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Techno-Economic Analysis of Dye Separation in Textile Recycling

A pre-feasibility study on dye separation and reclamation of process filtrate using electrocoagulation and sequential membrane filtration

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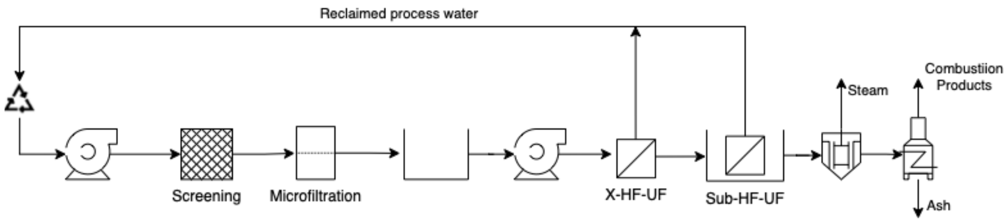
Abstract

This study determines the technical and economic feasibility of separating dye from a process filtrate in industrial textile recycling using electrocoagulation or sequences of membrane filtration with microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The lower requirements for treating this stream, compared to previously researched dyehouse effluents, left treatments not good enough for dyehouses viable for this process filtrate. Electrocoagulation effectively removes the dye from the filtrate but limited downstream research, coagulant pollution and excessive pH control left the process filtrate unfit for recirculation to the process. Therefore, the design of this treatment method was focused on the core process and should only be applied on waste streams leaving the process. The direct operational cost of electrocoagulation was estimated to 1.22 $\$/m^3$. For membrane filtration, a complete process was designed from incoming filtrate to handling of end products. An indirect series of first external and then submerged hollowfiber-ultrafiltration shows best performance. This both concentrates pollutants and reclaims the process filtrate. A CAPEX estimation of \$680 000 and OPEX of \$360 000 gives a total treatment cost of 0.49 $\$/m^3$ for operations in Sundsvall, Sweden. Both electrocoagulation and membrane filtration efficiently remove dye from the filtrate and can be industrially feasible.

Popular science summary

Cost efficient membrane filtration can make textile recycling more sustainable by separating the dyes from the solvents.

To make the textile industry sustainable it must become circular by recycling textiles. Currently textile recycling use, discard and emit water, chemicals, water-based solvents, and dye when these could instead be used cyclically. For example, the solvents used to remove the dye from clothes does not get consumed, only saturated of dye. If the dye can be separated from the solvent, then the solvent can be reused for the same purpose while also avoiding harmful release of dye through collection after the separation. A proposed design of a membrane filtration system achieves this at an estimated unit cost of $0.49 per m^3 for constructing and operating a plant in Sweden. This system uses advanced industrially available hollow-fiber ultrafiltration(HF-UF) membranes to treat large quantities of wastewater with high precision.



Another explored treatment method is electrocoagulation that coagulates pollutants with electrolysis and leaves a purified solution behind. While electrocoagulation is shown to be efficient at the main objective, the dye removal, it turned out that the solvent cannot be reused, partially falling short of the aim. The direct operational unit cost of electrocoagulation was estimated to $1.22 per m^3.

Current research is focused on separating dye and reclaiming solvents in dyehouses producing new clothing. Reusing the solvent for coloring have higher purity requirements than for decoloring in textile recycling. For this reason, in textile recycling specifically it is smarter to use an indirect membrane sequence to reclaim more solvent but with lower purity compared to dyehouses which must use direct series to meet strict purity limits. Dyes used for textiles are often toxic chemical compounds not easily broken down in nature or at treatment plants. The dye therefore needs to be separated to not exceed the capacity of the chemical loading of treatment plants. This thesis concludes that HF-UF is the best available option all in all and should be the long-term solution for industrial separation of dye in textile recycling.

“Theory will only take you so far.”

-Robert J. Oppenheimer

Abbreviations

A – Amperes, SI unit of current

EC – Electrocoagulation

V – Volt, SI unit of electric potential

h – Hour, unit of time

kDa – Kilo Daltons, unit of molecular mass

L – Liters, unit of volume

m^3 – Cubic meters, SI unit of volume

MWCO – Molecular weight cut-off

Pt-Co – Platinum Cobalt units, Unit of color strength

HF-UF – Hollow fiber ultra-filtration, ultrafiltration using hollowfiber membranes.

MF – Microfiltration, filtration process using filters with pore sizes on the micrometer scale.

UF – Ultrafiltration, filtration process using filters with pore sizes in-between micro- and nanoscale.

NF – Nanofiltration, filtration process using filters with pore sizes on the nano scale.

RO – Reverse osmosis, filtration process using filters with pore sizes on the micrometer scale.

ZLD – Zero Liquid Discharge, incentive to use all water in processes cyclically.

μm – Micrometer, a millionth of a meter

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1. Background

1.1 Introduction

The global textile industry has serious effects on our environment through pollution and consumption of water and natural resources. According to Fischer and Pascucci[1] the textile industry is responsible for generating 5% of the world's total waste and Boucher and Friot[2] reveals in an IUCN report that 34.8% of the microplastics ending up in oceans comes from the textile industry. For industries this big even process inefficiencies and minor pollutant have a huge effect on the environment. For example, according to Buscio et al.[3] about 15% of all indigo consumed in dyeing does not end up in the products and is sent for wastewater treatment and in countries where regulations are not followed it can end up in waterways.

The European parliament has reviewed the total impact of the textile industry and concluded that it was the third largest source of water degradation and land use in 2020. In terms emissions, the sector was responsible for a tenth of global greenhouse gas emissions, which was estimated to be more than the combined emissions from all global international airplane traffic and maritime shipping.[4]

Albeit bad, since clothing is a basic human necessity, the industry and the demand for these products is not likely to decrease. Therefore, clothing must be sourced in a more sustainable way. To avoid further overexploitation of natural resources, pollution, and waste generation, Renewcell among other actors are trying to provide customers with an alternative to linear consumption of clothes by recycling textiles. Textiles can be mechanically recycled and blended into new fabrics but as fibers get shorter and the product quality is inferior to virgin materials this is essentially downcycling the material. An alternative to this is chemical recycling. By dissolving the fibers new fibers with a higher quality that is comparable to virgin materials can be produced. These fibers can be used without the need of any other fibers, closing the loop on material sourcing in the textile industry.

Renewcell is producing dissolving pulp by recycling discarded textile waste. The dissolving mass is intended for production of new textile fibers that can replace virgin fibers in textile manufacturing. Depending on the process used to dissolve the dissolving mass and precipitate the new fibers, the products are fibers like lyocell and viscose.

When chemically recycling cotton the problem with blended garments is most easily avoided by only accepting textiles with high cellulose content. This gives a lower supply of textile waste, but one that is by no means met by the textile recycling industry. Discarded denim jeans are a great example of a garments applicable for chemical recycling. But not only post-consumer goods such as worn out and out of fashion clothing is suitable for recycling but also unsold product and waste from the production process such as cuttings and defect pieces.

Closing the loop on the textile fibers alone is not enough. Resources such as the water used within the recycling process should also be used in a cyclic way to have minimal impact on our environment. With more sustainable and responsible manufacturing becoming the global standard, all producing industries will have to use resources cyclically in the future and approach the zero liquid discharge incentive.

1.2 Dye

Many different types of dyes are used globally in the textile industry such as vat dyes, acid dyes, reactive dyes, and sulfur dyes. Different dyes present different uses, dyeing techniques, and of course different colors. Because of the different properties of the dyes, different categories of dyes are used in certain categories of garments or textile products.

In the textiles for clothing with high contents of cellulose there is an overrepresentation of vat dyes and sulfur dyes for their high color fastness and colors in the blue and black range. The best example of this is denim jeans made almost exclusively with cotton and historically dyed with the vat dye indigo although more and more sulfur dyes are being used in jeans production since these are cheaper. Because of this the dye to be separated in this study can be assumed to be mostly indigo and sulfur dye which have very similar physicochemical properties.

Renewcell are planning to incorporate a more diverse feedstock as the production is going to be continuously ramped up over the coming years. This will lead to a greater mix of different dyes in the filtrate in the future but for now Indigo and sulfur dyes remains in focus.

1.2.1 Indigo

Indigo, indigo blue, vat blue 1 or the IUPAC name 2-(3-hydroxy-1*H*-indol-2-yl)indol-3-one is a natural pigment historically sourced from plants. Today its commercially synthesized for a much lower cost. The most famous use of indigo is for dyeing blue denim jeans. Indigo belongs to the class of dyes called vat dye which changes properties when it is reduced or oxidized.

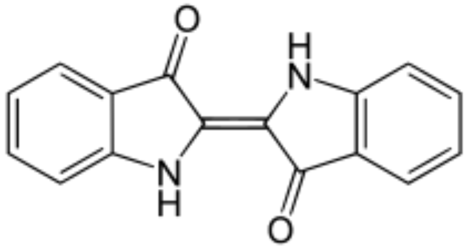

Figure 1. Structural formula of the Indigo molecule by Yikraazul[5].

Indigo is an organic aromatic compound, and the structure shows that it´s a fully conjugated pi-system which makes it a very stable compound. The molecule is flat, symmetrical and the adjacency- of the ketone group and the amine makes it rather neutral. Therefor it is neither soluble in water nor common non-polar solvents like benzene or DMSO. Indigo is only water soluble in reducing and alkaline environments. In the alkaline environment indigo is an electron acceptor and through the keto-enol equilibrium the double bonds are rearranged leaving negative charges on each of the two oxygen atoms, making it a divalent ion. This form is called leuco-indigo because it is rather colorless in solution. The form of indigo present in the process filtrate is not fully understood and might be a complex mix of different forms with.

1.2.2 Sulphur dye

Sulfur dyes are not as specifically defined as indigo, instead sulfur dyes are characterized by the starting material of the synthesis, di-nitro phenol. Sulfur dyes are synthesized by letting multiple di-nitro phenol molecules nucleate and then aggregate with more molecules resulting in larger polycyclic flat aromatic networks of different constellations. As with indigo sulfur dyes are not water soluble at moderate conditions but becomes soluble in an alkaline and reducing environment.

1.3 The Wastewater Stream

The stream to be treated in this thesis is the filtrate from the decoloring of textiles, the process filtrate. As mentioned, it is necessary that the solution is alkaline for the indigo to become water-soluble. All dyes in the filtrate are not fully dissolved and the filtrate is expected to contain larger particles of dye. To increase the solubility the solution is heated. These harsh conditions will cause some damage to cellulose leaving partially degraded macromolecules in the solution measured and treated as a biological oxygen demand (BOD). Apart from dye and BOD the stream will also contain small amounts of salts from the original coloring of the textiles, but these are not considered problematic pollutants but could still affect the performance in the system.

Currently this filtrate is not regenerated instead fresh solvent is added in equal amounts as the used filtrate that is continuously bled of. The filtrate volume from the process currently bled of and discarded is $50m^3/h$. The filtrate that is to be treated is not saturated of dye, but the performance and capacity is not sufficient for efficiently dissolving more dye. If the filtrate is being regenerated and recycled the performance of the process step is dependent on the extent of regeneration and how much of the total filtrate is being reclaimed, recycled, and bled off. There are many advantages in regenerating the filtrate; lower quantities of wastewater discharge, decreased chemical consumption and increased process performance. This could improve the economics of the process and enable ramped up production all while making the process more sustainable.

Comparing the filtrate in the decoloring process to the dyebaths in the conventional textile industry, the necessary salt for the dyeing operation is not present in the decoloring process. Because of this, high salt concentrations or high conductivity is not off concern in this work and the process does not have to achieve high removal efficiency of these. The dye concentrations in filtrate from the dying operations are higher than the filtrate from the decoloring process in textile recycling.

The dye concentration is not measured directly; therefore, it is estimated by making assumptions on the dye in the feedstock and other measured species in the filtrate.
The calculated dye concentration in the stream is based on the total nitrogen content of the stream and the fact that the mass fraction of nitrogen in indigo dye is similar to that of sulfur dye.

Table 1. overview of the contents of the process filtrate

Content	Concentration [g/L]
Dye concentration	1
COD	5
Suspended solids	0.5

1.4 Problem formulation

Before textile waste is dissolved to produce new textile it is turned into a dissolving pulp. The textile producers prefer colorless dissolving pulp for the dye not to get trapped within the new textile fibers and be able to dye the new textiles into any color. This is why the dye should be removed before dissolving the textiles. Currently in the process, the dyes are transferred from the textiles into an alkaline solution, the filtrate. In a large-scale industrial process, the dye concentration is built up in the solution upon recirculation and cannot as efficiently remove dye from the fabrics. To solve this problem a fraction of the filtrate is bled off and fresh solvent is continuously being mixed with the used filtrate. This filtrate is continuously being discarded and sent for wastewater treatment. Dyes have poor biodegradability and are harmful to humans and the environment. With discharge regulations becoming stricter and planned increased production, regular wastewater treatment may not be enough to treat this filtrate going forward.

If the dye that is removed from the textiles can also be separated from the filtrate, this stream can be regenerated and reused cyclically. This would significantly reduce the consumption water and chemical as well as producing a concentrated stream of dye that can be reused. Recirculating filtrate with lower dye concentration would improve the performance of the process step decreasing the need for bleaching. The current wastewater treatment plant receiving the filtrate is at capacity, meaning that the planed increased production and revisal of environmental permits could suspend production.

Separation processes does not eliminate the problem it only moves it to another phase. A solution thus needs to include a solution for getting rid of the dye or at least remove the dye from any water sent for discharge or treatment. Only concentrating the dye is not a solution as this would mean the same chemical loading for a treatment plant but it is a prerequisite for further handling.

1.5 Aim

The aim of this study is to propose and evaluate the technical and economic performance of sustainable methods for separating dye pigments from the process filtrate. The goal is to present a process that can separate the dyes from the filtrate and regenerate the process water to be recycled to the process step without making the stream ineligible for reclamation. This is to be done by using techniques from different published lab or pilot scale experiments and scale it up to an industrial level. This study also aims to evaluate the feasibility of recovering a dye product to be sold as dye pigment.

The outcome of the study should be the best possible design that can be implemented and solve the whole problem and at what cost.

1.6 Separation Processes

This study explores the use of membrane filtration and electrocoagulation as separation processes to remove the dye from the decoloring filtrate.

1.6.1 Membrane Filtration

Membrane filtration separates compounds by size through filtration using semi-permeable porous membranes. Membranes can be used to separate particles, suspended solids, dissolved solids and even ions from liquid solutions by the simple principle that small enough compounds can pass though the membrane while larger ones get shut out. The stream going through the membrane is called the permeate while the stream that is rejected by the membrane is called the retentate. Depending on the size of the pores the usage of the membranes is classified as either microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), in decreasing size of the pores. The pore sizes are also defined by the molecular weight cut off (MWCO), that is what molecular weight where 90% of molecules are too large to pass the membrane.[6] A combination of membranes in sequence can be used to separate a series of compounds from the solution. MF is the coarsest class of membranes; it clears the stream of rough suspended solids, microorganisms and lets everything else through the membrane. UF with slightly narrower pores blocks even smaller substances as macromolecules like proteins and is often used in wastewater treatment. NF has pore sizes on the nanometer scale and can thus remove molecules as small as polyvalent ions and larger organic molecules such as indigo and sulfur dyes. RO essentially only lets water though and rejects even monovalent ions. This makes membrane separation very useful in wastewater treatment, the contaminants can be separated and concentrated in one stream while purified water can be reclaimed in the other stream.[7]

1.6.1.1 Operation / dead end / crossflow

The straightforward method of operating a membrane filter would be dead end and batchwise much like a coffee where the rejected particles accumulate atop the filter to be periodically removed. This is the simplest way, but problems arise with separation of dissolved compounds that cannot accumulate in the same manner. To enable continuous membrane filtration of dissolved compound the membranes are operated at a crossflow where the part not passing the membrane is continuously flowing past the membrane avoiding any build-up.[7]

The performance of a membrane process can be evaluated by the rejection of a species, at what percentage the species ends up in the reject, and how the concentration of a species in the reject compares to that of the feed.

1.6.1.2 Fouling

Membrane fouling is the process where the permeate flowrate gradually declines over time. Along with build-up of particle on the membrane surface and in the pores, concentration polarization causes membrane fouling. Concentration polarization is a hindrance of a species entering the membrane through the adjacent film layer. This is because of the chemical potential lowering the driving force for a particle entering the film with a high concentration. Particles will not spontaneously diffuse from a liquid element of low concentration to one with high concentration.

1.6.2 Coagulation

Dissolved solids in a liquid can be separated from a liquid by coagulation. The dissolved particles are coagulated by the interaction with a coagulant, these coagulated particles then start to flocculate forming larger particles that can easily be mechanically separated from the suspension[8]. The principle of coagulation is that the coagulant lowers the colloidal zeta potential of the particles, i.e., canceling the repulsive forces of the particles making it more energetically favorable for them to coagulate and stick together. The introduction of coagulant can be performed by either direct chemical addition or using a sacrificial metal anode in electrocoagulation. Coagulation is a general treatment method often used in the early stages of wastewater treatment since it can remove a wide variety of compounds from the water by simply making them coagulate. Coagulation can simultaneously remove both BOD and dye from wastewater.

The products of coagulation are a purified liquid and a sludge containing the coagulant and the pollutants. Producing sludge is not considered very sustainable but it is often inevitable in wastewater treatment. When adding salts, the nonmetal part of the salt is left behind in the liquid, this can be anions like chloride, bromide, or sulfate.

2. Method

By using and combining information from different studies on reclamation and separation of wastewater, specifically dye bath water in the textile dyeing industry, a few alterative processes suitable for different scenarios are to be presented based on available research. The idea of this is to take advantage of all the insight and data from published work, combine it and though calculations and design get the techniques closer to industry than one new study on specific parameter would. To be explored are the above-mentioned separation processes membrane filtration, coagulation, and electrocoagulation.

Since these separation processes are not tested for the purpose of decoloring textile recycling wastewater the performance and implementation are still uncertain. However, these separation processes are tested to separate dye in lab trials and somewhat in pilot projects. By combining the specific information on the performance of dye separation in lab scale with industrial implementations of the separation processes in other industries the use of these treatments can be designed to separate dye from the decoloring filtrate on fully industrial scale. The performance and utility of the designs are evaluated by a techno-economic analysis to assess whether it is feasible.

To perform this, first the efficacy of each separation process is studied to see if it can perform separation at all. After this the optimal performance on a lab scale study or smaller pilot is studied. To get the process to an industrial level, scale-up studies or optimizations of larger pilot plants are used as a reference to scale the process based on experimental data. The final process is designed with regards to what equipment and techniques are commercially available to get a process that is achievable in the near future. Finally, the cost of constructing and operating the plant is estimated through CAPEX and OPEX and the financial feasibility of the process is explored.

2.1 Literature search

As a search engine for the literature Google Scholar was preferred because it has access to literature from multiple other databases instead of doing the same search in several database. The Google Scholar search algorithm was also preferred over other algorithms as it had a greater tendency to show relevant articles with industrially applicable results whereas other search algorithms seemed favor over-specific and very innovative articles that wasn’t useful for this project. Google scholar was used an all-in-one solution for handling literature, where articles could be saved, organized as well as exporting referencing compatible with the referencing software.

2.1.1 Referencing

Referencing was done automatically with EndNote by downloading the referencing data from google scholar. All references were done in according to American Chemical Society (ACS) style 1 with in text referencing.

2.2 TRL

To determine the technical maturity and feasibility of employing each method, NASAs concept of Technical Readiness Level, TRL, will be used to score the techniques from 1-9 in ascending maturity. For an adequate TRL assessment of a chemical plant, the specifications for technical readiness levels in chemical industry by Buchner et al.[9] was used.

2.3 Process design

To have as many degrees of freedom in the crucial parts, the process design should be conducted according to the onion principle.[7] Starting with design of the reactions and separations, then working outwards since there are no specific external design goals to integrate into the process.

2.3.1 Calculations & simulations

For the calculations Python using the Spyder IDE was used. Python was used to create a new customizable program for membrane calculations by setting up mass balances which allowed for design and dimensioning of a new process. With Python it was easy to solve complete systems mathematically for a specific solution, but this model was not capable of handling iterative calculations such as recirculation within the process.

The Python model does not account for the volume of the dissolved solids which limits the accuracy of the values within the model, but the output values should be correct. The calculated values for dye concentration will thus be slightly higher than the real values. Python with the matplotlib package was used to create the graphs comparing the performance of different process designs.

3. Literature review - Evaluation of the suitability for each of the separation processes

3.1 Membrane filtration

3.1.1 Introduction

Membrane filtration with NF and RO is widely known to be able to separate both dye and COD from wastewater.[10-14] NF and RO with MWCO as small as the dye molecules, or even smaller are used as the last step in the filtration while MF and UF are used as pretreatment prior to these. Since membrane filtration is separating the molecules by size exclusion, it is versatile and can be used to separate multiple types of dissolved dyes at the same time.[11, 15]
The uncertainty with using membranes for reclaiming decoloring filtrate in textile recycling is that it is not tested for this specific purpose, its unknown what membranes to use or how it is best integrated to Renewcell's process.

3.1.2 Pore size

Indigo has a molecular mass of 262.27 g/mol. The leucoindigo form is a bivalent ion. At this molecular weight a membrane with a MWCO of 262 is expected to remove 90% of the dye. A membrane with this MWCO and the ability to separate divalent ions would be classified as a NF membrane. The mechanisms of size exclusion are not as trivial for ions in polar solvents, here the hydrated ion radius is an important parameter. The hydrated ion radius is an average measurement on the complexes formed by molecular interactions between ions and water molecules. The hydrated ion radius of leucoindigo is not known, but hydrated ion radii for other dyes are known. Liu et al.[16] measured six different dye with charges from +1 to -2 and molecular weights in the same range as indigo and found that the hydrated ion radii where between 0.47 and 0.71 nm.

The capital and operating expenses for membranes increase with decreasing pore size as these membranes are more difficult to manufacture and more susceptible to fouling. Therefore, finer membranes should be avoided unless necessary.

The dye removal of the membrane is determined by the conditions of the surface, such as fouling, and the MWCO of the membrane, where the MWCO is dependent on the pore size of the membrane. The amount of water that is passed through the membranes is based of Darcy's law in Equation 1

Equation 1 Darcy's law

$$q = -\frac{k}{\mu \times L}\Delta p$$

saying that the flux, q, is dependent on the transmembrane pressure, Δp, the viscoelasticity of the fluid, μ, the permeability, k, and the thickness, L, of the membrane. This shows that the flux is increased by lager pore size increasing the permeability, higher transmembrane pressure, higher temperatures decreasing the viscoelasticity of the fluid while thicker membranes decrease the flux.

3.1.3 NF and RO Results

For spiral wound nanofiltration Uzal et al.[14] reported color retention of 91-93% using three separate commercially available nano-filters (NF90, NF99, NF270) on real textile effluent from indigo dyeing, and COD retentions between 88 and 94%. None of the tested NFs had good enough conductivity removal to meet the proposed reuse criteria for dyeing new garments. Uzal et al.[14] however decreased the color strength of the filtrate from 4887 Pt-Co to 1 Pt-Co by applying a metal filter, a dead end MF and two sequential NFs.

Chakraborty et al.[15] achieved similar results in 92 and 94 % retention respectively for reactive red and reactive black using a NF membrane with MWCO 400.

Table 2 Comparing three different NFs on indigo dyeing effluent at steady state with transmembrane pressure 5.07 bar, 0.62 m/s cross flow velocity. ∗Permeate flux of second stage NF 270 membrane.[14]

		Final permeate quality			**Cumulative retention (%)**		
Membrane (MWCO [Da])	Flux (L/m^2h)	COD (mg/L)	Color (Pt-Co)	Conductivity (mS/cm)	COD	Color (Pt-Co)	Conductivity
NF270 (200-300)	31	87	8	4.3	92	93	60
NF90 (100)	8	67	8	1.0	94	93	91
NF99 (159)	2	113	15	4.9	88	91	55
Sequential NF270	54∗	39	1	2.8	97	99	74
CA 995 PE	3	115	7	3.2	90	94	71
HR 98 PP	5	46	3	0.9	96	97	92

All three NFs in Table 2 showed great performance in color retention which is expected based on the MWCO and the molar mass of indigo 262.27 g/mol. Conductivity removal was not as efficient since NF generally only rejects polyvalent ions, like leucoindigo. As seen in

Table 2, NF in series or RO achieve significantly higher conductivity removal than single NF. [14] The permeate flux differed very much between the tested NF membranes and NF270 with the largest pore size had the highest permeance and was thus deemed as the best alterative by Uzal et al. [14]. High flux is desirable since it would require much less membrane units and lower cost while achieving sufficient color separation.

The two RO membranes in

Table 2, like the NF, membranes showed great retention of COD and color but also performed much better in conductivity removal because of the ability to reject monovalent ions. The flux was however much lower compared to the NF270 membrane, the best RO membrane had less than a sixth of the flux of the best NF membrane. The RO is, unlike in this trial, expected to operate at higher TMP than the NF which would increase the flux, although not likely to reach that of the NF270.

3.1.4 UF Results

Using a sequence of hollow fiber UF Buscio et al.[3] managed to remove 98 % of dye and 67% of COD on a semi-industrial scale. After screening to remove large contaminants, an external 0.03 µm hollow fiber UF(HF-UF) module was used and the concentrate from this was led to a tank with submerged HF-UF module where the concentrate accumulated while the permeate was passed to a permeate tank. From an indigo feed concentration of 0.082 kg/m^3 the final reject concentration of indigo was 20g/^{L}, via a concentration of 3g/L from the first UF, and this stream could be reused in an automated dyeing process. In the first UF the indigo is concentrated from 82 mg/L to 3g/L with the reject recycled to the feed tank that is continuously bleed of, this corresponds to a concentration factor of 37. The second UF with slightly larger pores are used to concentrate the reject from the first UF, this concentrated the solution from 3g/L to 20g/L. On a smaller scale two other smaller HF-UF membranes with slightly larger 0.04 µm pores were tested and achieved 96% and 99% dye removal.[3]

*Table 3. Summarizing the performance of the Hollow Fiber Ultrafiltration units presented by Buscio et al. *Combined dye removal for both the UOF-4 and FP-T00008 unit.*

Membrane	Configuration	Pore size (µm)	Membrane area (m)	Dye removal (%)
UOF-1b	External	0.04	0.5	96
ZeeWeed 1	Submerged	0.04	0.05	99
UOF-4	External	0.03	40	98*
FP-T0008	Submerged	0.1	1	

Vergili et al.[11] used UF as a part of a larger treatment scheme for dye removal on an industrial textile effluent. The UF removed 97% of the incoming dye from the pretreated effluent. The membrane used was a commercially available flat sheet membranes MWCO 5 kDa.

When Uzal et al.[13] tested the performance of UF after MF with five different commercially available membranes with MWCO between 1 and 100 kDa, Table 4.

the membranes removed between 68% and 83% of the color of the solution. Unlu et al.[12] got similar results with dead end UF after MF pretreatment in a lab scale trial, Table 5. The UF removed between 62% and 78% of color depending on the pore sizes in the range between 5 and 100 kDa.

Table 4 Steady state performance at pH 11 for UF membranes after 5 µm dead end MF along with cumulative value of the treatment with both MF and UF. [13]

	UF color removal (%)	**Waste-water flux(L/m²h)**	**Final permeate quality**		**Cumulative retention (%)**	
			COD (mg/L)	Color (Pt-Co)	COD	Color
Memb-rane		Feed	1211-1750	192-232	15	93
100 kDa	73	59	726	57	59	98
50 kDa	68	55	772	68	56	98
20 kDa	83	33	759	37	51	99
2 kDa	82	2	882	38	47	99
1 kDa	77	24	859	48	45	99

Table 5. Steady state performance of dead-end UF membranes after dead-end 0.45 µm MF.[12]

Pore size (kDa)	**pH**	**Conductivity (mS/cm)**	**Color (Pt-Co)**	**COD (mg/L)**	**Color removal (%)**	**COD removal (%)**
5	10.25	6.60	545	719	78	19
10	10.29	6.62	953	810	62	9
50	10.38	6.61	957	842	62	6
100	10.49	6.63	960	856	62	4

In Table 4 and Table 5 its shown that after MF, UF can remove a high percentage of the incoming dye and maintain high flux but the permeates have non-negligible concentrations of dye and COD limiting in process recycling and possibilities of safe discharge.

3.1.5 MF Results

Micro-filtration with membranes that have pore sizes in the range of micrometers is not previously regarded as a feasible method to separate small dye molecules like indigo but is instead used as a pretreatment method for UF, NF or RO to limit fouling.[11-14]. When MF is used as a pretreatment method, high separation of color has been shown. Uzal et al.[13] could remove 93% of dye with a 5 μm MF membrane operated dead end.

To find the optimal pretreatment for NF, Unlu et al.[12] tested the removal of color and COD for MF with different pore sizes in trials with different feeds R1, R2 and R3 and pressures P1=0.7 bar and P2 = 3.0 bar.

Table 6. Performance of micro filters with different pore sizes by Unlu et al.[12]

Filter pore size (μm)	**Color removal (%)**					**COD removal (%)**				
	R1	R2	R3	Mixture		R1	R2	R3	Mixture	
	P1	P1	P1	P1	P2	P1	P1	P1	P1	P2
0.45	-	66	64	62	64	-	25	50	32	29
2.5	48	61	58	53	62	30	29	47	30	27
8	47	61	59	53	-	21	22	48	30	-

The results in Table 6 show that MF perform significant dye removal no matter the pore size of the membrane. Separation of the principal species is more than what is expected from a pretreatment that should first and foremost prepare the feed for the main treatment.

Moreira et al.[17] achieved almost complete separation of dye using only MF, but this was performed at neutral pH meaning the indigo was precipitated and the filtrate could not be recirculated back to the decoloring step which require alkaline conditions. To reclaim the decoloring filtrate stream, it is not feasible to change the pH and precipitate the indigo but instead use finer membranes to separate the solubilized form.

3.1.6 Sequencing

Vergili et al.[11] tested 4 separate membrane sequences for separating dye from alkaline water solutions on the scale of thousands of cubic meters daily. The dye tested was neither indigo nor sulfur black, instead the reactive dyes kimsoline navy blue HFRN, synozol red KHL and synozol yellow KHL. The separation was achieved through a combination of sequential membrane filtration of various sorts and membrane distillation. The membrane distillation was applied to a mixture of all the reject streams from the previous membrane filtration to remove all liquid from the concentrate of the as the goal of the study was assessing whether Zero Liquid Discharge (ZLD) was techno-economically feasible. The four different designs only differing in the type of membranes used and how many filtration steps used in the sequence.[11]

Table 7 Overall performance of sequential membrane filtration. Initial dye conc 1.21 kg/m3 and feed flow of 42.8 m3/ h. Design 1 (D1) used UF & tight NF, D2 used loose NF & tight NF, D3 used loose NF and RO, D4 used UF, tight NF and RO. The membranes were applied in a direct sequence producing only one permeate and multiple rejects. Cartridge filtration was applied on the feed as a pretreatment.

Sequ-ence	**Final permeate dye concentration (mg/l)**	**Final Conductivity (mS/cm)**	**final permeate flow (m3/h)**	**combined reject dye conc (mg/l)**	**reject flow (m3/h)**
D1	7	49.3	30.9	4365	11.9
D2	0	46.8	30.9	4365	11.9
D3	0	7.7	30.9	4365	11.9
D4	0	4.3	26.3	3153	16.5

Table 7 shows that the membrane sequences are very effective at dye removal even at large-scale operations. The main benefit of using RO as in D3 & D4 is to remove monovalent ions and reduce the conductivity of the reclaimed and the drawback in adding another process unit is reclaiming less water and increasing the capital and operational costs.[11] This difference can however be critical depending on the use of the treated stream. Marcucci et al.[18] found the choice between NF and RO to be decisive whether or not the permeate could be directly reused in dyeing operations. With a primary treatment of sand filtration and Ultrafiltration, the dye bath water after secondary treatment with RO permeate could be re-used in dyeing of all types of coloring while the water treated with NF could only be reused for washing and dying with dark colors. This is because of the difference in the conductivity and hardness in the reclaimed water. NF only removed 36% of the conductivity while RO removed 96%.[18]

These direct sequences shown in Table 7 means that the permeate that is recycled has permeated all membranes in the system while there is one reject stream per membrane step.

In

Table 2 and Table 7 it is shown, through five different membrane sequences, that sequential membrane filtration efficiently can remove 99% or more of dye in textile effluent while maintaining high permeate flow enabling recycling of reclaimed process water. A combination of UF and NF was sufficient to remove more than 99% of the dye in the textile effluent.

In the studied decoloring process for textile recycling the effect of conductivity and hardness is less important and since the salts necessary for dyeing are not added. The salts present originate from residual amounts from the original dyeing of the fabric.

3.1.7 Concentrate treatment towards Zero-Liquid-Discharge

Further membrane treatment to the reject in an indirect series is an interesting possibility since this simultaneously recycles more water and concentrates the dye. This could be a very cost-effective treatment since it would be applied to the concentrated reject that is a much smaller volume than the feed stream. Buscio et al.[3] used sequential treatment of HF-UF to concentrate the reject of the first HF-UF filtration. The second HF-UF had larger pores than the first to be able to maintain a steady flux with the concentrated feed, compared to a direct series where finer pores would be used in the second step to remove even more pollutants from the permeate. This setup managed to concentrate the dye to 30 g/L making it eligible for more expensive treatments not feasible for dilute solutions, such as evaporation. Concentrating the dye does not in itself solve the problem entirely but removing a large portion makes more alternatives possible and cheaper when processing and transportation of water can be avoided.

In an indirect series there is one permeate stream from each membrane step but only one reject stream that has been rejected by each membrane step and concentrated of the pollutants on the way.

A possible end-treatment for the dye could be incineration since is an organic compound. With incineration all dye could be stopped from polluting waterways leaving flue gases and ashes as the only products. For efficient incineration the water content should be lowered enough that the combustion process is self-sustaining. For municipal solid wastes the maximum water content can be between 55%-85% . [19] To reach this limit evaporation could be used since it’s a rather small stream and an energy intensive process can be accepted.

Another alternative is to precipitate the dye by neutralization and separate the solids with filtration as done by Moreira et al.[17]. This would however make the permeate ineligible for direct reuse in the decoloring process because of the neutral pH and low dye solubility.

3.1.8 Pretreatment and fouling

To maintain an efficient process, the membranes must be protected from large particles that can damage and clog the filter resulting in fouling. Vergili et al.[11] proved that pretreatment was necessary by a trial without pretreatment for tight NF resulting in complete fouling and no flux after 10 minutes of operation. For the four designs presented an undisclosed cartridge filter and a sequence of membranes with declining MWCO were sufficient to avoid problematic fouling for operation up until steady state. The characteristic of this stream gives intrinsic anti-fouling behavior against microbial growth since the stream highly alkaline and at high temperature which is not a suitable environment for most microorganisms.

*Table 8. Permeate and fouling performance of single NF270, sequential NF270 and two RO membranes at steady state with transmembrane pressure 5.07 bar after pretreatment with metal screen and dead-end MF. *Permeate flux of second stage NF 270 membrane.*[14]

Parameter	Single NF	Sequential NF	CA 995 PE	HR 98 PP
Permeate flux with pure water (L/m2h)	64	70*	8	18
Permeate flux with wastewater (L/m2h)	31	54*	3	5
Permeate flux with pure water (fouled membrane) (L/m2h)	63	70*	7	17
Flux recovery (%)	98	100	96	97
Flux decline (%)	52	22	57	74
Irreversible flux decline (%)	2	0	4	3

Table 8 shows that there is significant fouling for all membranes but that it is almost completely reversible by cleaning through backwashing. The membranes used in RO suffer from higher fouling than the NF membrane. Prior to all of these membrane filtrations the stream was pretreated with a 0.8mm metal filter and dead end MF to reduce fouling.[14]

Uzal et al.[14] first used a 0.8mm metal filter to screen the feed and then a dead-end MF for the pretreatment for both NF and RO processes. The MF notably removed 88% of the color in the effluent.

To find the optimal pretreatment for the NF Uzal et al.[13] tested different sequences of two MF, 0.45 and 5 µm, combined with five different UF membranes ranging from 1-100kDa MWCO for a textile water with 3000-4000 Pt-Co and COD loading of around 1400 mg/L. The initial 5 µm MF removed about 93% of the color strength expressed in Pt-Co units. A single 5 µm MF dead-end membrane followed by a 100 kDa UF was deemed the best alternative for the subsequent NF to minimize fouling and maintain a high flux. Like the pretreatment with metal filter and dead-end MF the MF/UF treatment had very high dye removals between 93-99% even before the main NF. The 20 kDa UF was the membrane that maintained the highest normalized flux. Comparing the 100kDa and 20 kDa UF membranes after 5 µm MF, the course 100kDa experienced 36 % flux decline with 34% units experienced irreversible flux decline while the 20kDa only was fouled 5%, without any irreversible fouling. The 20kDa UF brought decreased the color from around 200 Pt-Co to 37 while the 100 kDa resulted in 57 Pt-Co from the same feed.[13]

Table 9 Performance of different UF membranes following initial 5 µm MF[13].

Pore size UF membrane	20 kDa	100 kDa
Flux at steady state [$L/m^2/h$]	33	59
Flux decline %	5	36
Irreversible flux decline %	0	34
Color removal %	82	72

*Table 10. Pretreatment and fouling for three selected studies using NF. *The flux decline on the UF is the last reported in the sequence.*

	Uzal single NF270	Vergili D1	Uzal pretreatment 2009

1st treatment	0.8mm metal screen	Cartridge filters	MF
2nd treatment	Dead end MF	UF	UF
Principal separation	NF	Tight NF	NF
Flux decline on last membrane	52 %	44 %	5-36%*

As can be seen in
Table 10 above, the NF pretreated by UF in the D1 design of Vergili et al. had better resistance to fouling than the NF treated by the dead-end MF by Uzal et al.[14], although many other factors affect this difference in performance it might give a hint on what pretreatment suits best.

3.1.9 Practical feats and operational parameters
3.1.9.1 Available Equipment & operational Conditions

Vergili et al.[11] reported that the pH increased slightly in the permeate compared to the feed. In lab trials and smaller applications of membrane filtration flat sheet membranes are most often used because it is easy to customize the area while they are simple and are easy to operate. Where large flows are required flat sheet membranes are not as suitable as they have a large footprint on the site. Because of this more compact membrane configurations such as spiral wound membranes and hollow fiber (HF) membranes are used. Spiral wound membranes are essentially regular flat sheet membranes that are wound-up leaving parallel channels where the permeate can flow through. In Hollow fiber membranes the membranes are instead manufactured as very fine tubes to give a very large surface area with a small footprint, the capacity is increased by bundling-up the fine tubes into modules, much like a pack of plastic straws or a shell and tube heat exchanger. HF membranes are preferably operated outside-in with a flow path such that only the permeate gets inside of the fibers to limit fouling. The membrane can then be backwashed from the inside out. Both spiral wound and hollow fiber membranes manage to fit a very large membrane areas into a compact module to enable high a high volumetric flow with a small footprint. HF membranes can be designed to operate in different ways for different applications. External HF membranes are made to be fit into modules and are operated very much like spiral wound membranes. Submerged HF membranes are not fit into modules but are instead submerged directly into the filtrate tank. Submerged HF membranes are useful for applications with higher concentration such as in membrane bioreactors.

3.1.9.2 MF

Because of the lack of details regarding the cartridge filter used in the trials by Vergili et al.[11] the performance or characteristics cannot be replicated in the design calculations. MF cartridge filters are however a widely available and used in wastewater treatment leaving abundant performance data available. The manufacturer Mann Hummel recommended a 200-µm cartridge MF as optimal pretreatment for their UF membranes. A 20 inch long, 5 µm cartridge filter from Diproclean have the capacity to treat 4 m^3 per hour.

3.1.9.3 UF

The UF membranes tested by Uzal et al.[13] are manufactured by Alfa Laval and intended for dairy processing. In the trials, small flat sheet modules were used but there are also spiral membrane modules available. These are Alfa Laval listed for continuous operation in the pH range of 2-9 although they were successfully operated at pH above 11 in the trials.

Buscio et al.[3] found that the best alternative for semi-industrial scale was a series of commercially available 0.03 µm polyvinylidene difluoride (PVDF) HF-UF and a submerged 0.10 µm hollowfiber UF purchased from Tanjin Motimo membrane technology in China. These membranes do not have much available product data online which makes it difficult to assess the suitability, but in series they were able to remove 98% of the dye in the solution.

The 5 kDa MWCO UF and the NF membranes used by Vergili et al.[11], that achieved 97% dye removal, are made of polyether sulfone (PES) with a polypropylene backing that can be continuously operated between pH 0 and 14. These are commercially available NADIR® flat sheet membranes manufactured by Mann+Hummel available in customizable sizes. Flat sheet membranes are not very size efficient regarding on site footprint compared to the membrane area. Mann+Hummel also have available systems for parallel hollow fiber UF modules with extensive product and performance data that match the requirements for the process. Hollow fiber membrane modules can fit large membrane areas on a small footprint making it more suitable for these large-scale implementations. The hollow fiber membrane modules can be arranged in the Mann-Hummel Pure ULTRA II skid 2 hollow fiber 0.025 µm pore size PVDF UF system, operating between pH 1-12, and cleaning between pH 1-13. This maximum transmembrane pressure for this membrane is 2.3 bar at a maximum total pressure of 6.4 bar. The dye removal efficiency is not tested for this specific membrane, but the hollow fiber UF, made by Tanjin Motimo membrane technology, out of the same PVDF, with slightly larger pores achieved 98% dye removal. Since the pore sizes of these membranes are approaching the nano scale high dye removal is to be expected as the performance approaches that of NF.

3.1.9.3 NF

The NF270 is a FilmTech™ spiral wound membrane from Dupont suitable for continuous operation between pH 3-10 and short-term operation from pH 1-12.

3.1.10 Economic performance

Vergili et al.[11] presented estimations for capital and operational costs of the four full scale design cases that had been operated. This capital cost estimation includes direct fixed capital, fees, and contingency, working capital and startup cost. The estimation of operational expenses includes Labor dependent expenses, facility dependent expenses, membrane cost, membrane disposal cost and utilities.

Table 11. Presentation of the Economic performance of the four processes operated by Vergili et al.[11]. The four processes have a feed rate of 42.8 m^3/h and a dye concentration of 1.21 g/L. Design 1 (D1) used UF & tight NF, D2 used loose NF & tight NF, D3 used loose NF and RO, D4 used UF, tight NF and RO. The membranes were applied in a direct sequence producing only one permeate and multiple rejects. Cartridge filtration was applied on the feed as a pretreatment.

	D1	**D2**	**D3**	**D4**
CAPEX	$ 408 000	$ 450 000	$ 1 043 000	$ 584 000
Annual OPEX	$ 316 000	$ 317 000	$ 529 000	$ 479 000
Treatment Cost of filtration ($/m3)	$1,06	$ 1,07	$1,85	$ 1,57

Table 12. Presentation of the Economic performance of the four processes operated including post treatment by membrane distillation(MD) to achieve ZLD by Vergili et al.[11]. The four processes have a feed rate of 42.8 m^3/h and a dye concentration of 1.21 g/L. Design 1 (D1) used UF & tight NF, D2 used loose NF & tight NF, D3 used loose NF and RO, D4 used UF, tight NF and RO. The membranes were applied in a direct sequence producing only one permeate and multiple rejects. Cartridge filtration was applied on the feed as a pretreatment.

	D1	**D2**	**D3**	**D4**
CAPEX	$ 682 000	$ 724 000	$ 1 317 000	$1 014 000
Annual OPEX	$ 398 000	$ 399 000	$ 611 000	$ 593 000
Treatment Cost including MD (/m3)	$ 1,37	$ 1,38	$ 2,16	$ 2,01
Unit revenue (/m3 influent)	$ 4,91	$ 4,9	$ 4,43	$ 4,37

Table 11 shows that the two processes containing RO (D3, D4) have both higher CAPEX and OPEX than the designs only using UF and NF. All the designs had treatment costs between $1-2 per m^3 feed treated while removing more than 99% of the incoming dye as shown in Table 7. Vergili et al.[11] also presented cost estimations for concentrating the reject with membrane distillation. When including the costs of membrane distillation in Table 12, the treatment cost was between $1.37 and $2.16. In Table 12 a unit revenue is also included this represents the value of the chemical separated from the filtrate and collected from the membrane distillation.

3.2 Electrocoagulation

3.2.1 Introduction

The use of electrocoagulation, EC, is promising since it has some advantages over traditional physicochemical treatment methods; the separation of organic matter is faster and more efficient than coagulation, only the metal ions forming the coagulant is added, lower chemical consumption, lower sludge production, and lower operating costs.[8] The downsides of EC are that metal ions are still added to the solution and will contaminate both water and sludge, and that the technology is not tested on an industrial scale to separate indigo and sulfur black dye. Most of the research is still in the lab phase, often performed on synthetic wastewater samples during short periods of time leaving a gap of knowledge in how the technique is to be implemented at full scale.

Garcia-Segura et al.[8] reviews the efficiency of EC in previous studies, on both synthetic wastewater and actual industrial effluents. From 103 different trials on synthetic dye wastewaters with 54 different dyes in different concentrations the average color removal was 92% and the median color removal 97%. From six different trials on actual wastewater from dye bath and general textile effluents an average of 92% of color or turbidity was removed, with a mean removal of 97%.

3.2.2 Effect of the feed pH

The pH values affect the EC removal efficiency of through the pH sensitive equilibrium reactions producing the coagulants. There are multiple possible ways for metal ions and hydroxides to combine and form complex ions with different charges. At high pH-values anionic iron hydroxides formed to a higher extent compared neutral and acidic conditions where positive iron ions and iron hydroxide complex ions are formed instead. More negatively charged coagulants in combination with negatively charged leucoindigo ions leads to the higher absolute zeta potential and less efficient coagulation.[20] The pH value also affect the solubility of the formed metal hydroxide complexes which can reverse the coagulation process.[21]

Table 13. The removal efficiencies of samples of synthetic wastewater and real textile dyeing effluent for different pH-values. Trial on synthetic indigo wastewater by Hendaoui et al.[20](2021). Trials on real indigo textile effluent by Hendaoui et al.[22](2018).

Origin of the Sample	pH	Removal efficiency [%]
Synthetic wastewater	2.5	89.3
	7.5	93.3

	12.5	70
Real textile dyeing effluent	3.972	71.8
	7	91.3
	10.027	44.7

Table 13 shows that the removal efficiency is heavily dependent on the pH of the solution. Comparing the dye removal in synthetic samples of the three different starting pH values; 2.5, 7.5, and 12.5 with all other parameters fixed the removal was 89.3% at acidic conditions, 93.3% at neutral and 70% at alkaline conditions.[20] The neutral pH range, between 6.4 - 8.1, was reported to be optimal for both the removal of dye and COD in trials with real textile wastewater effluents.[22] From the feeds with pH values 3.972, 7 and 10.027 the decolorization was 71.78%, 91.3% and 44.7% respectively.

Hendaoui et al.[20] could conclude that the zeta potential was only affected by the pH and that there was no chemical reactions reaction taking place at pH 7.5, all removal of color was due to coagulation by intermolecular forces. With hydroxide ions being formed in the solution the pH value will not remain unchanged. This is why studies focus on the initial pH of the solution rather than keeping the pH constant. For acidic solutions the pH would approach 7.4 while for neutral solutions it would turn alkaline and for alkaline solutions the pH would drop although remain alkaline.[22]

3.2.3 Volumetric Flowrate / residence time

The removal efficiency of EC is expected to increase with longer residence time, or lower volumetric flowrate, as longer residence time allowing for more coagulation and subsequent flocculation to occur.

The decolorization of a real textile effluent with 1750 Pt-Co decreased from 91.62 % to 75.13% when the flowrate of the feed was increased from 1 to 3 L/min with a maximum in decolorization at the flowrate of 1.3 L/min in a 2L reactor.[22] In synthetic indigo wastewater in the removal efficiency increased with residence time in the measured range 1-3 L/min with an indigo feed concentration of 60 mg/L. However, the effect was the largest at high flowrates and the tradeoff between the amount of water treated and the extent of removal did not significantly improve the process when lowering the flowrate from 2 L/min to 1L/min.[20]

Mudasir et al.[23] reported that the highest color removal was achieved at the very lowest feed flowrate for both dilute and concentrated actual wastewaters containing both indigo and sulfur black. The optimal reported flowrate was 0.1323 L/min corresponding to a residence time of 28 min. Meas et al.[21] found 5 or 6 minutes residence time to be sufficient for over 95% removal of color, COD and turbidity in a lab trial and seek to minimize the residence time to avoid additional electrolysis of water producing hydroxide ions elevating the pH considered detrimental for the performance.

With flowrates ranging from 1-3 liters per minute these trials mentioned above are still in an early pilot scale.

3.2.4 Effect of feed concentration

The removal efficiency is depending on the concentration of synthetic dye solution. It was observed that for a set voltage of 35 volts, up until the indigo concentration of 74 mg/L the removal increased with feed concentration but with any further increase the removal decreased.[20] The positive correlation between feed concentration and removal at lower concentrations was explained as a probabilistic result of more contaminants available for collisions to start of the coagulation. For the negative correlation at higher feed concentration, it was thought to be because the anodes were not supplying coagulant at a high enough rate. For better performance at this feed rate the current would have to be increased.

3.2.5 Voltage & Current density effect

The applied voltage, or the current density, corresponds to the in-situ release of metal ions necessary for generating the metal hydroxide flocks and higher voltage is expected to improve the coagulation. The voltage, *V*, is famously correlated to the current, *I*, through the resistance, *R*, as expressed in Ohm's law.

Equation 2 Ohm's Law

$$V = I \times \mathrm{R}$$

Current density, *J*, is defined as the current though the metal per surface area on the electrode.

Equation 3 Current density equation

$$J = \frac{I}{A}$$

The dye removal efficiency increases from 75-94% over the measured range 5-65 V as more coagulant is added , above 35 V no significant improvements are made for synthetic indigo waste water[20]. Furthermore advanced problems like water oxidation and formation of passivated layers on the sacrificial anodes could arise at high voltages.[20] The same trend is seen in the trials with real textile effluent as the decolorization increased from 80% to 93% when the voltage was increased from 33 to 117 V, although no significant improvement was achieved at voltages above 90 V. [22] Hendaoui et al.[22] also reported that the speed of decontamination as well as the quantity of sludge flotation increased with the higher voltage.

To avoid sulfate formation on the electrodes at low current densities and still keep the current density at a level with efficient color abetment Mudasir et al.[23] kept the current density between 400- 600 A/m^2 and could achieve efficient color removal up to 95%. On the other hand, Enviraj Consulting generally recommended current densities between 20-25 A/m^2 for efficient operation at larger scales.[24]

3.2.6 Conductivity

Since pure water is not a great conductor of electricity the wastewater is dependent on the presence of dissolved salts and other ions to complete the circuit for the EC to function. At the same time the amount of salt added should be limited to not pollute the water and enabling it for recycling or safe discharge. It was found that the unadjusted conductivity of 140 $\mu S\ cm^{-1}$ the color removal dropped below 80% and was deemed insufficient and the electricity consumption was increased. Instead the conductivity should be increased to 500 $\mu S\ cm^{-1}$ for the process to be efficient while not polluting the stream in vain.[21]

3.2.7 Electrodes

Generally, in EC either iron or aluminum sacrificial anodes are used with similar performance. Iron is most often the default alternative since it is more widely used and cheaper in raw material.

For the removal of indigo using iron electrodes there was no problems at any pH of the solution while for treatment of sulfur black dye it was not applicable at alkaline conditions.[23] Using only iron electrodes in a alkaline solution to treat sulfur dye the solution turned dark greenish indicating serious an obvious error and uncertainty. At acidic pH the color removal was only 50%, because of high concentrations of the reducing agent sodium sulfide. Without high enough current density a sulfate could form passivating layers on the electrodes disabling the metal dissolution. Therefor either a mix of iron and aluminum electrodes or only aluminum was considered for further research by Mudasir et al.[23] and it is recommended for the pH not to be to alkaline for the generation of the desired cationic aluminum hydroxide complexes. Aluminum has the advantage of being colorless in water solution compared to iron which has brown color in solutions.[21] Additionally aluminum is has a much higher charge per unit mass and thus the weight of the produced sludge will be lower. No matter the material the electrode material current can be alternated every hour to further avoid electrode scaling.[25]

The electrode consumption and thus the rate of which the metal ions are being supplied to the solution can be theoretically estimated based on Faraday's law for water with low salinity.[26]

Equation 4 Faraday's Law of electrolysis

$$\Delta m = \frac{M_W * I * t}{n_e * F}$$

Where the mass dissolution, Δm, is given by the molecular weight of the metal ions, M_W, the current through the electrode, I, the time, t, the charge of each metal ion, n_e, and Faraday's constant, F.

According to Enviraj consulting the ratio between the electrode area and the reactor volume is an important factor and its commonly between 0.1 and 0.2 m^2/L.[24]

3.2.8 Scale-up

The research on the application of EC for dye removal on textile effluents[20, 22, 23] is still in the phase of lab trials or early pilots with volumetric flows in the range of liters per minute. However, in other similar applications of the technique the up scaling has come further. Meas et al.[21] performed a scale-up design study from lab scale, via pilot scale, up to Industrial scale on EC to treat a wastewater stream polluted by a florescent penetrant liquid. Much like the textile effluents this waste stream was to be treated to get rid of COD, color, and turbidity to enable recirculation within the process. This process was designed for compactness, producing low amounts of sludge, high water recovery and easy operation. Through this more than 95 % of the color in the wastewater was removed.[21].

3.2.9 Practical feats

3.2.9.1 Agitation

For an efficient process of coagulation and flocculation it's important to find the sweet spot in the stirring speed. There is a trade of between promoting coagulation and flocculation since coagulation requires collisions between coagulants and the pollutants, thus favored by vigorous agitation while flocculation relies on Van Der Waals interactions between different flocks and get torn apart with excessive stirring. The optimal agitation should be determined during the startup phase of the plant. [21]

As mentioned above there can be problems with electrode scaling and the formation of passivating layers. For optimal performance the electrodes should of course be kept clean. Impurities from the wastewater matrix can accumulate and cause problems along with microbial growth. Regularly switching the current is one way to further avoid electrode scaling.[25]

3.2.9.2 Recycling Sludge

By recycling parts of the sludge or the supernatant of the sludge back to the EC reactor it can be made sure that there is always coagulant and flocks present while decreasing the consumption of electrodes and electricity.[21]

3.2.9.3 Post treatment

After successful coagulation the pollutants should be trapped in the coagulated sludge, but it still needs further solid-liquid separation to be removed from the stream. This is most easily done by gravitational separation, letting the sludge float or settle, by filtering of all particles or a combination of the two methods. Meas et al.[21] used a configuration of a settling chamber efficiently removing the vast majority of sludge followed by a sand filter and finally a activated carbon filter to remove the smaller residual particles. Mudasir et al.[23] also separated the sludge from the treated water by simple gravitational settling.

3.2.10 Optimized performance.

The performance of continuous EC with iron electrodes on real indigo dyeing effluent was first studied and optimized by Hendaoui et al.[22]. The results in color removal, COD removal, conductivity removal and operating cost were optimized based on the three operating parameters: initial pH-value, inlet flow rate and voltage. Using Response Surface Methodology (RSM) to determine the operating parameters for the optimal combination of dye removal, COD removal and conductivity removal. The effect of the operating parameters was similar for the removal of dye and COD, both favored neutral pH, low flowrate, and high voltage. With operating parameters of the process optimized according to RSM 89.2% of indigo color, 76.15% of COD and 29.76% of conductivity could be removed which made the stream eligible for discharge according to the Tunisian standards. This was achieved through an inlet flowrate of 1.1L/min, pH of 7.2 and a voltage of 66V. The conductivity removal for this case is not great, and it might not always be necessary. Therefore, the process was also optimized without regard to the conductivity removal. Then the removal of dye and COD was 93.7% and 92.07% respectively. This was achieved through a slightly lower inlet flowrate of 1 L/min, an increased pH of 7.6 and an almost doubled voltage of 101V.

Table 14. Optimized operational parameters through response surface methodology.

	Real textile wastewater	Real textile wastewater without considering conductivity	Synthetic indigo wastewater
Initial pH	7.2	7.6	7.5
Residence Time, minutes	1.8	2.0	1
Voltage, V	66	101	47
Dye removal %	89.2	93.7	94%
COD removal%	76.2	92.1	N/A
Conductivity removal %	29.8	N/A	N/A

In another article of Hendaoui et al.[20] based on treatment of synthetic wastewater with indigo blue the mechanisms of EC was investigated to better understand the cause of the improvements by altering the operational parameters. Here, only the effect on indigo dye removal was measured. Using RSM for optimization of the optimal operating parameters could be determined based on the effect on the removal efficiency and linked to a direct operating cost of electricity and anode materials. For \$0.0927/m^3, 94% of indigo was removed at 60 mg/L feed concentration, pH 7.5, 47 V and a flowrate of 2L/min. From this feed concentration the removal of 94% of color produce an effluent with the color intensity of 62 Pt-Co units which is below the Tunisian limit of 70 Pt-Co for discharge.[20]

3.2.11 Economic performance

Hendaoui et al.[22] estimated the operating cost based on only of the direct operational costs which in this case is the cost of consumed electrodes and electricity. With the process optimized with RSM considering the conductivity removal the operating cost was \$ 0.527/m^3. The process optimized for only removal of dye and COD had an operating cost of \$ 1.013 /m^3.[22]

For a synthetic filtrate with only indigo the cost of the RSM optimized process was \$0.0927/m^3 while achieving the removal of 94% of color produce an effluent with the color intensity of 62 Pt-Co units which is below the Tunisian limit of 70 Co-Pt.[20]

The industrial scale EC process on a wastewater containing penetrant liquid was reported to have weekly operational expenses of \$2.04 including electricity, electrodes and filters and investment costs to treat 8 m^3 of wastewater. This corresponds to \$0.26/m^3.[21]

Kobya et al.[27] conducted a small-scale study on EC on dyehouse effluent with a cost assessment. This study did not focus on removal off dye rather general treatment to reduce COD and BOD, but the cost assessment was thoroughly conducted, and it is the same for EC no matter the purpose of the treatment. With much longer residence times and lower voltages, the treatment cost using iron electrodes were \$1.562 /m^3 and \$1.851/m^3 using aluminum.

Table 15. Comparison of the costs associated with the EC treatment.

Study	**Effluent**	**Treatment cost /m^3**
Hendaoui et al.[20]	Synthetic with indigo	\$ 0.093
Meas et al.[21]	Penetrant liquid wastewater	\$ 0.26
Hendaoui et al.[22]	Real textile effluent	\$ 1.0
Kobya et al.[27] Fe electrodes	Real dyehouse effluent	\$ 1.6
Kobya et al.[27] Al electrodes	Real dyehouse effluent	\$ 1.9

Table 15 shows that the 5 trials report large differences in treatment cost with the lowest just below \$ 0.1 and the highest at \$ 1.9. The three reported cost for wastewaters from real textile industries are the three highest costs, all three above the dollar.

3.3 Technical Readiness Level Assessment

3.3.1 Membrane filtration - TRL 6

Industrial use of membranes for other purposes are very advanced and examples of desalination plants using RO is a proven and reliable technique in use around the world which would give it the highest score of technical readiness, TRL 9.

Membrane filtration to separate dye on the other hand is not as proven. Much less the implementation of reclaiming and recycling the decoloring filtrate in textile recycling. The work of Vergili et al.[11] operating four separate full-scale processes connected to a textile dyeing plant and meeting reuse criteria, moves the technology beyond TRL 7. The technology does not meet the criteria for TRL 8 since this really means that the commissioning is underway, and the plant should start the production. For implementation of this technique in textile recycling specifically, the decoloring performance of the recycled filtrate must be proven on a pilot scale or larger to achieve TRL 7 not just the membrane separation.

Therefore, I consider the implementation of membrane filtration for dye removal and reclamation of decoloring filtrate to be of TRL 6.

3.3.2 Electrocoagulation - TRL 6

It is rather intricate to assign electrocoagulation a discrete TRL value. The commonly used coagulation in regular wastewater treatment would be a clear TRL 9 since its widely used in wastewater treatment plants around the world and efficiently removes color and solids. Electrocoagulation used as a method for dye removal and decoloring filtrate reclamation is not as mature. Like the membrane filtration the main mechanisms are well understood and tested but process integration and side stream characteristics are largely overlooked.

Integrated industrial applications like the one performed by Meas et al.[21] really pushes the technical readiness forward even though it's not performed on a wastewater very similar to the process filtrate in textile recycling. This partially meets criteria for TRL 8 or even TRL 9. What's keeping the TRL down for specific applications in textile industry is that it's on a different wastewater, and because I remain questionable of the understanding regarding the coagulant dosage, and details of posttreatment and disposal are limited.

The design presented here, cannot reasonably be given a TRL score of more than TRL 6 since higher scores requires more insights and data from operating a pilot or demo plant on representative wastewater. Without this key operational parameter like current density cannot be assessed.

4. Design (Discussion, Decisions & Dimensioning)

4.1 Membrane filtration

4.1.1 Discussion

The most important design goals of the process it to:
- The concentrate to have high dye concentration to allow for further non discharge treatment
- Avoid unnecessary and complex treatment methods that drive the cost
- Discharge as little water as possible to approach Zero-Liquid-Discharge.

It is clearly shown in the literature that membrane filtration can efficiently separate various dyes from textile wastewater but there is not one superior solution for all cases of dye removal. The main uncertainty of membrane filtration is what flux that can be expected from a membrane on a specific stream of wastewater as there is a large difference between the flux of pure water given by the manufacturers and the steady flux of wastewater after months or years of operation. Here the operating flux is estimated by trials of similar membranes on similar wastewaters and expertise from manufacturers, piloting is however needed for an optimized process. An uncertainty in this estimation would not lead to failure in the process as the permeating water is treated it would just change how much water is being reclaimed and can be adjusted through changing the number of membrane modules in operation.

Separation with NF and RO can be used to achieve complete separation of dye. The difference between RO and NF is that RO has much higher rejection of smaller ions like salts. NF can be used in series for performance in-between NF and RO, this can remove more than 99% of the dye and most of the conductivity while maintaining a much higher flux than RO. The technical performance of RO is preferred when the conductivity, hardness or salt concentration is important for the process it is recycled to, while the economical and operational performance of the NF is preferred if these parameters are not important because of the much higher flux in NF.

The available research in this area is focused on achieving complete dye removal because this enables dye bath water to be reused within dyeing operations or discharged in accordance with local regulations. When the filtrate is only to be used for decoloring textile waste, complete removal of dye or conductivity is not essential. This makes solutions, not considered good enough for other applications, viable for this process. Since the purity of the reclaimed filtrate is not as important, the economic downside of both RO and sequential NF will outweigh the improved dye removal compared to a single NF treatment.

NF membranes seems to be the best option for complete dye removal since it rejects the dye particles of interest at high fluxes while avoiding the increased costs of RO processes. A NF process on textile effluent requires pretreatment to not get completely fouled. Fouling and cake formation lower the flux through the membrane and limit the treatment capacity.

In the three studies evaluating sequential membrane filtration with NF in Table 10, all use three filtration steps with decreasing pore size in a direct sequence. The first step is often a screening step with a metal filter or MF to remove large particles that can clog and damage the membranes. After screening, MF and UF are then used to lower the concentration of larger dissolved compounds to keep the NF or RO from fouling. The last step is the main membrane concentrating the dye in the reject, leaving the permeate with low enough concentrations to be reused in new dyebaths. The extent of the pretreatment is a tradeoff between complexity, cost, and water recovery versus how much fouling that can be accepted. Dead-end filtrations will not affect the volume significantly or make the process more complex but dead-end filtration requires more maintenance because of the accumulation. The need for a primary screening filter is down to the quantity of debris and suspended solids in the filtrate but won't affect the stream more than removing particles.

Interestingly, when applying adequate pretreatment to prevent fouling of NF membranes, reports show that almost all the color has already been removed from the solution by the pretreatment steps. Both Dead-end MF and various UF membranes has performed more than 90% color removal making them eligible as the complete solution for reclaiming the decoloring filtrate. MF and UF should not be considered as only a pretreatment to the more expensive NF or RO, but rather a crucial part of the membrane sequence responsible for most of the dye removal. The color removal in pretreatments like dead end MF is likely the result of the dye not being fully dissolved, cake filtration, concentration polarization and more complex phenomena rather than size exclusion, since the pores in these are not small enough to mechanically separate dye. No matter the uncertainty of the mechanisms involved in the separation, these results should not be overlooked. MF and UF have been proven to achieve high dye separation on streams with the same characteristics as Renewcell's in multiple published articles.

The reported dye removal capability of UF is unexpected since the MWCO of UF should be at most half of the smallest species to be separated or tenth of the smallest species for optimal performance according to previous knowledge.[28] The membranes in Table 4 and Table 5 that show efficient dye removal notably have MWCO 5 to 500 times the mass of the indigo molecule. This indicates that the dyes are not fully dissolved in the filtrate but instead suspended as particles.

Based on the similarities in physicochemical properties of the main components in the dye mix, separation of the different dyes is not considered feasible since there is no clear difference to exploit. For example, indigo and sulfur dye cannot be separated by the solubility as both are limited to alkaline reducing water solutions, and they cannot be separated by phase change as the range of melting temperatures of sulfur dyes overlaps the sublimation temperature of indigo.

In studies evaluating either different pretreatments or the principal filtration steps I see a trend where the filter with the largest pore size is most often chosen because of the highest flux and sufficient efficiency. To me this indicates that not all alternatives are explored and that the trials overrate the important of high fluxes and underrate the long-term fouling prevention. When evaluating pretreatment methods for NF, Uzal et al.[13] decided that the 100 kDa UF was the best fit of the alternatives in Table 4 because of the high flux. I would however not consider it feasible for the process because of the 34% irreversible flux decline after a single steady state trial. The 20kDa UF indeed had a lower flux but greater dye removal and most importantly no irreversible fouling which would be a more feasible choice for an industrial process.

The best performing flat sheet UF membranes presented above have MWCO in the range of 1-20 kDa. With such low MWCO the pore sizes are approaching the nano scale at the same time the best performing NF, NF270, was the one with the largest pore size. We get that the best membranes are somewhere around the border in-between what's classified UF and NF. Optimal performance might be not determined by pore size or its classification but rather by individual characteristics of the membrane and what is commercially available. All the HF-UF presented in Table 3 shows dye removal above 95% on a representative feed while using a membrane configuration that is industrially applicable. For all types of UF, with different pore sizes and dyes to be separated, single pass dye removal efficiencies are found in the range of 62-98 %. This Proves that UF is a reliable method for filtration of dye even though the exact performance depends on the characteristics of the stream. For UF membranes with smaller pores in particular, dye removal lies around 80% and for HF-UF removal efficiencies above 95%.

The choice of MWCO for the membrane presents a design trade-off where smaller pores give. better dye removal but lower permeate flux. Increasing the TMP on the other hand increases the flux without changing the dye removal but high pressure will cause more fouling.

To reclaim as much water as possible and approach ZLD some sort of concentration or posttreatment should be applied to the reject of the membranes. Separating the reject further has several benefits since it for example both reclaims more water and makes disposal through evaporation and incineration more viable. The problem with treating the reject with membranes is the high concentration of contaminants posing a risk of troublesome fouling. Vergili et al.[11] successfully performed this via membrane distillation and Buscio et al.[3] through sequential HF-UF. Concentrate treatments can be very cost efficient since the total outcome of the process is changed by only treating a smaller part of the total feed. As this step in the treatment handles a much lower volume it's not as important to recycle this stream. Because of this it could be valid to change the pH to precipitate dye and not meet criteria for recycling the filtrate to the decoloring step. Without post treatment the problem is not solved it has just been concentrated into a smaller stream.

Vergili et al.[11] estimated the cost full-scale treatment of textile wastewater to between 1-2 $\$/m^3$ where UF and NF were closer to \$1 and the processes using RO were closer to \$2. When including membrane distillation to concentrate the reject the cost increased by roughly half a dollar per cubic meter of feed. Even though these results are not for textile recycling specifically they should be highly valued since it is not possible to match the insights gained from constructing and operating a plant.

Based on the literature review I present three scenarios.

1. RO or sequential NFs should be used if more than 99% dye removal and high conductivity removal is desired.
2. NF along with proper pretreatment should be used if more than 99% of dye is to be removed but there are no requirements on high conductivity removal.
3. If there are no specific requirements on high removal off dye and conductivity the stream, the treatment can be designed for optimal technoeconomic performance. MF or MF and UF is sufficient to remove most of the dye and reclaim the water for decoloring.

4.1.2 Decisions

According to Marcucci et al.[18] there are three especially important parameters in selecting a membrane for a process; the pore size, the membrane material and the membrane shape. The pore size decides the MWCO and at what rates what particles are let through. The material determines the chemical resistance and at what conditions the membrane can be operated at without being destroyed. The shape of the membrane on the other hand determines the rheology which is one factor affecting the fouling and washing of the membrane.

Based on the process requirements it can be concluded that RO or sequential NF is not needed for reclaiming the decoloring filtrate in this process. MF and UF can either be sufficient as a stand-alone treatment or should be used as a pretreatment for NF that can reliably ensure more than 99% dye removal over the whole process. NF should only be applied if it's necessary to remove all dye from the reclaimed stream because of its cost and technical downsides. Scenario 3 best suits Renewcell's process. Because of the uncertainty and complexity regarding the capability of MF to separate dye it's hard to accurately predict the technical performance in this process. MF followed by UF would give more predictable results as the dye removal capabilities of UF are not as ambiguous as MF. UF reliably produces high dye removal, especially the UF membranes with smaller pore sizes and the HF-UF. This gives us pore sizes approaching the nanoscale somewhere around 0.02-0.04 μm.

For filtrations with membranes such as in UF and NF, hollow fiber membranes or spiral wound membranes should be used to reduce the footprint of the process. Spiral wound membranes are easily operated continuously with cleaning in place through periodic backwashing to reduce membrane fouling. Spiral wound membranes are commercially available, enable the use of large membrane areas at a small footprint and the modularity makes it easy to scale the capacity of the process.

Before the membranes the treatment of the filtrate should start with metal filter screening the stream. The Metal filter acts as a screen and removes larger particles and protects the following membranes while its cheap, won't impede the flow much and can easily be washed off when fouled as it's not as delicate as membranes. After the metal filter, dead-end MF should be used to separate dye, COD, and other suspended solids from the stream by cake filtration through the slurry that will accumulate on the filter and enhance the removal efficiency. For the MF that relies on dead-end filtration either a flat sheet membrane or a cartridge filter can be used.

After pretreatment by MF, UF should be used to concentrate the dye in the reject and recycle the reclaimed permeate. After the rigorous pretreatment with metal filter and MF the UF can very much be tailored to optimal performance. In this case the 20kDa UF membrane presented in Table 4 shows the best overall performance of the simple flat sheet membranes.

To improve the process in a cost-efficient way HF-NF an indirect series should be used to concentrate the reject. This reclaims more water and concentrates the polluting dye down to a small volume taking important steps towards ZLD. Here fractions of the concentrated reject can be recycled back within the filtrations process to increase the dye concentration and reclaim more water, but this puts more strain on the membrane as the solution becomes increasingly polluted and requires more membrane area as the feed increases. Here it could also make sense to recycle portions of the second permeate back to the initial feed since this stream will have a higher dye concentration because of the recycling of the reject. When recycling streams, the system becomes more dynamic and steady state might be harder to predict and more difficult to control with real time fluctuations propagating in the process. Reject recycling is thus something that should only be done if the system is operating below capacity for some reason. For example, if the system is designed with excess capacity for a planned scale-up.

A second HF-UF membrane to treat the reject in an indirect series should, unlike in the other presented sequences, have larger pores than its precursor since it is to treat a solution with higher dye concentration. This is because compared to dye separation in dying mills for textile recycling it is more important to recycle the process filtrate that to remove all dye form said filtrate.

Based on all these decisions the process should contain; pretreatment with screening and MF, UF (preferably HF-UF), reject concentration with submerged HF-UF, evaporation of the concentrate and incineration of the partially dewatered dye concentrate.

4.1.3 Assumptions in membrane Design calculations

As it is not possible to perfectly calculate or simulate transport phenomena of specific species in the fouled membranes the performance of the membrane units is based on data from reported steady state trials of these. The membranes are assumed to follow the black box model with the different processes and transport phenomena are uncoupled from each other. For example, this means that the dye removal efficiency is not dependent on the flux. The membrane is instead given a percentage of dye removal that previous studies have shown and are assumed to be valid in the same range of operation. This is a reasonable assumption for wastewaters with similar characteristics and feed rate, especially after pretreatment.

With data from the current process on the annual treatment of dissolving mass, hourly rate and dye concentration of the filtration being bleed of, a minimum need of dye removal can be calculated given only an annual production of dissolving mass. Given the hourly need of dye removal based on the annual production along with performance data of the membranes presented earlier in this report, mass balances be setup and solved to determine how much water that must be treated, how much water can be recycled and the required membrane area. COD and BOD where not considered to affect the stream since the majority was assumed to be removed by dead end filtration methods.

4.1.4 Dimensioning

Membrane treatment can be considered a long-term treatment and should be designed for application in the near future, because of this the process is designed for a planned twofold increase in production, producing 120 000 tons of dissolving mass.

The dimensioning of the membrane modules is based on the dye concentration in the rejects that not being recirculated to the process shown in Equation 5 for indirect series and Equation 6 for direct series, where the concentrations are dependent on the dye removal efficiencies of the membrane modules shown in Equation 7.

Equation 5 .Mass balance of the dye being separated by the indirect membranes system.

$$m_{dye\ removed} = n_2 \cdot V_{reject,2} \cdot C_{reject,2}$$

Equation 6. Mass balance of the dye being separated by the direct membrane system.

$$m_{dye\ removed} = n_1 \cdot V_{reject,1} \cdot C_{reject,1} + n_2 \cdot V_{reject,2} \cdot C_{reject,2}$$

Equation 7 . Mass balance off dye through the membrane for membrane, i, assuming the liquid is incompressible.

$$C_{permeate,i} = C_{feed,i} \cdot (1 - \eta_i)$$

If the mass removal rate of dye in the rejects are equal to the mass dissolution rate of dye from the textiles, and fresh filtrate of equal volume to the reject is fed, the dye concentration is unchanged in the filtrate of decoloring process to keep the whole process at steady state, presented in Equation 8.

Equation 8. Steady state mass balances of dye being removed by the main membranes, the micro filtration, and the dissolution of dye. The dye removal efficiency, η, over the membranes is defined as the percentage off dye being rejected by the membrane.

$$m_{dye\ removed} = m_{dye\ dissolved} - C_{Feed} \cdot V_{Feed} \cdot \eta_{MF}$$

Fully industrial membrane systems are scaled very straight forward since many parallel membrane modules are used. For higher capacity more modules are simply applied in parallel, making it possible to scale membrane systems very freely.

The design calculations are based around three main correlations; the mass balances of dye over the membrane filtrations expressed as concentrations in Equation 9, the volume balances between filtration steps in Equation 10 and Equation 11 for indirect and direct series respectively, and the overall mass balance of the system over time for steady state operation in Equation 8 and Equation 5.

Equation 9. Mass balance of dye for all streams in a membrane unit.

$$C_{feed} \cdot V_{feed} = C_{permeate} \cdot V_{permeate} + C_{reject} \cdot V_{reject}$$

Equation 10 Volumetric balance between the membranes in the indirect series with the volumetric flow per membrane unit, V_i, and the number on units, n_i.

$$n_1 \cdot V_{reject,1} = n_2 \cdot V_{feed,2}$$

Equation 11. volumetric balance between membrane modules for a direct series with the volumetric flow per membrane unit, V_i, and the number on units, n_i.

$$n_1 \cdot V_{permeate,1} = n_2 \cdot V_{feed,2}$$

Simply, the rate of dye being dissolved in the filtrate must equal the rate of dye removal in all the filters given that the volume is kept constant with addition of feed equal to the sum of all reject streams. To solve this system with multiple membranes in series based on the membrane performance the mass balances of each unit are setup. The mass balances determine the concentrations, permeate flow, and reject flow for the first unit. By using the calculated permeate concentration from the first membrane unit as the feed to the second and so on all concentrations in the system can be deduced without any correlations of the relative volumetric flows of each membrane unit. Combining the three correlations above into one equation all volumetric flows and the number of membrane modules are calculated.

For the indirect series the combined equation is shown in Equation 12

Equation 12. Combined design equation for dimensioning of the indirect membrane sequence

$$n_1 = \frac{m_{dye\ dissolved}}{V_{feed,1} \cdot \eta_{MF} + \frac{V_{reject,1}}{V_{feed,2}} \cdot V_{reject,2} \cdot C_{reject,2}}$$

For the direct series the combined design equation is shown in Equation 13

Equation 13. The combined design equation for the direct membrane sequence

$$n_1 = \frac{m_{dye\ dissolved}}{V_{feed,1} \cdot \eta_{MF} + V_{reject,1} \cdot C_{reject,1} + \frac{V_{permeate,1}}{V_{feed,2}} \cdot V_{reject,2} \cdot C_{reject,2}}$$

All liquids are assumed to be incompressible meaning that the volume liquid going in and out of each process unit is equal.

Membrane systems should be designed with inevitable fouling in mind so that the process can run at design capacity even after years of operation, around 20% excess capacity is usually accounted for. The downtime for the regular back washing and the occasional cleaning in place (CIP) must be accounted for with additional capacity. Mann Hummel expects their Pure Ultra II membranes to need CIP every few months. Back washing on the other hand is needed after 30-60 minutes of operation and takes about 90 - 180 seconds for air scouring, backwashing, and forward flushing. Chemically enhanced backwashing (CEB) is also recommended to improve performance in-between the CIP sessions. CEB is in essence a backwashing cycle with additional time for chemicals to soak the membrane for 5-20 minutes. CEB is done somewhere between every few hours and every few days. Assuming 3 minutes of backwashing each hour, 20 minutes of CEB daily and 12 hours of CIP quarterly the required downtime is 7.0% of the annual production time. To make up for this the system needs to be 7.5% higher capacity when running.

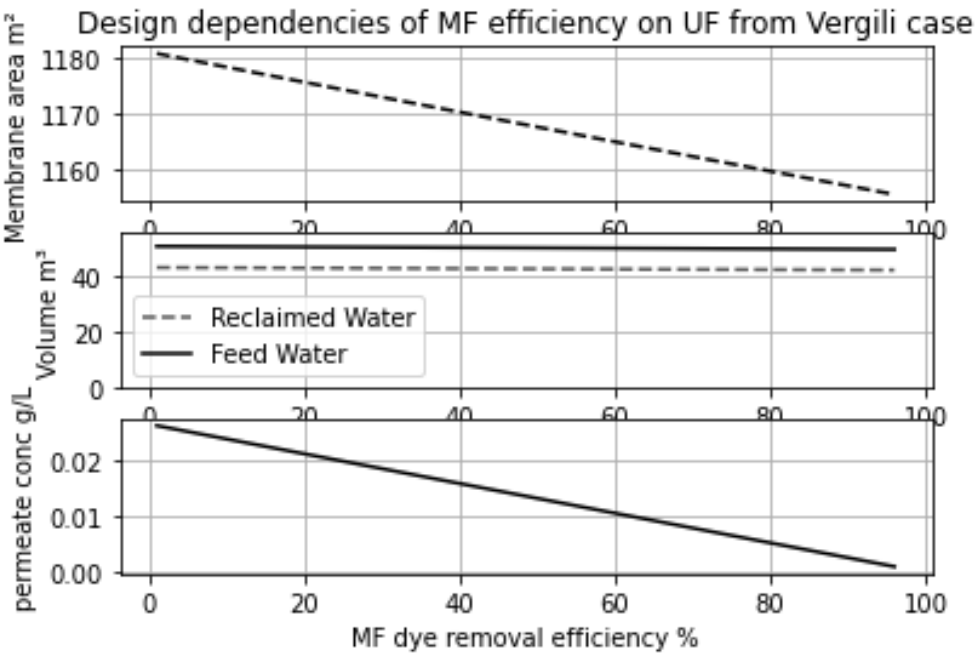

Figure 2 Results from a parameter sweep of the dye removal efficiency of the dead-end MF on the 5 kDa flat sheet UF membrane used by Vergili et al.

Figure 2 shows how dye removal efficiency effects the rest of the UF process. Given that the dye removal efficiency of the dead-end MF is uncertain and will have to be assigned a numerical value based on assumptions from similar studies it's important to assess the robustness of this assumption. The parameter sweeps show that the biggest effect is on the recycled permeate concentration while the effect on the membrane area and the volumes only differs around 10% from no dye removal at all to 96% dye removal in the MF step. The permeate concentration will not affect the performance of the process since all design calculations obey the same mass balances that give the same concentration in the decoloring bath. Further the figure shows the trivial effect of the dead-end MF, only lowering the dye concentration in the feed, making the response in the system linear. The robustness shown let us make a rough estimation of the MF dye removal efficiency without having to worry too much if we are 10-20% off on either side the results will not propagate. For the rest of the design the MF is assumed to remove 50% of incoming dye which is very much in line with the performance presented in Table 6.

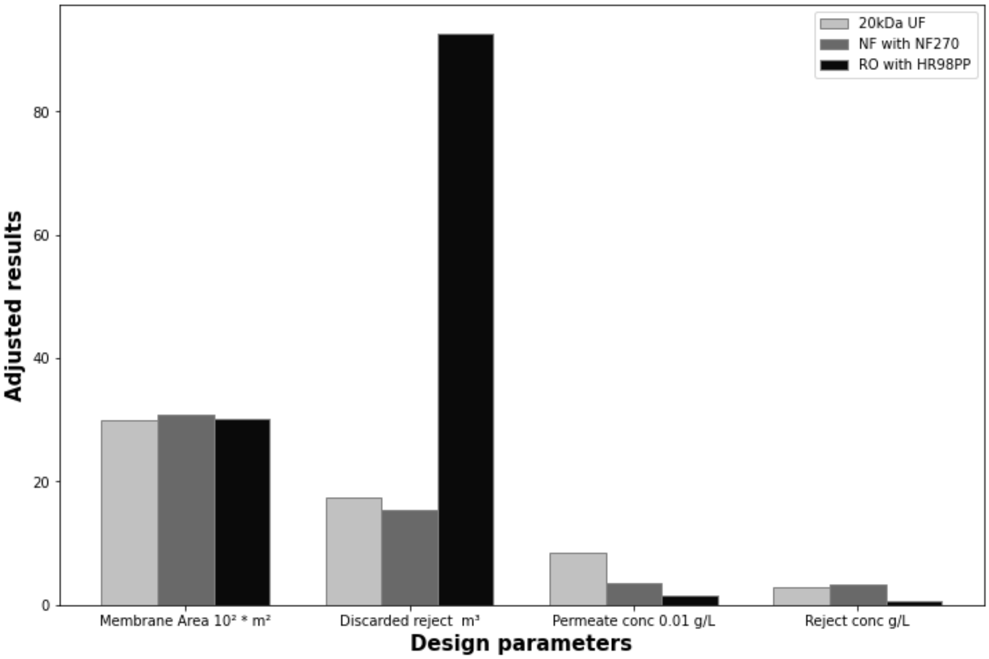

Figure 3. Comparison of Dimensioning and design parameters for UF, NF and RO to meet the design specifications. All designs have the same pretreatment with 50% dye removal from dead-end MF prior to the principal membrane. Note that the size of the bars is not true to scale between the parameters as the values are scaled to compare different multiple properties in the same graph.

Figure 3 shows the relative performance of UF, NF and RO. The most striking result is how much of the filtrate the RO rejects, this is because of the low membrane flux of the RO membrane and shows how important a high flux is for the whole process.

The high proportion of rejection means that an equal volume of fresh filtrate must be feed, defeating a part of the purpose for the treatment process. This could partially be fixed by recycling most of the reject back to the RO unit, but this would require a much larger membrane area, thus a larger capital cost, to generate a larger flux. This shows once again that RO is not suitable for this treatment process. The performance of UF and NF is very similar, but the NF has a slightly better technical performance reclaiming more filtrate with a lower concentration and leaving the reject with a higher concentration. On the other hand, the UF membranes are likely to be cheaper and may thus give better economic performance leaving a trade-off between technical and economic performance.

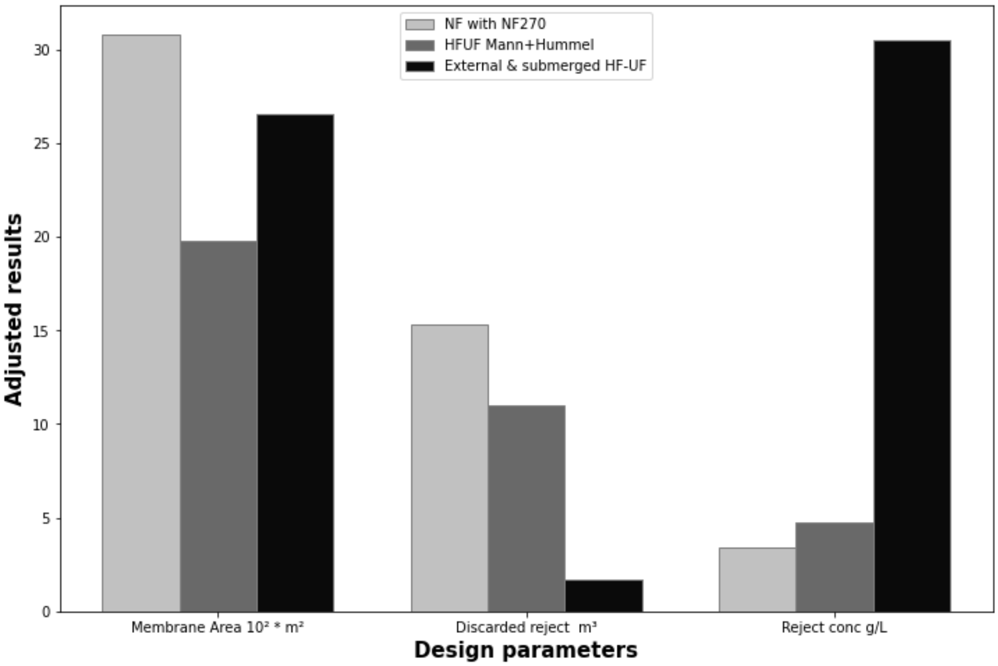

Figure 4. Showing the most important design result of three membrane cases. Note that the bars are not true to scale as the total membrane areas is divided by 100 to fit into the graph.

In figure 5 the three most important technical dimensions for the three most promising constellations of commercially available membranes. As the previous discussion implies NF with NF270 is not the best option. NF needs the largest membrane produces the least concentrated reject and discharges the most wastewater. The difference between the two other systems is that a second submerged HF-UF system is added as a post-treatment to concentrate the reject further. Here there is a trade-off which must be assessed with a cost benefit analysis. The extra membrane system increases the needed area, thus the capital cost, while it recycles much more filtrate and produces a much more concentrated final reject. Although the reject concentration does not affect the performance process a high concentration is important for disposal of the dye making the design with an indirect series of two HF-UF the best treatment method.

Table 16. Calculated process results of the presented design. This dimensioning includes increased capacity to offset the downtime for Backwashing, CEB & CIP and 20% extra membrane capacity to account for inevitable fouling over time.

Design case		Sequential HF-UF
Feed flow	**m^3/h**	112
Reclaimed filtrate flux	**m^3/h**	111
Concentrated reject flux.	**m^3/h**	1.68
External HF-UF membrane area	**m^2**	2430
Submerged HF-UF membrane area	**m^2**	764
Reject concentration of dye	**g/L**	30.5

This design should be compared to Renewcell's current process to highlight the changes in the process not just the pure numbers. For water reclamation the 111 m^3/h being recycled does not mean that this process reclaims 111 m^3/h more than the current process which has no reclamation because it also treats more water. This design sends the 1.68 m^3/h, collected as evaporator vapor, for external water treatment compared to the current treatment which would have to send 100 m^3/h for external water treatment scaled to meet the same production. Therefore, this design comparatively reduces the water consumption by 98.32 m^3/h.

The optimal transmembrane pressures for the membranes in this process are to be determined for the specific wastewater matrix in the commissioning phase of the plant construction and it should be within the operational range given by the manufacturer. Since this design neither uses RO nor NF, high transmembrane pressures are not required to maintain a high flux. High transmembrane pressure is instead an indication that the membranes are heavily fouled.

A detailed process design for the post treatment with evaporation and incineration is considered outside of the scope of this project but a basic design is provided to enable a cost analysis from untreated wastewater to reclaim water and incinerated dye.

The dimensioning of the evaporation step is based on the hourly flowrate of 1.68m^3 reject from the second HF-UF process. The extent of evaporation is determined from the concentration of dye in the reject, 30.5 g/L and the required moisture content level to sustain stable combustion, assumed to be 30% [19]. This would require that the evaporator can remove 1.61 m^3 of water hourly. The power consumption is estimated by the energy demanded per volume of waste water removed through the presented values from Global Water Intelligence.[29] The evaporation is assumed to be ideal with no entrainment of dye to the vapor below the point of saturation.

Incineration is a large-scale industrial process and it's not deemed feasible to build a process to treat only 50.4 kg per hour present in the concentrated reject. Instead, the incineration is proposed to be outsourced to an external actor. For sludge from industrial wastewater treatment plants the cost of incineration is approximated to $90-130 per ton. This could be compared to $ 40-70 per ton for the cost of disposal in landfills, which is about half of the cost but risking the disposed waste to contaminate local groundwater.

4.1.5 Process Flow Chart

Table 17. Process flow chart of the membrane system including post treatment with evaporation and incineration.

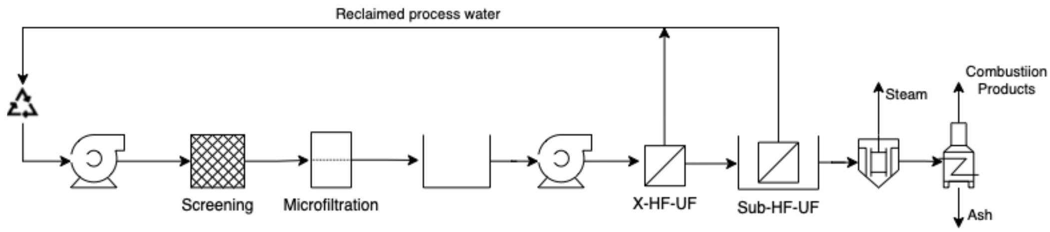

Table 18. List of necessary equipment for the cost estimation.

Process Equipment
Self-cleaning screening filter
MF cartridge filters
120 m^3 storage tank
External HF-UF
12 m^3 storage tank
Submerged HF-UF
Evaporator
Incinerator
6 pcs chemical dosing tanks
2 Centrifugal feed pumps
2 Centrifugal backwashing pumps
2 Permeate tanks for backwashing
2 CIP tanks

4.2 Electrocoagulation

4.2.1 Discussion

The most important design goals of the process it to:

- Coagulate maximum amount of dye from filtrate.
- Reclaim the filtrate.

Garcia-Segura et al.[8] showed in great numbers from lab trials that electrocoagulation can effectively remove dye from a water solution by presenting the average removal of 97% from the 103 trial reviewed. While the use of EC on textile effluents is still in early development other implementations like the presented by Meas et al.[21] is important to show the feasibility and the maturity of the technique. This shows that EC can be successfully operated on an industrial scale given the insights from piloting on the specific wastewater.

As electrocoagulation is an emerging technology not widely used in the industry, most research have been in lab scale focusing on how to approach 100% removal efficiency with a short residence time. I believe that there is a problem with EC processes being optimized in lab scale trials since researchers lose sight of the intended industrial applications. By non-global parameter optimization without scale-up in mind, the process gets stuck in local maxima. The results are not discussed, understood or not necessarily feasible for industrial application. One of the main reasons to use EC is to be able to achieve the same coagulation as for chemical coagulation but with lower addition of coagulant and better process control. In the EC trials however, the coagulant dosage is rarely discussed and never reported. The same goes for the remaining coagulant concentration in the effluent.

As a trend in the results, I see short residence times coupled with high voltages, leading to high coagulant dosages. Scale-up of the process according to these optimized parameters would require extreme currents and lead to overdosing of coagulant.

Because of the limited knowledge off important parameters for designing and integrating EC to a full scale process this design will focus on designing the core electrocoagulation process necessary for a pilot.

All the studies on the effect of pH[20-22] showed that the performance of electrocoagulation was best at the range of neutral pH because of how the pH affects which metal hydroxide complexes are formed and their ability to coagulate. At alkaline conditions the common sulfur dye caused unknown reactions and the removal efficiency was heavily reduced. Therefore, EC should strictly be operated at neutral pH. To operate the EC at neutral pH would require pH control of the filtrate which is a buffered solution. The incoming filtrate must be neutralized and then the effluent would need addition of base to get back to meet the requirements of the decoloring process. Although this seems tedious for a buffered solution, it should be compared to the current process where nothing is recycled, and pH control is still needed.

The optimal current density is more uncertain and not always reported. As the current density determines the coagulant dosage, the optimal value is dependent on not only the concentration and matrix of the polluted solution but also the material of the electrode. The optimal current density for this process will have to be determined experimentally.

Compared to iron, aluminum seems to be the best choice of electrode since it is colorless in solution, has a higher valence and a significantly lower molar weight leading to more coagulant per kilogram of electrode. Iron electrodes on the other hand have better performance for sulfur dyes and could be a cheaper alternative due to the lower raw material price.

Electrocoagulation can be used to separate various types of dye from solutions in the textile industry but when the process is optimized for efficient industrial performance the properties of the filtrate will not match the criteria to be recycled to the decoloring process. The need for neutralization from pH 12 off a buffered solution in combination with the filtrate becoming contaminated with metal coagulant makes electrocoagulation an unfeasible method for reclaiming the decoloring filtrate. This does however not disqualify EC from being used since it efficiently removes dye from the water stream, which could be considered the most urgent objective. Electrocoagulation is better implemented on streams that are not to be recycled. Comparing EC to membrane filtration EC treatment doesn't get the double benefit both reclaiming the filtrate and separating the dye. However, depending on the value of reclaiming the filtrate EC could be cheaper since it avoids costly membranes. EC should be implemented on the stream currently being bleed off and mixed with the other wastewater streams before being sent for treatment and the effluent should be mixed. The EC effluent could still be mixed and sent for treatment but after EC the content of dye and COD would no longer be a problem for the receiving wastewater treatment plant.

4.2.2 Design and dimensioning

Based on the literature, removal efficiencies of 90% and above seem achievable for various types of filtrates. These removal efficiencies are good enough for relieving the receiving wastewater treatment plant from most of the chemical loading even though complete removal is not achieved.

The design of the electrocoagulation process should start with the design of the reactor according to the onion model of process design.[7] The coagulation process is dependent on what coagulant species are formed and at the concentration of these as well as the matrix of the water to be treated. The electric current quantitively determines the release of metal ions while the pH value greatly affects what specific metal hydroxide complexes are formed. The metal ion release at the anode can be derived from Faraday's law in Equation 4 as a function of only the electric current along with intrinsic constants of the metal and Faraday's constant. Because of this the optimal current and current density must be found through experiments for a specific solution with a given pH value and pollutant concentration. The pH should be kept neutral as the literature proves the removal efficiency is superior and the preferred coagulant complexed are formed.

Because the coagulant dosage is only dependent on the current, the current must be increased by the same factor as the volume to keep the coagulant concentration constant in scale-up. While scaling up the current, the surface area of the electrodes also has to be considered since the current density is considered a master variable and should be kept rather constant when electrocoagulation reactors are scaled up.[25] This is because the rate of metal dissolution should produce the same coagulant concentration in the EC reactor for the same wastewater matrix regardless of the scale. The result of this is that the current, the electrode area, and the volume are all conveniently scaled up 1:1:1 once the optimal current or current density has been determined on a smaller scale.

To keep up with the dye incoming wastewater the electrocoagulation must treat the $50m^3/h$ currently being bled of from the decoloring process and replaced with fresh solvent. Just as the case for the membrane treatment this design is dimensioned for a planned twofold increase in production. The EC should thus be dimensioned to treat 100 m^3 of filtrate per hour. Flowrate and the reactor volume should be scaled such that the residence time in the reactor is the same as the reference process.

4.2.3 Dimensioning

Using current density as a master variable following the scale-up criteria presented in the previous section the only parameter that is needed for scale-up is the scale-up factor the ratio between flowrate of the process to be designed and the known reference process. This scale-up factor then must scale volume, current, and electrode area equally while all other parameters are left to accommodate this scale-up.

To calculate the consumption of electrodes Equation 4 Faraday's Law of electrolysis was used combining the scaled-up value for current was used along with intrinsic constants for the metal. To calculate the energy needed to dissolve each kilogram of the metal anode a formula for the Specific Electrical Energy Consumption (SEEC) is used.[30]

Equation 14. Formula for Specific Electric Energy Consumption. n, is the number of electrons per mole, F is the Faraday's constant, U is the voltage, Mw is the molecular mass of the anode material, phi is the fraction between theoretical and actual mass loss. With the SEEC given in energy per hour and kg of anode consumed

$$SEEC = \frac{n*F*U}{3600*M_W*\varphi}$$

The total energy consumption is calculated by multiplying the SEEC from Equation 14 with the anode consumption.

The chemical consumption comes from the need to neutralize the feed for optimal technical performance. The dosage of HCl for neutralization does not consider the buffering capabilities of the filtrate, to better approximate neutralization of a buffered system the dose is assumed to be twice that of the dose without buffer capabilities.

By scaling the process according to theses presented calculations and using the largest EC process available, Meas et al.[21] as a reference, the following design was made.

Table 19. Design results of electrocoagulation process scale-up

Electrode material	**Aluminum**
Treated filtrate	100 m^3/h
Scale-up factor	520
EC reactor volume	12 m^3
Current	690 A
Energy consumption	17 kW
Aluminum consumption	230 kg/hour
Coagulant concentration	2.3 kg/m^3
Initial dye concentration	1 kg/m^3
HCl consumption	17 L/h

Table 19 shows that the coagulant dosage is 2.3 times that of the dye. This is an effect of the lab trials being optimized towards short residence times. There is a risk involved with high dosages if some of the coagulant coagulate. If there is a large surplus of coagulant, metal hydroxides in this case, these will instead contaminate the water and need treatment. If it is determined that all coagulant is not consumed effluent can be recycled to make sure that the process can run at high concentrations without eluting much coagulant. Again, the lack of insight apart from the core processes of EC makes any predictions and verdicts uncertain. Assuming a 95% removal efficiency the dye concentration in the effluent will be 50 mg/L.

The positive side of this design choice is the short residence time and the small reactor volume of $12m^3$ to treat 100 m^3 each hour. With the current being scaled equally to the volume of treated water the process will require high currents and powers.

5. Technoeconomic analysis

Renewcell must treat the outgoing filtrate to be able to sustain their practices, the current chemical loading of the wastewater is not feasible for coming years of production. Because of this the company does not consider filtrate reclamation as only a financial benefit, it's a necessity. Therefore, it is not necessary for this process design to make a profit, but it must be cost effective for large scale implementation.

There is also a great value in reducing the water consumption making the operations more sustainable environmentally and financially. Currently the municipal water price in Sundsvall is \$ 7/m^3 making the water price an important parameter in economic analysis.[31]

5.1 Cost estimation of membrane filtration

5.1.1 CAPEX

The capital expenditure was estimated using the Ulrich method of multiplying all direct cost of purchased equipment by a module factor to better represent what it costs to get the equipment operational. The purpose of the module factor is to make up for all costs connected to the equipment such as installation, engineering, freight, fees and contingency, insurance, ground improvements, buildings, and auxiliary equipment. All these factors add up to a factor of 3.795 to be multiplied on all capital costs. By summing all the costs, the result is the Total Grass Root Plant Cost.

The economic plant life was assumed to be ten years with an interest rate of 8%, equal payments of interest and amortization and linear depreciation of the material assets. The plant was assumed to be a brownfield plant as the site is already in commercial production with necessary infrastructure.

All process units were dimensioned according to the design results presented in Table 16 and rounded up to match commercially available equipment. Therefor the design capacity of the CAPEX estimation is 120 m^3/h of incoming filtrate.

The Total Grass Root Plant Cost was estimated to \$ 680 000 as of 2024. The specific costs of all equipment are listed in appendix A2.

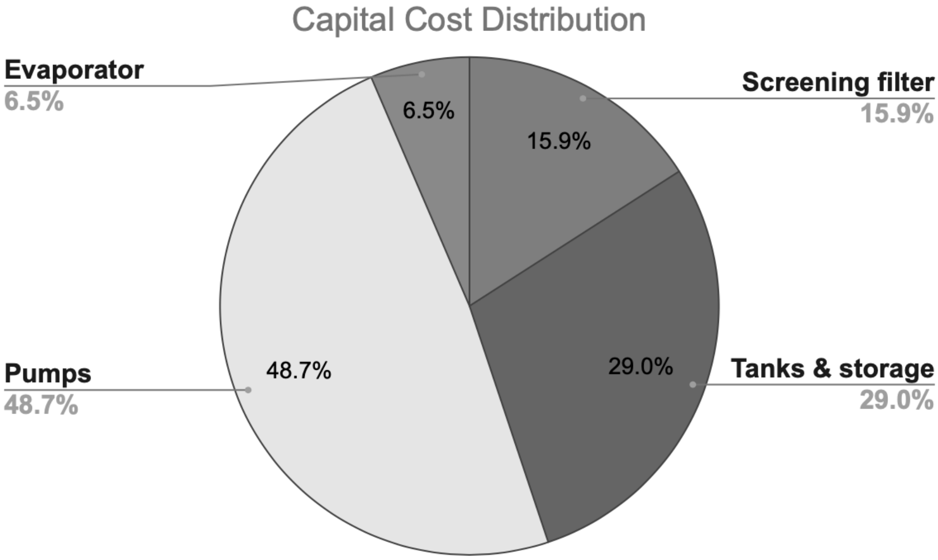

Figure 5.Diagram showing the distribution of capital costs for the membrane process.

5.1.2 OPEX

The Operational expenses were also estimated using the Ulrich method. The cost of fixed capital, direct operational cost and indirect cost are based of the costs of total capital expenditure, operator salaries, membranes, utilities, chemicals used along with estimations for licensing fees and R&D.

The cost of an operator in Sweden was estimated to $ 5000 a month with three shifts a day working around the clock and the amount of operators required is based on workers per process unit according to the Ulrich method.

Water is not included as a feedstock cost instead lowered water consumption compared to the current process can be considered as cost saving in the cost analysis.

5.1.2.1 Chemical consumption

The major chemical consumption is the sodium hydroxide and sodium hypochlorite for CEB and CIP. The costs of these were based on the bulk price available on Alibaba.com.

5.1.2.2 Membrane consumption

Membranes were included in the operational expenses and not the capital expenses since these are going to have to be replaced during the lifetime of the plant. The direct purchase costs of all proposed membranes are given by industrial retailers. Deviating from the Ulrich cost estimation method for OPEX, the direct purchase costs of the membranes were also multiplied by the module factor as a special case since membranes are advanced equipment with needs of installation, commissioning, and engineering etc. The membrane costs were divided by the lifetime of the membranes given by the manufacturers to give the annual cost of membrane.

5.1.2.3 Electricity consumption

For all electricity consumption the average electricity price of electricity region 2 in Sweden of 0.456 SEK/kWh or 0.044 $/kWh was used.
Electricity consumption by evaporation in wastewater treatment is in the range of 15 - 40kWh per m^3.[29] For this design 30 kWh/m^3 is assumed.
Membrane filtration with UF membranes are estimated to consume 1.1kW per m^3 of feed.[11]

5.1.2.4 Other operational expenses

Indirect costs associated with the salary of the operators such as overhead for staff and personnel, supervisors and administration were excluded from the operational cost since the proposed design is extension of an already operating plant with these costs in place. Instead, the R&D cost was set at its upper limit of 3% of direct & capital cost to account for the hardship of operating a plant with new treatment methods. Cost of capital fixation though product storage and the cost of product distribution was also excluded as there isn’t any product for sale.

The annual operational cost was estimated to $ 360 000 as of 2024.

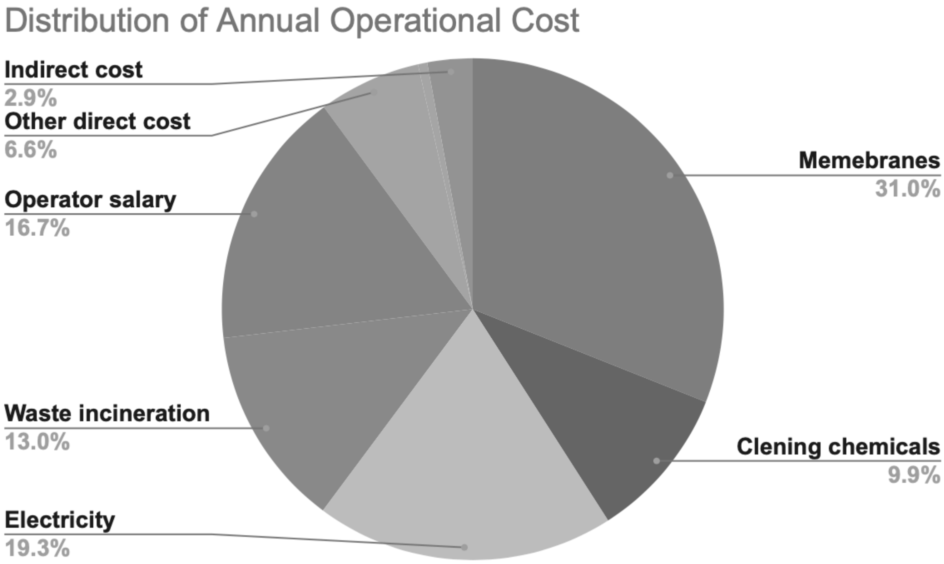

Figure 6. Diagram showing the distribution annual OPEX.

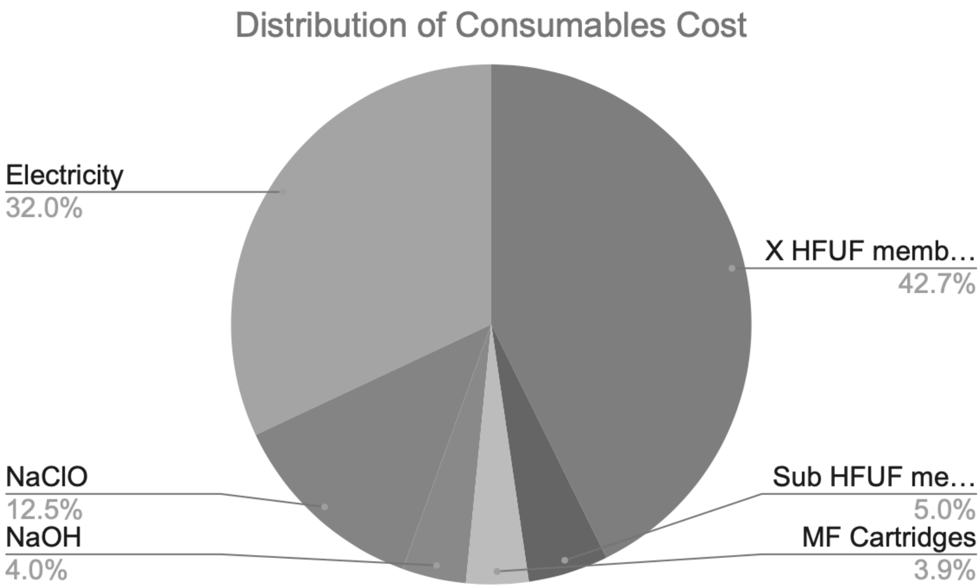

Figure 7. Diagram showing the distribution of the cost considered consumables.

5.2 Cost analysis of membrane filtration

Table 20. Cost analysis of the membrane filtration design.

Cost bearers	Cost
Total Grass Root Plant Cost	$ 680,000
Annual interest on loan + amortization	$ 100,000
Annual Operational Costs	$ 360,000
Annual cash expense	$ 460,000
Cash expense per m^3	$ 0.49
Annual Depreciation	$ 68,000

Comparing the costs in Table 20 to the presented costs by Vergili et al.[11] in Table 11 & Table 12 this design has less than half of the cost per treated m^3. The capital and operational cost are very similar only that the design presented in this study hourly treats 112 m^3 compared to the ones of Vergili et al.[11] treating only 42.8 m^3. Comparing the ratio of CAPEX to OPEX for this design, 1.89, to the Vergili et al.[11] designs with post treatment, on average 1.85, indicated that the balance between CAPEX and OPEX in the cost estimations for this design is reliable.

The treatment cost being this much lower is surrounded by large uncertainties. The municipal water price is 14 times higher than the estimated treatment cost is. Although, the largest share of the operational cost is the membranes, and this process uses hollow fiber membranes that are significantly more size efficient than the flat sheet membranes used by Vergili which should result in a lower cost. Another reasonable explanation for this process to be cheaper is that the membranes are arranged in an indirect series meaning less membrane is required and more water is recirculated with the downside of higher dye concentration in the permeate. This method is cheaper since it does not treat the water to the same extent, but this is good enough for the purpose of being recycled to the decoloring process.

To assess the financial feasibility of this process the cost has to be compared against potential cost saving and revenues that can pay back the initial investments. The first and most obvious cost savings are the reduced filtrate consumption, both water and the chemicals necessary for the dissolution of dye, and the reduced costs for sending water for external treatment.

Given the treatment cost of \$0.49 /m^3 for the presented design with an annual production of 120 000 tons of dissolving mass and the water price of \$7/m^3 in

Sundsvall the payback time of the investment is 0.12 years. With the same assumptions the annual change in cashflow of the investment is \$ 5 300 000. This economic performance is not realistic since it's not likely that Renewcell pays \$ 7 /m^3 of water for all their operations. Even if the water is not purchased at this cost, the markets evaluation should be considered as an opportunity cost when consuming this much water. Instead, doing the calculations the other way around to calculate at what acquisition cost of water the process breaks even, given the \$0.49/ m^3, a break-even cost of water of \$ 0.56 / m^3 is obtained. \$ 0.56/ m^3, equal to 0.0056 SEK / L, is less than a tenth of the current cost of water in Sundsvall indicating that the process can be profitable.

5.3 Cost analysis of Electro coagulation

The cost analysis of electrocoagulation will be concentrated to the operational expenses of running EC and compare these to available cost estimations performed on a smaller scale. To make a more detailed cost analysis of the whole EC process would require more information and results of EC which is simply not available.

The main operational expenses for EC are the costs of electric energy, the metal electrode, chemicals, and the sludge disposal.

The annual operational costs for treating 100 m^3/h of decoloring filtrate with electrocoagulation was estimated to $ 1 000 000 as of 2024 resulting in a unit cost of $ 1.22/m^3.

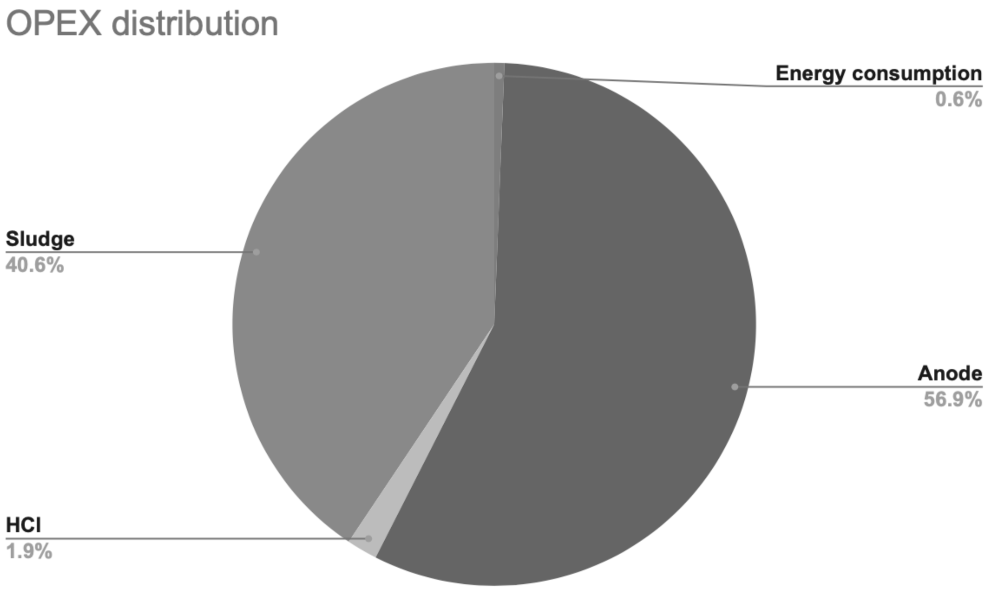

Figure 8. Distribution of operation cost for electrocoagulation.

In Figure 8. Distribution of operation cost for electrocoagulation.Figure 8 it is shown that the largest part of the OPEX is the raw material cost for the aluminum electrodes followed by the sludge incineration. The energy and chemicals cost are very small compared to the total cost.

6. Complete Design Proposal

Based on the available research, mature technology, results of the cost analysis and the discussion of the technical performance, an indirect sequence of hollowfiber UF membranes is the best design option for treating the process filtrate. This process both reclaims process filtrate for in process recirculation and concentrates the dye in a small portion of the process filtrate enabling the posttreatment of evaporation and incineration. The low treatment cost compared to the cost savings possible through reclamation of water and chemicals indicates that this process can be profitable and sustainable.

For optimal performance all the reclaimed process water should not be mixed with the decoloring filtrate left in the decoloring filtrate. The cleaner filtrate should be used after an initial decoloring with the old filtrate. The old filtrate is then the filtrate that is being bled off and reclaimed. This will increase the concentration of the filtrate to be reclaimed.

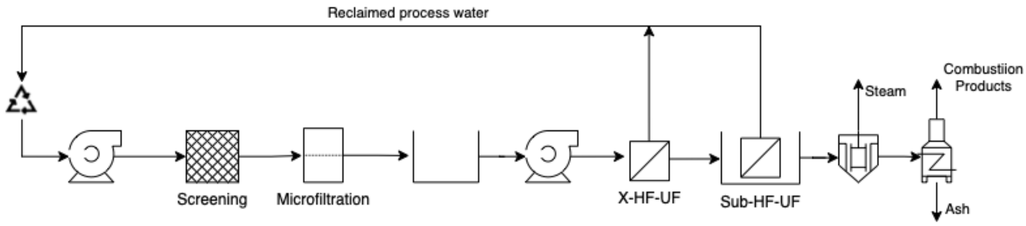

Figure 9. Process flow chart of the proposed process design

6.1 Short-Term

Renewcell should start pilot testing HF-UF membranes on the process filtrate.
Install instrumentation for continuous measurements of turbidity or color strength in Pt-Co units to be able to see the analyze performance of the tested treatment and enable real time process control. Electrocoagulation can be a short-term option to reduce the chemical loading to receiving wastewater treatment plant if necessary but is likely to be more expensive and the process filtrate cannot be recirculated to the decoloring process.

6.2 Long-Term

Renewcell should use sequential membrane filtration to separate dye from the process filtrate. This can reclaim valuable filtrate and concentrate the dye for further posttreatment. For a sustainable practice, the goal should be to reclaim all process filtrate to approach the Zero-Liquid-Discharge incentive. Further a final solution is needed for the separated dye that does not risk contaminating the environment. For this evaporation and incineration is proposed.

The treatment methods proposed are rather large and extensive for not being a part of the company's main activities. With the production quantities set to rise and the regulations surrounding discharge of water and pollutants becoming ever tighter, wastewater treatment will become a larger part of Renewcell's operations each year. How to deal with this is not only a technical decision, but a financial decision to decide if Renewcell should themselves treat water as part of their business going forward.

Renewcell should assess the cost of external water treatment, and the acquisitional cost of all components in the decoloring filtrate and compare these to the presented cost of treating and recycling the filtrate. If treatment is considered profitable the solution should be pilot tested on the specific filtrate before making any capital investments. For this purpose, there are available mobile treatment units fitted into containers equipped with advanced membranes, pretreatment, and cleaning systems with capacity up to 50 m^3/h.

7. Conclusion

Both electrocoagulation and membrane filtration are proven to be very effective at removing various types of dyes from textile effluent. Before assessing different treatment methods, it is important to understand the value of each component in the wastewater and why it is consumed rather than used cyclically. In this process the focus should not only be to remove the dye but also recycle the process water that contains all necessary chemicals back to the process. Because of the similarities of the physical properties of dyes, which is partly what makes them dyes, the separation of these is very intricate and is currently not deemed to be feasible for industrial application and should be destroyed to not pollute the environment.

The requirements for reclamation of filtrate for decoloring are not the same as for reclaiming of dye bath water which a lot of the current research is focusing on. This opens new possibilities as the lower requirements on the stream makes techniques not good enough for dye bath reclamation feasible for reclamation of decoloring filtrate. For example, membrane filtrations used as pre-treatment for dyehouse effluents can be used as a complete solution for this purpose.

Membrane filtration has a double effect of at the same time removing the dye and reclaim the process water without adding or changing the stream. Post treatment methods such as membrane filtration in indirect series with evaporation can increase the performance very efficiently since it can be applied to a concentrated stream.

Electrocoagulation can be used to efficiently remove dye, but the interplay between dosage and residence time is not explored enough for sustainable industrial application. Electrocoagulation should only be used to treat streams leaving the process as it disqualifies the treated water to be recycled and reused since the water is contaminated by metal coagulants and neutralizing acids for efficient coagulation.

The cost of electrocoagulation was estimated to \$1.22 per m^3 based on only the direct operational cost of the core process. This cost was within range of the previously presented operational cost of EC performed on a smaller scale. For membrane filtration the capital cost and annual operational cost was estimated to \$ 680 000 and \$ 360 00 respectively. These costs meant a total cost of \$ 0.49 per m^3, lower than previous cost estimations on large scale operating plants. The cost estimations for electrocoagulation and membrane filtration compared to the water price shows that dye separation from the decoloring filtrate in textile recycling can be economically feasible.

Altogether, an indirect sequence of hollowfiber ultrafiltration membranes seems to be the best option for Renewcell to separate dye from the process filtrate and reclaim the process water necessary for the operations.

*Table 21. Summary of the factors affecting the techno economic feasibility for the technologies evaluated. *Indicating that the cost is only based of direct operational expenses.*

	Sequential Membrane Filtration	**Electrocoagulation**
Specification	Indirect hollowfiber UF membrane sequence	Continuous EC with aluminum anodes
OPEX	$ 360 000	$ 1 000 000*
CAPEX	$ 680 000	-
Treatment cost $/m3	0.49	1.22*
Technical readiness level	6	6
Main uncertainties	Wastewater flux and the resulting concentration factor	Optimal coagulant dosage

8. Declaration of Competing Interest

The author has no known competing financial or commercial interests.

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Appendices

A1 Process Equipment & Solutions

For membranes and filters the direct purchase price is based on quotations received from the suppliers.

Apart from membranes in-process storage tanks, pumps and evaporator etc. must be included in the capital expenses. Piping and basic valves are excluded from the cost estimations as these are to be designed by external contractors.

The two in-process storage tanks are designed to offset one hour of downtime.

There is no need for an additional feed tank since the current filtrate tank can be used for this purpose.
There should be a buffer tank in-between the MF and the UF. This should be able to offset one hour of feed, 120 m^3, so that all the process won't have to be stopped for the daily CEB.

The reject of the first HF-UF membrane needs a tank where the HF-UF membranes are submerged. This tank should just be designed for steady state operation with continuous output of permeate and removal of the sludge left behind. A tank volume corresponding to one hour of feed, 11.2 m^3/h, is sufficient.

The permeate from the process does not need in-process storage, it should be recirculated back to the filtrate tank.

Dosing tanks are needed for the cleaning chemicals for the CEB and CIP to MF, UF and post treatment.

MF, UF and Post-treatment needs pumps and storage tanks for the CIP operation, valves are excluded again.

CIP tank: 70L per membrane module + 20 % excess volume + the volume in the pipes=20*0.07*1.25=1.75 $m^3 \approx 2 m^3$

Pumps & Blowers

2 HF-UF feed pumps: A centrifugal pump with a frequency inverter for flow control is recommended by Mann Hummel

2 Backwashing pump for HF-UF with twice the capacity of the feed pump

4 Dosing pumps for each cleaning chemical: i.e., 2 pcs (alkali and Chlorine wash) per HF-UF step

Air blower: discharge flow rate of 12 Nm^3/h (7.1 scfm) per module and a maximum air scouring pressure of 1.0 bar (14.5 psi).

Screening pump is included in the purchased equipment.

The screening comes with built in automatic cleaning.

MF cartridge pump is included in the purchased equipment.

Utilities consumption electricity
Pumps (heuristic for membranes)
Evaporator
Motors for filters

A2 Capital cost estimations

*Specific equipment costs given by manufacturers through quotes cannot be published openly

Unit operation	Purchased equipment cost	Module factor	Bare module cost	Number of units	Total unit cost ($)	Operators required
External HF-UF module	*	3.795	*	24	*	0.1
MF cartridge **filter**	*	3.795	*	1	*	0.05
Motor driven **self-cleaning screening filter**	*	3.795	*	1	*	0.05
Backwashing equipment to screening filter	*	3.795	*	1	*	
Submerged Reinforced PVDF Hollow Fiber	*	3.795	*	30	*	0.1
HF-UF Feed/buffer tank 120m3	$ 32,999.00	3.795	$ 125,231.21	1	$ 125,231.21	0

12 m3 tank for submerged HF-UF	$ 6,900.00	3.795	$ 26,185.50	1	$ 26,185.50	
CIP tank 1.75 m3	$ 500.00	3.795	$ 1,897.50	2	$ 3,795.00	0
permeate tank for backwashing	$ 500.00	3.795	$ 1,897.50	2	$ 3,795.00	0
Chemicals dosing tanks (2(MF+ xHF-UF + subHFUH)	$ 500.00	3.795	$ 1,897.50	6	$ 11,385.00	0
Centrifugal pump w/ frequency inverter	*	3.795	*	2	*	0
Backwashing pump for HF-UF with twice the capacity of the feed pump	*	3.795	*	2	*	0
Dosing pumps for each cleaning chemical: i.e., 2 **pcs (alkali and Chlorine wash) per**	*	3.795	$ 12,713.25	4	*	0

membrane step						
Evaporator	$ 10,000.00	3.795	$ 37,950.00	1	$ 37,950.00	0.2
Total Grass Root Plant 2024 Costs					$ 676,205.62	

A3 Assumptions in Cost estimations

Brownfield plant	
Plant life (years)	10
Operating days per year	350
Interest rate	8%
Annuity factor	0.1490
Daily labour shifts	3
Days in storage	30
Operators per shift	0
Operator salary(dollars/month)	$3,333.00
Nordic operator slary	$5,000.00
Fees and contingency	1.15
Auxillary facilities	1
1 Euro	$1.10
1 SEK	$0.10
Additional Costs Based on Equipment Costs	
Auxiliary **Factor**	1.3
Installation Factor	0.6
Buildings for Liquid Processes	0.2
Installation Overhead	0.6 * 0.7
Ground Improvements	0.15
Freight and Insurance	0.05
Engineering	0.15
Resulting Module Factor	0

A4 Summarizing table for Electrocoagulation trials

*Table 22, Summary of operating parameters and performance of studied processes. * indicating that there were no reports on current or current density only a operational voltage in volts. ** indicating that the color strength of the solution was measured in Pt-Co units instead of measuring the actual concentration *** Indicating that only direct electricity consumption and direct electrode consumption is the only cost bearer.*

Process	**Reactor Volume [L]**	**pH**	**Flow rate[L/min] (Residence time [min])**	**Current density [A/m²]**	**Feed conc [mg/L]**	**Anode material**	**Cost [$/m³]**	**Removal %**
Hendaoui et al.2021	2	7.5	2 (1)	47 V*	60	Fe	0.0927***	93.9
Meas et al.	23 (6m³/d)	7-7.5	3.2 (7.2)	110	Pt-Co: 380** COD: 1060	Al	0.25	> 95
Hendaoui et al.2018 optimal	2.4	7.58	1 (2.4)	101 V*	Pt-Co: 1750** (COD: 2000)	Fe	1.013***	93.7
Hendaoui et al.2018 Test 15-20	2	7	2 (1)	75 V*	Pt-Co: 1750** (COD: 2000)	Fe	0.401***	91.3
Mudasir et al. Diluted	3	10.43	0.63 (4.8)	400-600	500	Fe + Al	N/A	90
Mudasir et al. Concentrate	3	10.27	0.2 (15)	400-600	1100	Fe + Al	N/A	72

A5 Typical search queries

Membrane separation of indigo dyes

Coagulation of textile wastewater

Separation of ‘sulfur dye’ from textile wastewater

Sulfur dye recycling

Recovering indigo from textile recycling

Denim dye recycling

Electrocoagulation of Indigo

Electrocoagulation industrial scale

Scale up electrocoagulation.

Techno economic analysis of tertiary wastewater treatment processes

Techno economic analysis of electrocoagulation for textile effluent