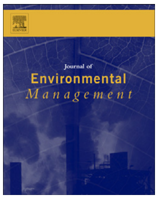
Journal of Environmental Management 207 (2018) 334–340

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman



Research article

Investigation of electrodialysis anti-fouling configuration for desalting and treating tannery unhairing wastewater: Feasibility of by-products recovery and water recycling

Sabrina Tamersit*, Kamel-Eddine Bouhidel, Zakaria Zidani

Laboratory of Chemistry and Environmental Chemistry LCEE (Team: Water Chemistry/Desalination & Environment), Dep. of Chemistry, Fac. of Matter Sciences, University Hadj Lakhdar, Batna 1 05400, Algeria

A R T I C L E I N F O

Article history:
Received 12 May 2017
Received in revised form
12 October 2017
Accepted 22 November 2017

Keywords:
Electrodialysis
Unhairing wastewater
Anti fouling
Ultrafiltration membrane
Tannery
Sulphide

A B S T R A C T

The desalination and treatment of tannery unhairing wastewater by electrodialysis (ED) is investigated in this research in order to separate, concentrate, recover and reuse low molecular weight charged species (S^{2-}, HS^-, OH^-, Cl^-, Ca^{2+}, Na^+ and amino acids), and to separate proteins and recycle treated water. Therefore, a novel electrodialysis membrane configuration was proposed. This was based on a double anti–fouling membrane. The ED anion exchange membrane (AEM), which is very sensitive to organic fouling, was protected by an ultra filtration membrane impermeable to the negatively charged proteins that could not reach the AEM surface. The experimental results were quite promising, and in spite of only one desalination compartment ED cell; the demineralization efficiency was 56 ± 1.25% (5.5–2.4 mS/cm), with a sensitive removal of sulphide, calcium and chloride. The organic matter (protein, peptides…) was isolated in the dilute compartment. The most important result was the total absence of membrane fouling.

The experimental results remarkably proved the initial hypothesis, and suggested promising solutions for industrial pollution, where the membrane processes have never been successful.

1. Introduction

The tanning industry aimed at transforming animal hides to finished leather. This transformation needed successive chemical operations using important quantities of water and producing much polluted wastewaters (Galiana-Aleixandre et al., 2013; Saxena et al., 2016).

The hide itself (by its natural organic matter and by-products) and the used chemicals are the main sources of pollution. The unhairing step is an alkaline attack of the epidermis and hair to partially dissolve keratin. High chemical oxygen demand COD (20,000–80,000 mg O_2/L), alkalinity/toxicity ($Ca(OH)_2$ and Na_2S), conductivity (8 mS/cm and many more) and pH (≥13) characterized the resulting unhairing wastewater. This constituted a worldwide dramatic environmental (Cassano et al., 2001; Galiana-Aleixandre et al., 2013; Mukesh and Anil, 2005; Saxena et al., 2016) and economic (Cassano et al., 2001) issue. Instead of preventing pollution, the industrial delocalization from Europe to South Mediterranean and Asian countries was the main alternative.

Catalytic air oxidation of sulphides by Mn^{++}, followed by a neutralization/precipitation step with acidic tanning waste waters, constituted the main treatment in Algerian tanneries, however, unrecyclable treated waters; sulphide related corrosion problems, important volumes of sludge, high investment and chemicals costs were serious drawbacks. Furthermore, the slow oxidation kinetic of $S^{=}$, which is at least 6 h, requires large reactors and massive energy.

Biological and/or physicochemical combination has been the main conventional treatment worldwide. Sludge generation, salty and COD polluted treated waters and absence of recycling are the main drawbacks (Cassano et al., 1997; Lofrano et al., 2013; Suthanthararajan et al., 2004) in nowadays treatments in spite of severe legislations and evident efforts towards pollution prevention politics (Cassano et al., 1997, 2001; Lofrano et al., 2013; Suthanthararajan et al., 2004). In fact, recent and intensive research efforts were made towards pollution reduction, recycling and reuse of water and valuable solutes; advanced oxidation processes (AOP), electrochemical and membrane techniques were largely investigated. In order to separate and recover low molecular

---

* Corresponding author.
E-mail address: sabrina.tamersit@gmail.com (S. Tamersit).

https://doi.org/10.1016/j.jenvman.2017.11.058
0301-4797/

weight ions and molecules and recycle water from skin products (proteins, peptides…), pressure driven membrane processes (reverse osmosis RO, nanofiltration NF, ultrafiltration UF and microfiltration MF) combined with various pre-treatments have been thoroughly studied but rarely applied (Fig. 1) (Brites Alves and Silva, 2006; Cassano et al., 1997, 1999, 2001; Galiana-Aleixandre et al., 2013; Mendoza-Roca et al., 2010; Taleb-Ahmed et al., 2005). Membrane fouling and high costs were the main obstacles. The electrodialysis (ED) has also been experimented (Streit et al., 2014) after nanofiltration (Streit et al., 2013), photo-electro-oxidation (Rodrigues et al., 2008) and centrifugation. In spite of the successful applications in milk industry, there were not many successful ED stories in tannery because of the fouling problems (Brites Alves and Silva, 2006; Galiana-Aleixandre et al., 2013; Mendoza-Roca et al., 2010). Recent ED organic separations with charged bio-molecules (Eliseeva et al., 2009; Kattan Readi et al., 2011) and the combined ED – UF membranes (Doyen et al., 2013; Poulin et al., 2007) in the ED stack, where UF membranes replaced the anion exchange membrane (AEM) for peptides separation, opened promising perspectives. Low ED pressures would minimize the membrane fouling by proteins.

These anion exchange membrane IEM/UF membrane combinations inspired the present work; however, the present stack configuration is totally different and quite novel. Indeed, in this research work one compartment conventional ED cell (Fig. 2) was used, but AEM was protected by a UF membrane which constituted a barrier against anionic proteins and high molecular weight organics which could not reach the AEM surface. Oppositely to the cation exchange membranes, it is established that the AEMs were very sensitive to anionic fouling (Lee et al., 2009; Lindstrand et al., 2000). This was the main research hypothesis that was extensively verified.

In order to optimize this lab scale cell (Bouhidel and Lakehal, 2006), feasibility tests were carried out and current–voltage curves were plotted to determine limiting current densities. Furthermore, the influence of flow rate, salt nature, and applied voltage were studied systematically in batch mode ED.

2. Materials and methods

2.1. ED setup configuration

The ED module with ultrafiltration membrane (EDUF) was developed in our laboratory. This cell was constructed of Plexiglas (8 symmetrical plates), inert material of great chemical and mechanical resistance. The ED cell contained 5 compartments, the central desalination compartment, two concentrations and two electrode rinsing compartments (Figs. 2 and 3).

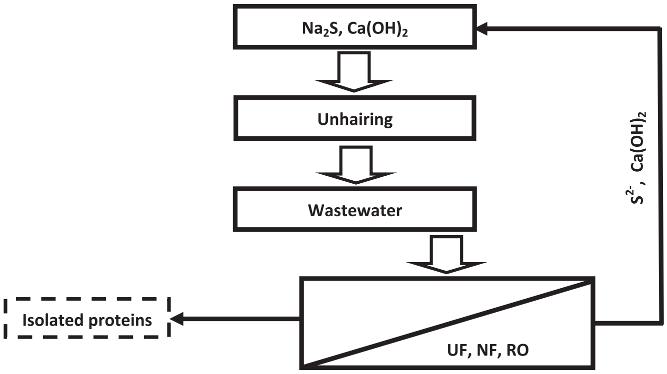


Fig. 1. Chart of unhairing operation integrated with membrane process.

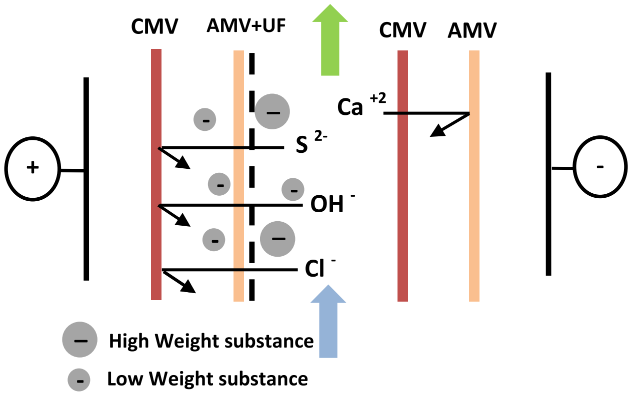


Fig. 2. Scheme of the proposed ED/UF cell, explaining the behavior of different component of unhairing bath during ED/UF process.

The electrode rinsing compartments contained at their inside two extremities embedded rectangular and vertical carbon electrodes ($h = 3$ cm, $l = 2$ cm and $S = 6$ cm^2). On each cell plate there were identical rectangular apertures limiting the active 6 cm^2 surface of the membrane and providing a solution volume of 3 cm^3. The distance between each two membranes was 0.7 cm. The ED cell is shown schematically in Fig. 3.

The ED unit contained three tanks for: electrode rinsing solution (250 cm^3), concentrate (250 cm^3) and diluate (150 cm^3).

The fluid passage was gravity driven. Four Selemion membranes, two CMV and two AMV were used. The location of the membranes is illustrated in Fig. 1. The ultrafiltration membrane is superposed on the anionic membrane of the stacking.

2.2. Chemicals and membranes

The chemicals used are of highest purity. NaCl (analytical grade) was obtained from Sigma-Aldrich (99.5% of purity). Na_2SO_4 was obtained from RP.NORMAPUR (purity 99.5%). Na_2S and $Ca(OH)_2$ were obtained from Fisher Scientific Labosi with 99% and 98% purity respectively.

The electrode and concentrate compartments contained 20 g/L and 2 g/L of NaCl aqueous solution.

In this study, cation selective membranes and anion selective membranes (Selemion AMV, CMV, Asahi Glass) were used. In order to achieve the equilibrium condition, both membranes were maintained in contact with the solutions for 48 h. Therefore, a tight ultrafiltration membrane (UH004, Microdyn-Nadir. Germany) was used with 4 KD of molecular weight cutoff.

2.3. ED electrical devices

The electrical devices consisted of a DC power supply 0–30 V (MCP. M106SP6303E) connected directly to the two electrodes of the ED cell. An ammeter and a voltmeter were used to complete the set up.

2.4. Analytical methods

The conductivity and pH of the Solutions were periodically measured using a Hanna electrical conductivity meter and an Inolab WTW pH meter.

First, the reduction agent (mg/L of Sulphides) was analyzed by iodometric titration, where concentrations were obtained by the titration of the excess iodine using the $Na_2S_2O_3$ solution (Mendoza-Roca et al., 2010; Rodier et al., 2009). The COD is determined