison of electrical conductivity (EC), ions recovery, current efficiency and energy consumption for 8 and 10 hour tests using mixed configuration.

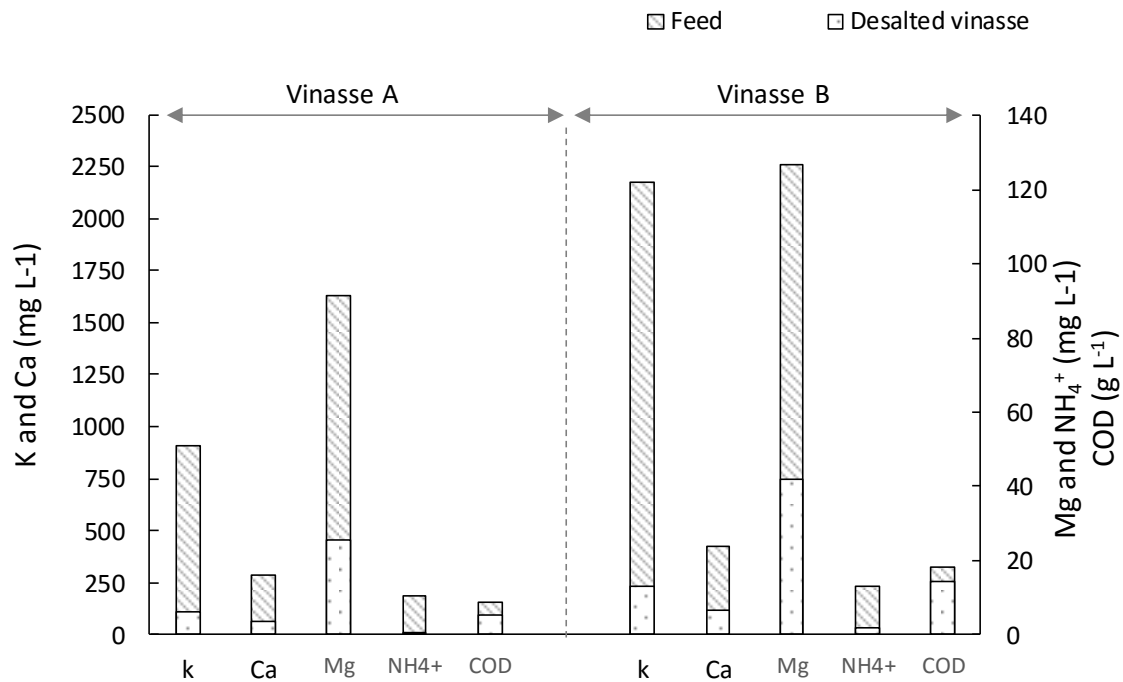
PARAMETERS		Mixed configuration 8-hour test	Mixed configuration 10-hour test
EC (mS.cm <sup>-1</sup> )	Initial CC	5.1	5.0
	Final CC	7.3	7.2
	Initial E	3.3	3.2
	Final E	2.1	1.6
Ions recovery (%)	Potassium	72	78
	Calcium	69	68
	Magnesium	47	34
Current Effic. -K (%)		54	47
Current Effic. -Ca (%)		27	10
Current Effic. -Mg (%)		21	12
Energy (kWh.m <sup>-3</sup> )		0.5	0.6
E/K <sup>+</sup> (kWh.kg <sub>K<sup>+</sup></sub> <sup>-1</sup> )		1.0	1.1
K <sup>+</sup> /i (mg <sub>K<sup>+</sup></sub> .L <sup>-1</sup> .mA <sup>-1</sup> )		5.2	5.7
$S_{Ca}^K$		1.71	1.20
$S_{Mg}^K$		1.10	1.12

Even though the mixed configuration 10-hour test presented lower conductivity in compartment “E”, 6 percentual points more recovery of potassium and higher amount of potassium carried by each unit of current, the energy consumption, energy demanded per gram of potassium recovered and the current efficiencies for all three ions still favors the 8-hour test.  $S_{Ca}^K$  is higher for 8-hour test, due to a higher flux of potassium and lower flux of calcium, comparatively, meanwhile for  $S_{Mg}^K$  the value is quite the same for both tests, since the higher flux of magnesium for 8-h test compensates the higher flux of potassium. It is interesting to note that for the mixed configuration, the duration of tests influenced on the selectivity, so  $S_{Ca}^K$  reduces considerably from 8 to 10 hours of test and there is a slight increase in the  $S_{Mg}^K$ . Making a comparative of all tests it is noted that mixed configuration 10-hour test showed same potassium recovery compared to selective configuration test, additionally, current efficiency for potassium of mixed configuration 10-hour test and non-monoselective configuration test were quite similar. For all

tests there is a higher  $S_{Ca}^K$  compared to  $S_{Mg}^K$ , so all the membranes exhibit a preference to permeate potassium, then calcium and magnesium.

Finally, considering that the 8-hour mixed configuration test showed 72% recovery of potassium, a calcium recovery of 69%, the highest magnesium recovery (47%), the lowest energy consumption, lowest energy demanded per quantity of potassium and the higher current efficiencies for the three cations, this was the configuration chosen for the recovery of ions from vinasse.

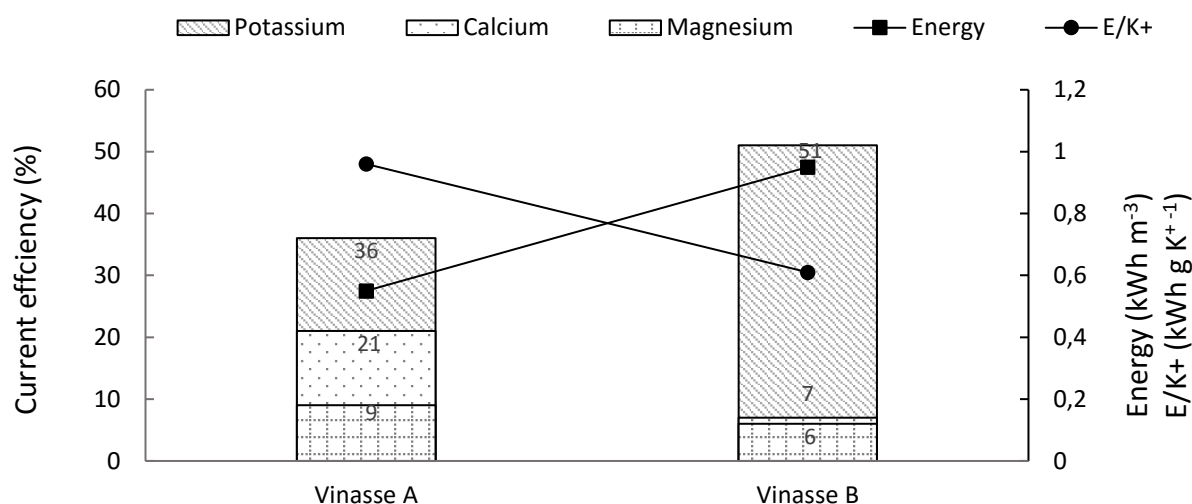
Another important aspect is that the vinasse used to evaluate the three configurations was more diluted than the usually observed for vinasse (Table 2.1 and table 2.3). The vinasse is very susceptible to variation of its composition as can be observed by the high coefficient of variation. Therefore the vinasse treatment by ED can be economically more favorable when treating vinasse having high salt concentrations as these will result in a more favorable specific power consumption, since the solution resistance would be lower and diffusive flux of ions would be higher. The ED was evaluated for the treatment of a more concentrated vinasse (vinasse B). The mixed configuration was selected to be used in this experiment since it shows advantages related to low energy consumption without relevant treated vinasse quality loss. Figure 2.13 shows the ions and COD concentration of diluted (vinasse A) and concentrated (vinasse B) vinasse before and after the ED. The ions removal depends on the initial concentration; high initial ion concentration in the feed solution resulted in a lower removal of ions, besides necessitating longer residence time.



**Figure 2. 13** - Ions and COD for vinasse before (feed) and after (desalted) ED for vinasse A and B.

The flux of COD transferred to anionic compartment was 69 and 74 g m<sup>-2</sup> h<sup>-1</sup> for ED fed with vinasse A and B respectively. The COD deposited on the membrane surface was 325 and 352 g.m<sup>-2</sup> for ED fed with vinasse A and B, respectively. These results showed that the higher soluble COD (ultrafiltrated vinasse) in the vinasse B does not offer restriction for ED operation in relation to organic fouling.

As expected, the vinasse treatment by ED was economically more favorable when treating vinasse having high salt concentrations as these resulted in a more favorable specific power consumption (Figure 2.14). This effect may be attributed to reduction of the solution resistance ( $R_f$  is 1.98 and 1.14  $\Omega$  for vinasse A and B respectively) and amplification of the overall ionic transfer rate by higher diffusive fluxes caused by an increased concentration gradient. The current efficiency of potassium was higher in the vinasse B compared to vinasse A in relation to the divalent cations. These results are in accordance with observation by Sata and others (2002) that at high ion concentration, the monovalent ion is less rejected because of the high ionic strength successfully screening the field of the monovalent charge much better than it screens the coating from the divalent charge.



**Figure 2. 14** - Calculations of current efficiency, energy and E/K+ for vinasse A and B.

### 2.3.3 Potential application of desalted vinasse in agriculture

The PAR value for the raw vinasse A and B were 7 and 14, respectively. According to Arienzo and others (2012), at SAR and PAR values less than 5 (meq.L<sup>-1</sup>)<sup>0.5</sup>, there are little adverse effects of Na or K in soil. Vinasse has small values of SAR (1.20 and 0.05 for raw vinasse A and B, respectively), but PAR values which exceeds the limit suggested by the literature, reinforcing that application of vinasse in the soil should be controlled and that the reduction of potassium in vinasse by ED would enable the enlargement of application rate in soil.

The use of desalted vinasse in irrigation/fertigation is an interesting alternative for vinasse disposal. SAR and PAR values were chosen as parameters to quantify the hazard to soil structure of vinasse disposal, as well as other agricultural criteria.

SAR shows the ratio of monovalent cations (Na) with divalent (Ca and Mg). A low electrical conductivity associated with a high SAR can bring problems to the soil, which is presented in table 2.5 in a broader classification and that does not take into account the particularities of each soil.

**Table 2. 5** - Reference for degree on restriction of use (adapted from Matos and Matos, 2017).

SAR ( $\text{meq.L}^{-1}$ ) <sup>0.5</sup>	Degree on restriction of use		
	None	Slight to moderate	Severe
	-----EC ( $\text{dS.m}^{-1}$ )-----		
0-3	>0.7	0.7-0.2	<0.2
03-6	>1.2	1.2-0.3	<0.3
06-12	>1.9	1.9-0.5	<0.5
12-20	>2.9	2.9-1.3	<1.9
20-40	>5.0	5.0-2.9	<2.9

The SAR values were 3.78 and 2.95 ( $\text{meq.L}^{-1}$ )<sup>0.5</sup> and final electric conductivities were 1.92 and 3.16  $\text{dS.m}^{-1}$  for desalted vinasse A and B respectively, thus, both desalted vinasse samples show no restriction of use. The PAR values were 1.71 and 2.75 ( $\text{meq.L}^{-1}$ )<sup>0.5</sup> for desalted vinasse A and B, respectively, being under the value of 5. The sulfate in the desalted vinasse A and B were 75.5 and 238  $\text{mg.L}^{-1}$ , respectively. The high  $\text{SO}_4^{-2}$  concentration in the desalted vinasse is not a problem since calcium levels are < 100  $\text{mg.L}^{-1}$ .

Reduction in vinasse PAR indicates the desired separation between mono and divalent cations and consequently the monoselectivity in the removal of cations. It is impossible to do the same evaluation for SAR indicator since  $\text{Na}_2\text{SO}_4$  solution is used as electrode solution and Na ions migrate to effluent compartment, and then, the sodium concentration increases in the effluent. Regarding SAR and EC values, there is no restriction of use in soil, despite that, desalted vinasse A and B display the values of 240  $\text{mgNa.L}^{-1}$  and 147  $\text{mgNa.L}^{-1}$ , respectively, which could indicate the sodium as limiting nutrient for application in soil. Therefore, the use of  $\text{Na}_2\text{SO}_4$  as solution offer challenges and require further investigation in order to select a more adequate electrolyte solution. Next chapter will present alternatives for electrolyte solutions in order to enable completely the use of vinasse in fertigation and the future recovery of potassium as fertilizer.

Avoiding the migration of sodium to compartment E, desalted vinasse will present the conditions, including SAR and PAR values, that enables the higher dosage of vinasse in soil in an environmental friendly way and reducing the cost with transportation of vinasse in the sugarcane plantations. With the considerable reduction of the content of potassium of vinasse from raw vinasse to desalted vinasse, the maximum vinasse application rate ( $\text{VAR}_{\text{max}}$ ) increases from 502  $\text{m}^3.\text{ha}^{-1}$  to 2510  $\text{m}^3.\text{ha}^{-1}$  for vinasse A, and from 231  $\text{m}^3.\text{ha}^{-1}$  to 1255  $\text{m}^3.\text{ha}^{-1}$  for

vinasse B. That means that the  $VAR_{max}$  can be at least 5 times higher for the desalted vinasse, leading to a reduction in the total transportation cost associated to vinasse disposal in agricultural soil. These assumptions still consider the potassium as chemical element of reference.

The COD in the desalted vinasse B was more than double compared to vinasse A. With the treatment route UF-ED there is a decrease of COD in vinasse, on the other hand, with 5 times increase in the dosage of vinasse in soil, the applied organic load (AOL) into the soil rises.

It is generally assumed that organic compounds (AYANABA and JENKINSON, 1990) and soil organic matter (TRUMBORE, 1993) have a faster turnover in tropical than temperate soils due to the enhanced decomposition under the higher moisture and temperature regimes of the tropics (SIX et al., 2002), besides, 97% of vinasse organic matter content are biodegradable (MOTA, SANTOS and AMARAL, 2013). Primary plant production and soil microbial activity are the two main biological processes governing inputs and outputs of organic matter. The balance between them determines organic matter turnover and is controlled by biotic and abiotic factors. Climate, parent material, biota, topography and time are the major controlling factors on production and decomposition (by microorganisms) of organic matter (JENNY, 1941). Climate, parent material and biota (e.g. vegetation) are the factors that differ the most between tropical and temperate regions. Due to the mentioned above and considering that our country is situated in tropical region, the input of higher COD in soil should not compromise the soil quality, but further studies should consider the continuous disposal and assess the real consequences in order not to disturb the environment.

## **2.4 CONCLUSIONS**

The lowest deposition of COD on the membrane surface for the ultrafiltrated vinasse and the more pronounced membrane fouling for the raw vinasse reveal the importance of the ultrafiltration to protect the membranes. The accumulation of both organic matter and salts near membrane also justifies the smaller removal efficiency of ED applied to raw vinasse. Anyway, it should be interesting to assess the permanent fouling, by studying the chemical cleaning of the membranes.

The comparison done with the three distinct configurations of membranes took into account the potassium recovery, current efficiency and energy consumption. The results revealed that the

different configuration (one cationic monovalentselective membrane and the other non-monoselective) was able to recover after 8 hours, with a current of 0.11A, 72% of potassium with the lowest energy consumption ( $0.5 \text{ KWh.m}^{-3}$ ) and the best potassium current efficiency (54%).

Raw vinasse exhibits low SAR, but elevated PAR values inconsonant with the literature, and the high amounts of potassium limits, then, larger dosages of this effluent in soil. The employment of electrodialysis and consequently the achievement of desalted vinasse reduces the concentration of potassium in the effluent, enabling higher dosages in the soil, as fertigation. The use of sodium sulfate as electrolyte solution is not ideal since occurs migration of sodium onto vinasse compartment and the Na could become the chemical element of reference, restricting large applications in the soil. Wherefore, the use of other electrolyte solutions might solve the problem of sodium supply onto the effluent and enable the expansion of vinasse dosage in soil, without compromising the crop, the soil and the environment, since the reference element, potassium, was successfully greatly removed from vinasse.

## **CHAPTER 3**

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### **INVESTIGATION OF DIFFERENT ELECTROLYTE SOLUTIONS FOR POTASSIUM RECOVERY AND UPGRADING VINASSE FOR IRRIGATION**



### 3.1 INTRODUCTION

Potassium is the seventh most common element occurring in the earth crust, being widely distributed, but due to its high reactivity and affinity with other elements, it never occurs in its elementary form. It is present in rocks, soils, oceans, lakes and saline of salty lakes, although in these occurrences it is rarely found in concentrations superior to 10%. Higher levels are observed in evaporite minerals and in potassium silicates. The two salts of potassium in current use are potassium chloride (containing 60 to 62%  $K_2O$ ) and potassium sulphate (50 to 52% of  $K_2O$ ). Worldwide, more than 95% of potash production is used as fertilizer, 90% of which is produced in the form of potassium chloride (DNPM, 2009).

In 2015, Canada (27.0%), Belarus (20.3%) and Russia (16.2%) occupied the top three positions in the ranking potassium salt reserves. They are also the world's largest producers, since together they sum 64.3% of the total potassium fertilizer produced in the year. Brazil was ranked 10th in terms of reserves and ranked 11th in relation to world production. The reserves of potassium salts in Brazil are located in Sergipe and Amazonas and in the regions of Taquari/Vassouras and Santa Rosa de Lima, both in Sergipe, official reserves of sylvanite ( $KCl + NaCl$ ) totalize 62.92 million tons, with an average content of 9.3%  $K_2O$  equivalent. Of these, 7.7 million tons of  $K_2O$  equivalent represent the Taquari/Vassouras mine/plant complex, which is the only one in current production of potassium fertilizer. From this mine, which has been in operation since 1985, about 46.73 million tons of sylvanite have been explored. The total installed capacity of the mine is 3.2 million tons per year and the beneficiation plant has an installed capacity for production of 850 thousand tons per year of  $KCl$  with expected exhaustion for 2020, after studies that allowed the mine life to be extended (DNPM, 2016).

Still in Sergipe, Mosaic (company that bought VALE FERTILIZANTES S.A in 2018) has a mining project for exploitation of the carnallite reserves through the dissolution process . The project has expected annual production of 1.2 million tons of  $KCl$  per year and useful life of 40 years. Other projects, such as the exploitation of sylvanite reserves in Santa Rosa de Lima and the use of sylvanite reserves in the State of Amazonas is pending definition (TMSA, 2018).

Although Brazil has a domestic supply source of potassium, it currently accounts only for around 9% of national demand of the fertilizer industry. Therefore, the country still relies heavily on imports. Potassium chloride is responsible for a considerable amount of Brazilian imports (US\$-FOB 3,32 billions in 2013, corresponding to 4,9 Mt de K<sub>2</sub>O equivalent (DNPM, 2014) and, as it occurs for China and India, demand tends to increase (DNPM, 2009). In relation to the import value of potassium, when compared the second semester of 2017 with the second semester of 2016, it increased 28.6% (DNPM, 2018). Of the three basic sources of nutrients for the production of agricultural fertilizers (N, P, K), potassium is the one which import Brazil most depends on.

With population growth and subsequent increased demand for food, fertilizers are used to increase agricultural productivity, thus fertilizers are pivotal in meeting the global food demand (FAO, 2015). At present, most of the nutrients used in fertilizers relies on the use of non-renewable energy and finite natural reserves, where extraction problems create environmental contamination and risks to the health of the workers, and also the extraction process is expensive and involves numerous steps (OTHMAN AND AL-MASRI, 2007; LEDEZMA et al., 2015). Thereafter, a paradigm shift towards recovery and reuse of nutrients is urgent, regarding the search for manufacture of fertilizers from the reutilization of nutrients present in materials initially considered as waste, with less environmental impact (SILVA et al., 2017; VERSTRAETE, CLAUWAERT and VLAEMINCK, 2016).

In this sense and focusing on more sustainable solutions, ‘ economy is an alternative to a traditional linear economy (make, use, dispose) in which the resources are maintained in use for as long as possible, people extract the maximum value from them whilst in use, then recover and regenerate products and materials at the end of each service life. Thereby, the aforementioned concept, combined with the context of manufacture of fertilizers and the scarce sources of potassium, enhance the use of recycled K as a substitute of chemical K fertilizers.

The rise of the sugarcane sector, with the augmentation of ethanol production, has led to increased vinasse generation, which has a variable chemical composition, depending mostly on the raw material used in the ethanol production (ESPANA-GAMBOA et al., 2011). The main use of vinasse is as a fertilizer through fertigation of fields (HOARAU et al., 2018). Vinasse is of great agricultural interest due to nutrients (nitrogen and potassium) and organic matter presence, representing an alternative to inorganic fertilizers (MADEJON et al., 2001). Even

though, because of its high concentration of monovalent cations, mainly potassium, when applied at high rates or under dryland conditions, it leads to relevant negative impacts, such as soil salinization (MADEJON, et al., 2011; LYRA, ROLIM and SILVA, 2003), essential nutrient losses (Ca and Mg; GARIGLIO, 2008), an increase in soil erodibility (AUERSWALD et al., 1996), and hydraulic conductivity losses due to the dispersion of fine particles (ARIENZO et al., 2012). Potassium presented in vinasse comes from the juice extraction step in which the K from plant tissues is solubilized into the liquid phase, after which it is concentrated in distillation. The K concentrations in vinasse range from 814 to 7612 mg.L<sup>-1</sup> (CETESB, 1982).

The dosage of vinasse to be applied as fertilizer in the soil is regulated in Brazil by means of potassium content (Section 2.3; CETESB, 2015). However, maximum normative vinasse soil application rate might not be economically feasible, since in some cases the vinasse transportation cost may become more expensive than the cost of mineral fertilizers (FUESS, RODRIGUES and GARCIA, 2017). Consequently, the reduction of potassium and other salts allows an increase in the dosage of vinasse applied in the soil close to the industry, representing less transportation cost, as well as the usage of this organic byproduct in fertigation in a more efficient and environmental safety way.

Electrodialysis, a membrane separation process, can generate desalinated vinasse, with a much lower concentration of ions, which can be applied in fertigation with higher rates, without compromising the needs of the crop, the health of the soil and the environment. Concurrently, it is also produced a solution rich in salts, among those the potassium recovered from vinasse. This solution is of interest for agriculture purposes. The most tradable artificial potassium fertilizer product, KCl with 60 to 62% of potassium quantified as K<sub>2</sub>O, has the disadvantage of causing seed germination impairing when used in high doses, because of excessive chlorine (MALAVOLTA and SHERWOOD, 1984). Therefore, a concentrated stream from the ED, rich in potassium and other important ions for agriculture, might be a great natural fertilizer, progressing towards the necessary paradigm shift of recovery and reuse of nutrients.

Electrodialysis is a consolidated technology that relies on electrolyte solutions that maintain the conductivity and movement of cations and anions through the membranes, promoting the circulation of electric current in the ED unit. The common saline solutions used by ED systems are NaCl, Na<sub>2</sub>SO<sub>4</sub>, KCl and others depending on the focus. In the context of potassium removal

from vinasse and its recovery in the concentrate, aiming at the generation of a byproduct that could be commercialized as a fertilizer, the electrolyte solution should be studied in order to optimize not only the performance of the system in terms of potassium recovery and energy requirements, but also the best application in the soil.

The solution rich in cations from ED can be further concentrated by some technologies as distillation, reverse osmosis and membrane distillation, in order to reduce the volume to be transported onto the fields, or it can be precipitated to generate salts of interests for agriculture. Of all the methods employed in nutrient recovery from wastewater, chemical precipitation is the most widely used due to its high efficiency and stability (YE et al., 2016; JOHANSSON, RUSCALLEDA and COLPRIM, 2017). Tran et al. (2014) demonstrated that the combination of ED process and chemical precipitation can achieve over 80% of phosphate being recovered by calcium phosphate precipitates.

For the recovery of nitrogen and phosphorous, precipitation through struvite is widely used. Struvite is considered a slow-release fertilizer because of its low water solubility (METCALF and EDDY, 2015). These fertilizers release the nutrients in the soil gradually, reducing the nutrient losses due to leaching (GIRARDI and FILHO, 2003).

Zhang et al. (2013) proposed an ED-based hybrid system containing an ED process and a struvite reactor to recover phosphate. Their results indicated high efficiency (93%) of phosphate recovered for the P-rich effluent from the ED process. Barros, Silva and Araújo (2012) analyzed the recovery of nutrients through the chemical precipitation of struvite in an artificial sample of sewage, synthesized from the reagents containing elements essential to the formation of this mineral: monobasic potassium phosphate ( $K_2HPO_4$ ), ammonium chloride ( $NH_4Cl$ ) and magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ), which were molar ratio of 1:1:1. The results indicated a removal of ammoniacal nitrogen and phosphorus between the ranges of 40%-78% and 41%-88% respectively. Schilling (2008) evaluated the struvite precipitation in a leachate sample from Gramacho Metropolitan Landfill (RJ), using  $MgCl_2 \cdot 6H_2O$  and  $Na_2HPO_4 \cdot 12H_2O$ , respectively, as sources of magnesium and phosphorus. The reaction between the precipitants used and the sample showed a yield of 90%, and the presence of struvite was also identified in the solid formed. Castro (2014) studied the recovery of nutrients, among them potassium, through the chemical precipitation of struvite and it was concluded that at a pH of 8.5 and stoichiometric  $Mg^{2+}:NH_4^+:PO_4^{3-}$  ratio of 1.5:1.0:1.25, condition that reached a  $N-NH_4^+$  removal

equal to 98.6%, was taken as optimal. Furthermore,  $\text{Mg}(\text{OH})_2$  and bone meal were used as sources of magnesium and phosphorus, necessary for the formation of the mineral. However, the formation of struvite was compromised due to the presence of interferers in the medium, which implied a decrease in the yield of the precipitation reaction, making it impossible to remove the nutrients of interest.

Because potassium is a very soluble alkaline earth metal with a high ionization constant (SKOOG et al., 2004), it is unlikely to be incorporated in the solid matrix, remaining in the aqueous phase, the main reason for not being removed from the broth, must, wine or vinasse as precipitated salt during the production of ethanol, for instance. However, additives can promote the immobilization of the element as inorganic precipitates of low crystallinity, such as struvite ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  or  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ). Thus, the potassium precipitation potential was also observed as K-struvite, forming a complete complement of low-release NPK fertilizer, from nutrient recovery in wastewater (BENNET, 2015; CASTRO, 2014).

K-struvite and struvite are isostructural minerals, differing only in the presence of potassium and ammonium ions, which have similar atomic radio. Therefore, the possible substitution of one ion for the other does not cause significant distortions along the crystalline lattice of the molecule and, therefore, both structures have similar chemical properties (GRAESER et al., 2008 apud BENNET, 2015). While struvite crystallization has been extensively investigated for the removal of N and P, further studies are still needed for K-struvite crystallization, because the thermodynamics and kinetics of K-struvite crystallization differ from those of struvite (RONTELTAP, MAURER and GUJER, 2007).

According to previous studies, the K-struvite precipitation obtained a significant efficiency within a pH range of 5.5 - 11 (GUNAY et al 2008, LE CORRE et al., 2009; DI IACONI et al., 2010 apud XU et al., 2011). In this way, Xu et al. (2011) carried out their tests in a synthetic urine sample within this pH range and observed that high pH values favor the precipitation of this product, although the removal efficiency has declined at pH 12. According to Li et al. (2015) precipitation at pH 10 is more favorable using a Mg:K:P molar ratio of 3:1:3; and about 97% of the K in urine could be recovered when the Mg:K:P ratio reached 3:1:3 (Xu et al., 2012b). Whereas for Xu et al. (2011) this ratio is 2:1:2, achieving removal efficiencies of P and K of 77% and 98%, respectively. Some K-struvite were produced, though not pure, in a molar ratio of 1:1:1, and results showed that ammonium replaced potassium in K-struvite matrix (LIN,

BASSIN and VAN LOOSDRECHT, 2012). Bennett (2015) obtained K-struvite quite pure with a K:Mg:P ratio of almost 1:1:1.

The matrix used in the precipitation operation must be carefully known so that interferences from other ions are inhibited. For Xu et al. (2011) removal efficiency of K decreased from 77% to 65% as the ammonium concentration increased from 0 to 500 mg N.L<sup>-1</sup>. According to Svehla (1996), ammonium salts form a K-struvite-like precipitate and in their presence, even in small concentrations, struvite is preferably formed (BENNET, 2015). Moreover, Mg and Ca materials are usually employed as the precipitator to form MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O (struvite) and Ca<sub>5</sub>(OH)(PO<sub>4</sub>)<sub>3</sub> (HAP), respectively.

A study by Xu et al. (2015) identified the co-precipitation of MgNaPO<sub>4</sub>·7H<sub>2</sub>O (Na-Struvite or MSP), MgNH<sub>4</sub>PO<sub>4</sub>·7H<sub>2</sub>O (Struvite or MAP) and MgKPO<sub>4</sub>·6H<sub>2</sub>O (K-struvite or MPP) in a synthetic urine sample over a pH range of 8.5-11 using MgCl<sub>2</sub>·6H<sub>2</sub>O as the precipitant. This occurred due to the presence of ammonia nitrogen and sodium, limiting the formation of K-struvite. Therefore, the author recommends that the precipitation occur in a free sample of NH<sub>4</sub><sup>+</sup> and that NaOH is not used to control the pH of the reaction. By substituting NaOH by Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub> to increase the pH in the precipitation reactor or adding another calcium or magnesium source, up to 90% of the phosphate can be precipitated (ETTER et al. 2011).

The co-crystallization of two isomorphous analogs, i.e. magnesium ammonium phosphate hexahydrate and magnesium sodium phosphate heptahydrate, significantly weakened the crystallization of magnesium potassium phosphate hexahydrate (Xu et al., 2011). Further, Wilsenach and others (2007) developed a continuous stirred reactor, and achieved a high efficiency of P removal from synthetic urine through the magnesium potassium phosphate hexahydrate crystallization and also MgO has been successfully applied in initiating the precipitation of MPP as both sources of Mg and alkaline.

A study of Li and others (2015) recovered products of MgKPO<sub>4</sub>·6H<sub>2</sub>O and hydrogen from nanofiltration (NF) concentrate generated from a landfill plant. It was found that from treating 400 m<sup>3</sup> per day of the NF concentrates containing approximately 2761 mg K.L<sup>-1</sup>, approximately 1540 t.y<sup>-1</sup> of MgKPO<sub>4</sub>·6H<sub>2</sub>O could be produced, based on a potassium recovery rate of 56%.

The immobilization of macro and micronutrients in hydrochars produced from the hydrothermal carbonization of the vinasse and sugarcane bagasse mixture also was investigated by Silva et al. (2017). The molar ratios between the nutrients K, Mg and P of the hydrochars

produced from reaction medium containing  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  were 1:1:1, suggesting the formation of the precipitate struvite-K. The molar ratios of the nutrients N, Mg and P in the hydrochars produced with the addition of the same additives mentioned above were 2:1:1. The immobilization of nutrients occurs both by adsorption on the surface of the hydrochar and also the precipitation of insoluble compounds.

Most works dealing with potassium precipitation tested urine as source of potassium and nutrients. The presence of several dissolved components in the vinasse may consume, probably in high levels, the precipitating and/or complexing additives, leading to prohibitive costs of the process for recovery of potassium. That is why, in this master thesis, the first step is to recover the potassium from vinasse by electrodialysis and use the concentrate, rich in potassium, in the precipitation stage, reducing the interference occurred with raw vinasse. Furthermore, the assessment of different electrolyte solutions might enable better conditions for precipitation in order to obtain a fertilizers with added value.

Thus, the aim of this chapter is to investigate the electrolyte solutions for potassium recovery for further precipitation as a fertilizer salt and also upgrade vinasse for agricultural use.

## **3.2 MATERIALS AND METHODS**

### **3.2.1 *Experimental apparatus***

More details about the electrodialysis experimental apparatus used are cited in topic 2.2.3 of chapter 2.

### **3.2.2 *Experimental procedure***

Tests with different electrolyte solutions were done with ultrafiltrated vinasse A and mixed configuration (one cationic membrane - between compartments E and CC - was monovalent selective NEOSEPTA® from ASTOM Co., Japan and the others were non-monoselective heterogeneous HDX membranes provided by Hidrodex® - Figure 2.3 c)). The electrolyte solutions tested include sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) 0.03 M, ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) 0.05 M, magnesium sulfate ( $\text{MgSO}_4$ ) 0.047 M, potassium sulfate ( $\text{K}_2\text{SO}_4$ ) 0.027 M and tap water. In all cases, the selection of the reagents took into account the possibility to aggregate ions of interest for agriculture in the concentrated compartment, such as ammonium, magnesium or potassium, rather than sodium as in the first electrolyte solution tested.

For each electrolyte solution, 8-hour tests were performed with  $6.9 \text{ mA.cm}^{-2}$ . This current density was chosen since the triplicate of the polarization curves for definition of the limiting current for each electrolyte solution presented no similarities, then the current value of the tests were the same as for sodium sulfate. The only test that couldn't reach this value was the test with tap water, then it was performed with the maximum current density as possible ( $1.3 \text{ mA.cm}^{-2}$ ).

It was simulated the precipitation of struvite and k-struvite from the electrolyte solutions selected in the previous step. Predictions of the amounts of precipitated formed and costs were done, taking into account the reagents needed and selected by best conditions exhibited in the literature and considering the volume of vinasse generated in a year.

### **3.2.3 Calculations**

More details about the calculations of percentage of recovery, current efficiency, specific energy consumption, energy per quantity of potassium recovered, selectivity, apparent stack resistance, SAR and PAR are cited in topic 2.2.5 of chapter 2.

### **3.2.4 Analytical methods**

Effluent and solution were analyzed according to the parameters sulfate, ammoniacal nitrogen, COD, potassium, calcium, magnesium and sodium. More details about the analytical methods applied can be seen in topic 2.2.6 of chapter 2.

## **3.3 RESULTS AND DISCUSSION**

Figure 3.1 displays the recovery of ions and COD for all electrolyte solutions for 8-hour tests. It is observed that for sodium sulfate test there were considerable transport of cations. Especially, this electrolyte solution leads to the higher recovery of ammoniacal nitrogen, potassium and magnesium. Only sodium presented low recovery (7%), which may be due to diffusional back transport of sodium from the electrolyte compartment to the effluent compartment due to concentration gradient. Because of the already high concentration of sulfate in the original electrolyte solution and consequent diffusional back transport from electrolyte solution to effluent solution, the liquid amount of sulfate crossing the membrane was not expressive. Thus, the transport of COD was important to ensure the electroneutrality of effluent



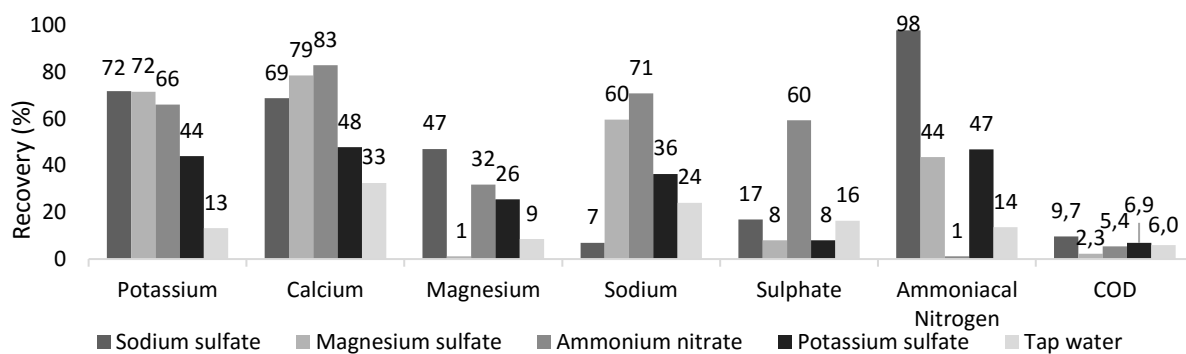
and cation transport across the membrane. Therefore, the transport of lesser permeable anions (charged COD) resulted in high ASR for this solution (Figure 3.2). Also, the observed increase in the ASR during experiment time could be associated to fouling and/or depletion of the anions most easily transported by the membrane from the feed to the concentrated stream. Once such ions are depleted, the current must be transported by other anions that have a lower membrane permeability resulting in an increased membrane resistance.

For the test with ammonium nitrate, the transport of calcium and sodium were expressive, favored by the transport of sulfate anion instead of COD. As expected, no ammoniacal nitrogen recovery from the effluent was observed for this solution.

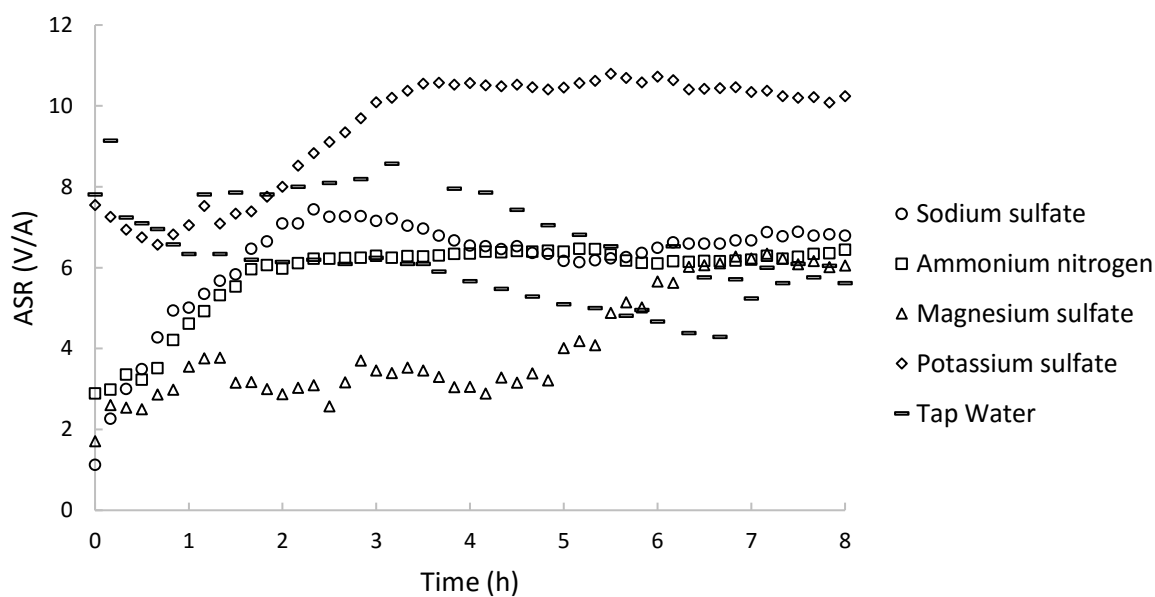
Magnesium sulfate displays a preference to permeate calcium and then potassium, probably to compensate the irrelevant liquid flux of the magnesium itself.

For the potassium sulfate solution, there is no recovery of more than 50% for any ion, achieving similar recoveries for calcium, ammoniacal nitrogen and potassium. As the passage of sulfate is hampered, some transport of COD is favored. As the potassium is the major ion in vinasse, with higher permeation, potassium sulfate shows higher ASR during all test (Figure 3.2), especially after the second hour of test, when some migration of potassium already occurred from vinasse to CC compartment and it gets even more difficult to permeate the membrane with the high accumulation of  $K^+$ .

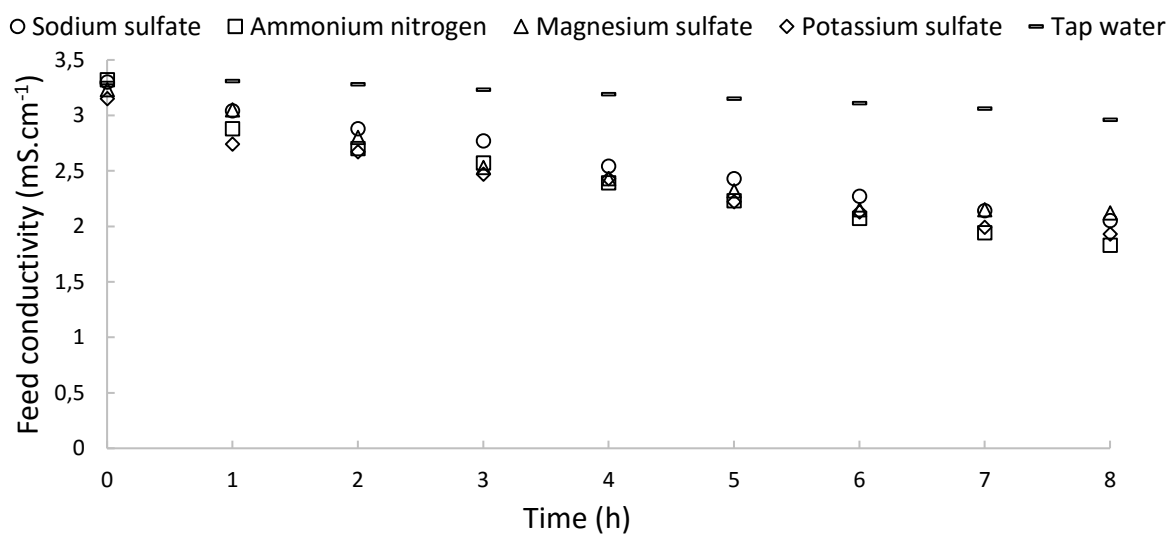
Tap water shows the lowest recovery values for almost all the variables, consequently a low reduction of feed conductivity (Figure 3.3), due to a smaller current density applied (explained in topic 3.2.2). Except from tap water, all the electrolyte solutions were made with the same electrical conductivity, then, the higher ASR for tap water (Figure 3.2) is due to the solution resistance, since it has much lower conductivity and consequently much less ions to favor the transport in the ED system.



**Figure 3. 1** - Recovery of ions and COD for electrolyte solutions.

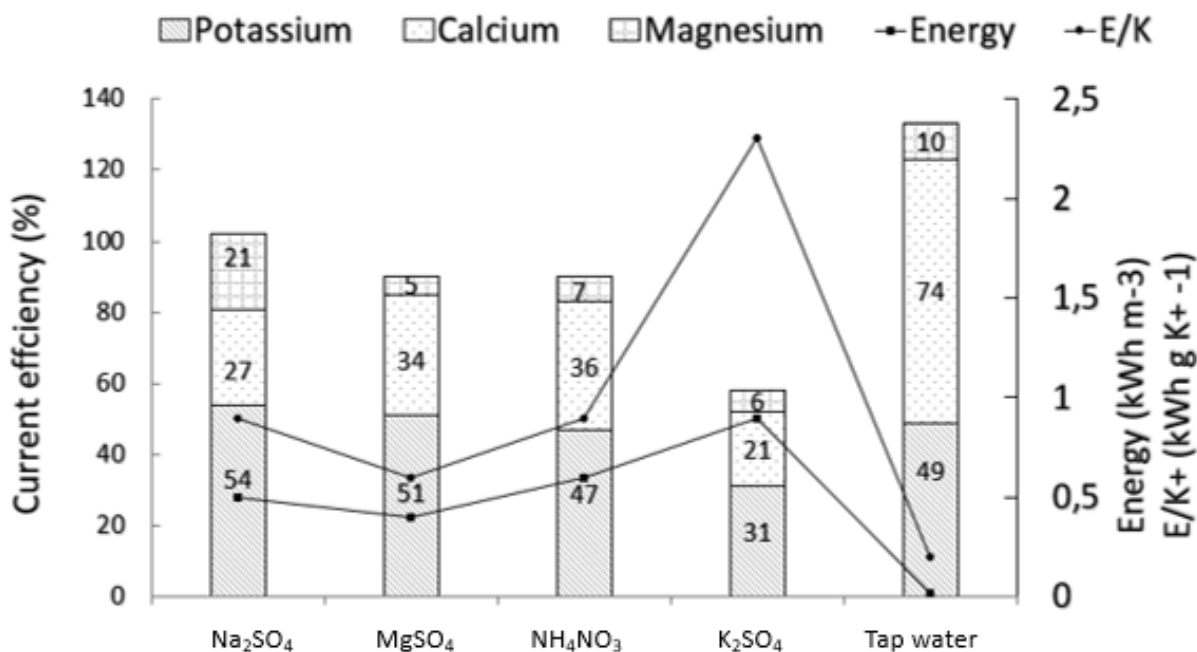


**Figure 3. 2** - Apparent stack resistances (ASR) for all electrolyte solutions.



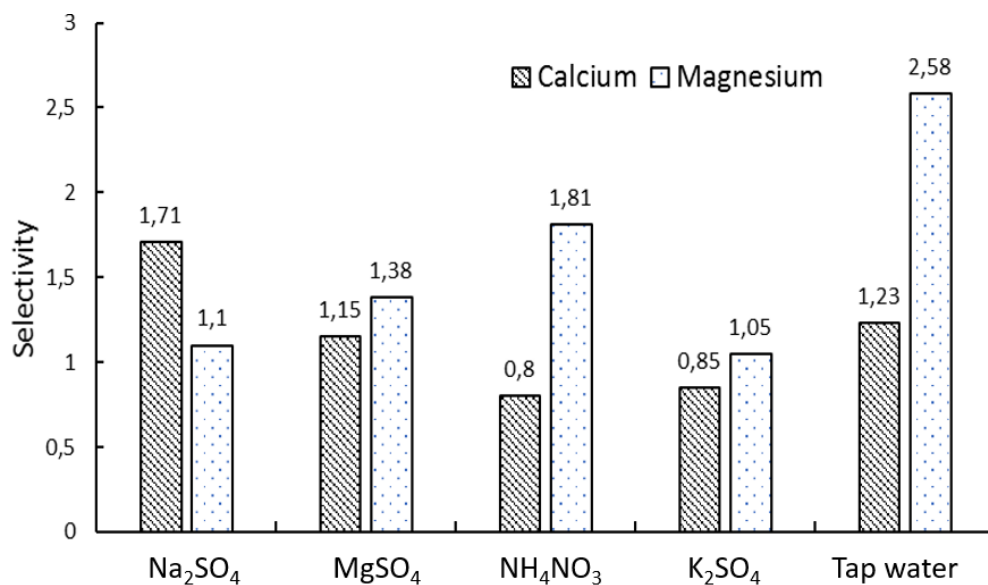
**Figure 3. 3** - Progression of feed electrical conductivity during tests for electrolyte solutions.

Besides analysing the recovery efficiencies, it were calculated, for all electrolyte solutions, energy consumption, current efficiency for potassium, calcium and magnesium and the selectivity between potassium and calcium and between potassium and magnesium. The analysis of Figure 3.4 elucidates that the sodium sulfate exhibits higher current efficiencies for potassium and magnesium, meanwhile tap water has higher current efficiency for calcium. The energy consumption for tap water is really low due to the low current density applied and even with only 13% of potassium recovery, the specific energy consumption is still the lowest. The amount of potassium transported per unit of current is similar for all tests (around  $5.5 \text{ mgK}^+ \cdot \text{L}^{-1} \cdot \text{mA}^{-1}$ ), except for  $\text{K}_2\text{SO}_4$  solution ( $3.6 \text{ mgK}^+ \cdot \text{L}^{-1} \cdot \text{mA}^{-1}$ ) that recovered less potassium with the same current density applied. All the electrolyte solutions presented better current efficiency for potassium, apart from tap water solution that presented higher current efficiency for calcium, in accordance with the recoveries in figure 3.2. The  $\text{K}_2\text{SO}_4$  solution showed lowest values of current efficiencies, the highest values of energy consumption and energy consumption per mole of  $\text{K}^+$  recovered. The high energy consumption is due to the highest voltage needed by the system when used this electrolyte solution, caused by high ASR. The specific energy consumption was more than double for potassium sulfate solution due to the less potassium recovery achieved with this solution.



**Figure 3. 4** - Calculations of current efficiency, energy and  $\text{E/K}^+$  for electrolyte solutions.

The permselectivities between calcium and magnesium and potassium ions ( $S_{Ca}^K$  and  $S_{Mg}^K$ ) are presented in Figure 3.5.



**Figure 3. 5** - Comparison of selectivity of all electrolyte solutions.

Not all the electrolyte solutions showed a higher selectivity in separating monovalent from divalent ions ( $S_{Ca}^K$  and  $S_{Mg}^K$ ) > 1). Even though the majority of the calculations demonstrates the preference in permeating potassium, calcium and then magnesium (higher  $S_{Mg}^K$  compared to  $S_{Ca}^K$ ), for K<sub>2</sub>SO<sub>4</sub> solution selectivity  $S_{Ca}^K$  is 0.85 and selectivity  $S_{Mg}^K$  is slightly higher than 1. This occurs due to the high concentration of potassium in the electrolyte solution, diffusional back transport and low liquid flux of K<sup>+</sup>, favoring the passage of the divalent ions, especially calcium, the divalent cation in larger amount in vinasse.

For ammonium nitrate solutions selectivity  $S_{Ca}^K$  is 0.80, showing a preference in permeate calcium (more than 80% of calcium is removed from vinasse and recovered in compartment CC) than potassium.

The higher selectivity for calcium is for Na<sub>2</sub>SO<sub>4</sub> solution and for magnesium is for tap water, The high selectivity  $S_{Mg}^K$  for tap water is justified by the low permeation of magnesium, a low mobility cation, to the CC compartment.

The choice of the adequate solution should consider not only the conditions and parameters discussed above, but also the ideal conditions for application in soil of the two by-product (desalted vinasse and concentrated solution).

SAR shows the ratio between sodium and divalent ions (Ca and Mg). A low conductivity associated with a high SAR can bring problems to the soil, as presented in table 2.5. Though there is no agreement of safe PAR value, water with a maximum PAR of 5 seems suitable to use in irrigation (SMITH, OSTER and SPOSITO, 2015).

Table 3.1 Shows values for PAR and SAR for all tests in the concentrated cation compartment, CC, and in the central compartment, E, where is obtained the desalted vinasse.

**Table 3. 1** - PAR and SAR values for vinasse and all electrolyte solution tests in compartments CC and E.

<i>Test</i>	<i>PAR (<math>\text{meq.L}^{-1}</math>)<sup>0.5</sup></i>	<i>Degree of restriction of use</i>	<i>SAR (<math>\text{meq.L}^{-1}</math>)<sup>0.5</sup></i>	<i>EC (<math>\text{dS.m}^{-1}</math>)</i>	<i>Degree of restriction of use</i>
Raw Vinasse	7.07	Slight to moderate	0.68	3.4	None
<b>Desalted vinasse (E)</b>					
Sodium Sulfate	2.33	None	4.75	2.05	None
Magnesium sulfate	2.60	None	0.37	2.12	None
Ammonium nitrate	3.82	None	0.36	1.83	None
Potassium sulfate	4.99	None	0.28	1.93	None
Tap water	4.79	None	0.74	2.96	None
<b>Concentrate (CC)</b>					
Sodium Sulfate	5.82	Slight to moderate	28.31	7.27	None
Magnesium sulfate	2.00	None	0.16	7.66	None
Ammonium nitrate	5.80	Slight to moderate	0.26	8.32	None
Potassium sulfate	35.72	Severe	0.39	7.03	None
Tap water	1.90	None	0.33	0.55	Slight to moderate

As it can be observed, vinasse has no restrictions of use in relation to SAR value, but has a slight to moderate restriction of use in the soil due to PAR between 5 and 10. The application of electrodialysis can, in all cases, adequate vinasse for application in fertigation, as potassium and other cations migrate out of compartment E to compartment CC. It is important to observe

that potassium sulfate and tap water, both with lowest recovery of potassium (Figure 3.1), almost achieve the limit of PAR value. For the cation concentrated compartment, tap water presents the lowest PAR value, because the potassium recovery is the lowest, followed by magnesium sulfate solution that has a low value of PAR due to a major presence of magnesium that compensates the potassium concentration. For potassium sulfate solution, the PAR value in CC compartment is explained by  $K^+$  of the initial electrolyte solution.

Even though for PAR and SAR values there is no restriction of use of desalted vinasse in soil, when using sodium sulfate solution, the migration of sodium to compartment E increases the concentration of  $Na^+$  in desalted vinasse, which could alter the chemical element of reference in soil application. For the other electrolyte solution, on the other hand, the desalted vinasse presents lower values of sodium than raw vinasse, allowing this effluent to be applied in fertigation.

Due to the above mentioned, for agricultural application and aiming the enlargement of vinasse rate application in an environmental safety way, the electrolyte solution of sodium sulfate, even with good results in terms of ions recovery, especially potassium and energy requirements, might be not adequate. Tap water and potassium sulfate PAR value almost reach the maximum, considering the lack of restriction of use, so they also shouldn't be chosen. All the other electrolyte solutions fulfill the conditions for the application of desalted vinasse in soil.

The choice of the ideal electrolyte solution, thus, should consider the concentrated compartment with the higher added-value as possible. Considering the application on sugarcane fields, the irrigation water could be used in the preparation of the electrolytic solution and then, with the application of ED and generation of the concentrate, this solution could be used in the fertigation. However, if the recovered potassium is used for other agricultural areas, the concentration of the solution or the precipitation of potassium is extremely important to reduce the cost of transport. Bringing into account that magnesium potassium phosphate products are considered valuable and scarce slow-release fertilizers (XU et al., 2011; XU et al., 2012a), the formation of K-struvite by precipitation of the obtained concentrate is indeed interesting.

Table 3.2 resumes the concentrations of all variables analyzed in the concentrate for all the electrolyte solutions.

**Table 3. 2** - Concentrations of ions and COD in the concentrate for all electrolyte solutions.

<i>Concentrate (CC) mg.L<sup>-1</sup></i>	<i>Potassium</i>	<i>Calcium</i>	<i>Magnesium</i>	<i>Sodium</i>	<i>Sulphate</i>	<i>Ammoniacal Nitrogen</i>	<i>COD</i>
Sodium sulfate	575	145	69	1650	3219	10.1	102
Magnesium sulfate	650	226	1537	12	5567	5.7	99
Ammonium nitrate	600	238	29	16	57	567.0	43
Potassium sulfate	2900	138	23	19	2960	0.8	5
Tap water	120	94	8	12	663	0.3	229

The solution of sodium sulfate is already discarded due to the contribution of sodium in the desalted vinasse, as pointed before. Regarding the precipitation simulation, the use of tap water, even with good energy requirements, recovered only 120 mg.L<sup>-1</sup> of potassium and 8 mg.L<sup>-1</sup> of magnesium, so other concentrated solutions exhibit much higher concentration of potassium, being more adequate for precipitation of K-struvite. Potassium sulfate, has the highest concentration of potassium, but in the ED step presented worst results of energy consumption, which is not economically feasible. Wherefore, electrolyte solutions of magnesium sulfate and ammonium nitrate were considered for precipitation simulation stage.

As recommended by Xu et al. (2011) for precipitation of K-struvite, sample should free of NH<sub>4</sub><sup>+</sup>. Combination of an ammonium-removal/recovery process and an MPP precipitation process needs further studies and discussions, especially on the technical and economic feasibility, anyway struvite would be the dominate precipitate in the presence of ammonium (WILSENACH, SCHUURBIERS and VAN LOOSDRECHT, 2007; XU et al., 2015). Due to that, the electrolyte solution of ammonium nitrate, would generate preferentially struvite at pH of 8.5, stoichiometry Mg<sup>2+</sup>:NH<sub>4</sub><sup>+</sup>:PO<sub>4</sub><sup>3-</sup> ratio of 1.5: 1.0: 1.25 (CASTRO, 2014), taking into account the constituents in the concentrate solution (Table 3.2) and simulating the application of MgCl<sub>2</sub>.6H<sub>2</sub>O and Na<sub>2</sub>HPO<sub>4</sub>.7H<sub>2</sub>O as sources of magnesium and phosphate, respectively and application of either NaOH or Mg(OH)<sub>2</sub>, the latter as alternative reagent source for pH correction. For the precipitation of struvite and K-struvite of the concentrate of ammonium nitrate solution, Table 3.3 resumes the necessary inputs, such as reagents, energy and electrolyte solution prices in \$.m<sup>-3</sup>. For ammonium nitrate solution, the use of Mg(OH)<sub>2</sub> rather than NaOH reduced the need of MgCl<sub>2</sub>.6H<sub>2</sub>O, making this option more profitable.

**Table 3. 3** - Reagents and energy costs for precipitation with ammoniacal nitrogen solution.

Inputs	NaOH as base		Mg(OH) <sub>2</sub> as base	
	mg.L <sup>-1</sup>	US\$.m <sup>-3</sup>	mg.L <sup>-1</sup>	US\$.m <sup>-3</sup>
<b>NH<sub>4</sub>NO<sub>3</sub> solution</b>	4002.15	1.60	4002.15	1.60
<b>Energy (ED)</b>	-	47,308.80	-	47,308.80
<b>MgCl<sub>2</sub>.6H<sub>2</sub>O</b>	16977.99	6.62	14702.69	5.73
<b>Na<sub>2</sub>HPO<sub>4</sub>.7H<sub>2</sub>O</b>	22898.38	8.93	22898.38	8.93
<b>Base</b>	895.41	0.35	652.82	0.25
<b>TOTAL</b>	40771.78	47,326.30	38253.89	47,325.32

For magnesium sulfate it is possible to obtain K-struvite, considering the ideal/average conditions for precipitation stated in literature: pH 10 and Mg:K:P molar ratio of 2:1:2 (XU et al., 2011). The application of an electrolyte solution with already large amounts of magnesium diminish or even avoid the application of magnesium salt in the precipitation step. Furthermore, the use of magnesium sulfate showed good results for potassium recovery, exhibiting lower ASR and best energy consumption (0.4 kWh.m<sup>-3</sup>) and specific energy consumption (0.6 kWh.kg<sup>-1</sup> K<sup>+</sup>) in comparison with the other electrolyte solutions, except from tap water.

As for ammonium nitrate, it was simulated for magnesium sulfate the application of MgCl<sub>2</sub>.6H<sub>2</sub>O and Na<sub>2</sub>HPO<sub>4</sub>.7H<sub>2</sub>O as sources of magnesium and phosphate, respectively and application of either NaOH or Mg(OH)<sub>2</sub>, the latter as alternative reagent source for pH correction, in order to avoid formation of MSP. Table 3.4 shows for magnesium sulfate the necessary inputs, such as reagents, energy and electrolyte solution prices in US\$.m<sup>-3</sup>.



**Table 3. 4 - Reagents and energy costs for precipitation with magnesium sulfate solution.**

Inputs	NaOH as base		Mg(OH) <sub>2</sub> as base	
	mg.L <sup>-1</sup>	US\$.m <sup>-3</sup>	mg.L <sup>-1</sup>	US\$.m <sup>-3</sup>
MgSO <sub>4</sub> solution	4929.4	0.39	4929.4	0.39
Energy (ED)	-	33,264.00	-	33,264.00
MgCl <sub>2</sub> .6H <sub>2</sub> O	0	0	0	0
Na <sub>2</sub> HPO <sub>4</sub> .7H <sub>2</sub> O	8914.76	3.48	8914.76	3.48
Base	283.16	0.11	206.44	0.08
<b>TOTAL</b>	<b>9197.92</b>	<b>33,267.98</b>	<b>9121.20</b>	<b>33,267.95</b>

As the magnesium sulfate already presents large amounts of magnesium, there is no need to add magnesium chloride in the precipitation step. For both electrolyte solutions, magnesium hydroxide as base was more cost-effective than sodium hydroxide. Consequently, in Table 3.5 it was calculated the price per tons of fertilizer recovered considering the total cost of inputs (with Mg(OH)<sub>2</sub> as base) and the total precipitated as struvite and K-struvite.

**Table 3. 5 - Total precipitated formation and cost per ton recovered.**

	K-struvite formation	Struvite formation	Total cost of inputs	Price per ton
	(t.m <sup>-3</sup> )	(t.m <sup>-3</sup> )	(US\$.m <sup>-3</sup> )	recovered (US\$.t <sup>-1</sup> )
<b>Ammonium nitrate</b>	0.0039	0.0073	47,325.32	4,248,028.40
<b>Magnesium sulfate</b>	0.0044	0	33,267.95	7,508,233.08

Even with lower cost associated with reagents, energy and electrolyte solution and slightly higher K-struvite formation for MgSO<sub>4</sub>, the total cost per tons of nutrients recovered is still more favorable to NH<sub>4</sub>NO<sub>3</sub>, due to the higher total precipitated (MPP and MAP). Even though this higher cost associated, it should be taken into account that potassium fertilizers could be partially substituted by K-struvite and Brazil still relies heavily on imports to meet domestic demand, with potassium chloride being responsible for a considerable amount of Brazilian imports (DNPM, 2009). Brazil, in 2013, imported US\$-FOB 3,32 billions, corresponding to 4.9 Mt de K<sub>2</sub>O equivalent (DNPM, 2014). Beyond that, in the distillery industry there is the generation of electricity in the production plant, so if this residual energy could be used in order to eliminate the cost with energy in the ED step, total cost would diminish considerably reaching

for ammonium nitrate and magnesium sulfate solution 1,482.86 \$.t<sup>-1</sup> and 891.84 \$.t<sup>-1</sup>, respectively.

Because MgKPO<sub>4</sub>6H<sub>2</sub>O (K-struvite), is a new scarce resource, the related market price is unavailable and the price of struvite (MgNH<sub>4</sub>PO<sub>4</sub>6H<sub>2</sub>O) is \$350.t<sup>-1</sup> (JONES, 2004). Even though still the price seems not competitive, the real gain with this technology includes the increase with vinasse rate in soil, with less transportation spent, since in some cases the vinasse transportation cost may become more expensive than the cost of mineral fertilizers. Furthermore, as in practical terms, the inputs of K (and other compounds) into the soils are much higher than the values calculated from the normative instruction, the use of ED might reduce the negative environmental impacts. Even so, recovery of potassium in the form K-struvite from wastewaters is promising owing to the higher and increasing price of potassium resources in the global market.

What can be studied after indeed is the appliance of MgCl<sub>2</sub> instead of MgSO<sub>4</sub> in the electrodialysis as electrolyte solution, since the literature uses MgCl<sub>2</sub>.6H<sub>2</sub>O as reagent in the precipitation step, and it is not known if with MgSO<sub>4</sub> the precipitation will occur with the same efficiency.

The other alternative is to concentrate the solution, in order to obtain a value-added solution with high amounts of nutrients. For that it is possible to test electrolyte solutions with multiple reagents, in order to supply to the value-added solution multiple ions of agricultural interest. At the end of experiment, CC solution can be concentrated by distillation in order to obtain a fertilizer rich in phosphate, potassium, magnesium, calcium, ammonium and other components useful for soil application.

### **3.4 CONCLUSIONS**

The use of electrodialysis enabled the generation of a desalted and a concentrated stream. The desalted one, the vinasse, with less potassium content can be applied in the soil in higher rates, meanwhile the concentrated one can be used as fertilizer, substituting the mineral fertilizer, since it is rich in nutrients.

Tests with different electrolyte solutions showed that the sodium sulfate, one largely use in electrodialysis systems, even with SAR and PAR values with no restriction of use in soil, due to diffusion of sodium towards vinasse compartment, presents high amounts of sodium, which could compromise the enlarged rates of desalted vinasse administration in soil.

The use of ammonium nitrate might enable the formation of struvite, preferably, due to high quantities of ammonium in the concentrate. For K-struvite formation the ideal was the use of magnesium sulfate. This solution presented 72% of potassium recovery, best energy consumption ( $0.4 \text{ kWh.m}^{-3}$ ) and specific energy consumption ( $0.6 \text{ kWh.kg}^{-1} \text{ K}^{+}$ ) in comparison with the other electrolyte solutions, except from tap water and less requirement of magnesium input in the precipitation test. The use of energy in the ED step increases the price to obtain K-struvite reaching US\$4,248,028.40 per tons of nutrient recovery for ammonium nitrate and US\$7,508,233.08 per tons of nutrient recovery for magnesium sulfate. Using the residual energy generated in distillery plants these values reduce to 891.84 US\$.t<sup>-1</sup> and 1,482.86 US\$.t<sup>-1</sup>, respectively. This preliminary economic evaluation does not consider the gain with less transportation cost of vinasse, since in some cases the vinasse transportation cost may become more expensive than the cost of mineral fertilizers.

This application of electrodialysis, then, enabled an application of vinasse in the soil without compromising the needs of the crop, the health of the soil and the environment. More than that, created a fertilizer stream that can be replaced by mineral fertilizers, generating profits for the distilleries.

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