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Recovery of Cr(III) from Tannery Effluents by Diafiltration Using Chitosan Modified Membranes

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Abstract: The selective recovery of chromium remaining in tannery effluents after the leather tanning process is highly desirable to potentiate its reuse, simultaneously minimizing the ecotoxicity of these effluents. To the best of our knowledge, this work evaluates for the first time the ability of a chitosan-based membrane for selective recovery of chromium from a tannery wastewater by subsequent diafiltration and selective chromium desorption, envisaging their integration after tannery wastewater treatment by reverse osmosis (RO). A polyethersulfone (PES) microfiltration membrane top-coated with a chitosan layer (cs-PES MF022) was used for selective recovery of Cr(III), from concentrate streams obtained by treatment of synthetic and real tannery effluents through reverse osmosis (RO), through a diafiltration process. The diafiltration of the RO concentrates was conducted by an intermittent addition of water acidified to pH 3.6. The prepared cs-PES MF022 membranes were able to retain 97% of the total mass of Cr(III) present in the RO concentrates, from a real tannery effluent, with a selectivity of 4.2 and 5 in reference to NH_4^+ and Cl^-, respectively, 12.9 and 14.6 in reference to K and Na, and >45 in reference to Mg, Ca, and S. Such a high selectivity is explained by the preferential adsorption of Cr(III) onto chitosan, and by the relatively high permeability of cs-PES MF022 membranes to the other ionic species. Proof of concept studies were performed to investigate the desorption of Cr(III) at pH 2 and 5.8. A higher Cr(III) desorption degree was obtained at pH 2, leading to a final solution enriched in Cr(III), which may be re-used in tannery operations, thus improving the process economy and reducing the hazardous impact of the effluents discharged by this industry.

Keywords: tannery effluent; chromium recovery; chitosan membrane; diafiltration; selective adsorption; selective desorption

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1. Introduction

Leather tanning requires the use of a large variety of chemicals, such as tannins, sulphates, phenolics, surfactants, and ion salts. In particular, Cr(III) is used in the form of chromium sulphate $Cr_2(OH)_2(SO_4)_2$ for the conversion of collagen from skin into commercial leather. This process results in the production of high wastewater volumes with appreciable chromium content [1] that increases the ecotoxicological impact of the tannery effluents [2]. Wastewater treatment is thus mandatory before discharge this water stream, which must possess physicochemical characteristics that conform with local regulations for a safe discharge into the ecosystems. In addition, the recovery of chromium allowing for its subsequent reuse can reduce the costs associated with the leather tanning process.

Several physicochemical and biological approaches have been used to reduce the organic and inorganic content of tannery wastewaters, including coagulation/flocculation induced by specific chemical agents [3], electrocoagulation [4], solvent extraction [5], adsorption [6], aerobic or anaerobic biological treatment [7], incineration [8], chemical oxidation [9], membrane filtration [10–12], and via process integration, such as by combining coagulation with microfiltration [13] or electrodialysis [14,15]. Among the adsorption-based methods, different adsorbents, such as clays [16,17], activated carbon derived from different biological [18] and non-biological materials [19] with distinct morphologies [20], and chitosan-based compounds [6,21–26] have proved to allow for an efficient capture of metals from target effluents.

Chitosan is an eco-friendly and inexpensive biomaterial obtained from the partial deacetylation of the acetoamine groups of chitin. Chitosan-based flakes/beads [6], nanofibres [22], membranes [12,23], or films [24] produced by chitosan crosslinking have been prepared and tested in terms of their capacity to adsorb metal ionic species. The outstanding capacity of chitosan to adsorb heavy metal ions [22], including copper [25,26] and chromium [23], such as Cr(III), has been mainly ascribed to the ability of amine to act as chelators of these ionic species. However, a potential interaction with hydroxyl groups should also be considered. The chelating efficiency was found to be dependent on the electric charge of the species involved and, thus, dependent on pH [6]. In strongly acidic solutions, Cr(III) is mainly present in the form of cationic species Cr^{3+}, $Cr(OH)_2{}^+$, and $Cr(OH)^{+2}$, whereas the Cr precipitation observed at more alkaline conditions (pH > 6) is explained by a decrease of the solubility of chromium hydroxides at increasing pH values. Thus, due to the prevalence of positively charged amine ($R\text{-}NH_3{}^+$) and hydroxyl ($R\text{-}OH_2{}^+$) groups of chitosan, the adsorption of the positively charged Cr(III) species is unfavoured at lower pH values, but increases with the deprotonation of these chemical groups as the pH increases. Nevertheless, Cr(III) removal by adsorption is still more efficient at a pH lower than 6, due to the absence of intense Cr precipitation [23]. Mirabedini et al. [24] produced magnetic chitosan hydrogels crosslinked with glyoxal, which showed pH dependent Cr(IV) removal efficiency from water, with optimal values of 80–90% reached at pH 4.

The high affinity of chitosan to heavy metals brings additional interest in the development of chitosan-based membranes for the removal of these metals from wastewaters, taking advantage of both, their adsorptive and water filtration capacity. In a work from Juang et al. [27], chitosan flakes were added to a filtration system to increase the efficiency of regenerated cellulose membranes to remove divalent ions, such as Cu(II), Co(II), Ni(II), and Zn(II). Chitosan flakes were shown to increase the removal degree of these metal ions six to tenfold under acidic conditions. In another work from Li et al. [28], electrospun chitosan membranes were prepared and used as membrane adsorbers for the removal of Cr(IV) from model aqueous solutions. Regarding the Cr(IV) loading capacity of these membranes, their bed saturation and efficiency showed a higher dependence on pH, solution flow rate, fluid flow distribution, and membrane packed patterns, as compared to the Cr(IV) concentration in the feed solution and bed length. The maximum bed loading capacity was found to be 16.5 mg Cr(IV)/g of chitosan under dynamic fluid conditions. Chitosan/polyethylene oxide (PEO) nanofibres (90:10) assembled to spunbonded polypropylene (PP) substrate containing 90% chitosan developed by Desai et al. [29] showed a Cr binding capacity of 35 mg Cr(VI)/g chitosan. The same authors have also shown that the binding capacity of chitosan/PEO nanofibres is dependent on the chitosan content in the chitosan/PEO blend and decreases with the increase of the fibre diameter [29]. In a previous work by Ghaee et al. [30], chitosan/cellulose acetate composite nanofiltration membranes with various amounts of cellulose acetate were prepared and evaluated in terms of their rejection capacity to copper. The membranes obtained exhibited a molecular weight cut-off of 830.74 Da, and a Cu rejection of 81.03%. Cellulose membranes, enriched with chitosan-silver ions, were designed by Căprărescu et al. [31] and used for the removal of iron ions from synthetic wastewaters with an electrodialysis system. The presence of silver ions increased the electric conductivity of the membranes, resulting in iron removal rates > 60% at an applied voltage of 15 V.

In our previous study [12], a polyethersulfone (PES) membrane coated with a thin chitosan layer—a chitosan modified membrane designated for simplicity as cs-PES MF022—

was prepared, and its performance for the treatment of model tannery effluents was compared with that of a SW30 reverse osmosis (RO) membrane in terms of species rejection efficiency and selectivity. The cs-PES MF022 membrane showed rejection coefficients <45% for most of the ionic species present, i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NH_4^+, and SO_4^{2-}. These rejection coefficients were significantly lower than those obtained with the SW30 membrane, which provided rejection values above 90% for all these ions. As a result, the cs-PES MF022 membrane was considered unsuitable to produce treated water with the characteristics required to allow the discharge of the effluents into the ecosystem. However, this membrane exhibited an outstanding Cr(III) rejection > 90%, and, thus, a Cr(III) removal selectivity much higher than that obtained with the SW30 membrane. These results evidenced the potential suitability of cs-PES MF022 membranes for the selective recovery of Cr(III) from tannery wastewaters, prompting us to investigate and suggest a two-step process for this purpose. This process consists of the integration of reverse osmosis (RO) (1st step), in which an SW30 membrane is used to obtain a permeate stream with a chemical composition which allows its direct discharge into the environment [12], followed by a diafiltration of the RO concentrate (2nd step) for a selective recovery of Cr(III), using the chitosan modified membrane (cs-PES MF022) mentioned above. Diafiltration involves a solvent (acidic water) consumption higher than that required by membrane processes when operated in conventional mode, and for this reason, it may be regarded as a disadvantageous separation process. However, the possibility to treat complex aqueous streams—such as tannery wastewaters—under conditions of reduced concentration polarization and fouling-related effects [32,33], made us anticipate the suitability of diafiltration for the enhanced removal of contaminants, i.e., other ionic species with a lower affinity to chitosan and low-molecular mass compounds, from these effluents, facilitating the isolation of Cr-containing compounds and, thus, allowing for its subsequent re-use in tannery processes. Therefore, this study aims at evaluating the performance of the cs-PES MF022 membranes for selective removal of Cr(III) from concentrates obtained by RO treatment of synthetic and real tannery effluents by diafiltration, and the possibility to recover Cr(III), by selective desorption, taking advantage of the pH-responsive ability of chitosan [34].

2. Materials and Methods

2.1. Materials

The synthetic tannery effluent was prepared using magnesium chloride ($MgCl_2$; purity 99%) provided by Alfa-Aesar (Kandel, Germany); calcium chloride 2-hydrate ($CaCl_2.2H_2O$; purity > 99%), ammonium sulphate ($(NH_4)_2SO_4$; purity > 99%), and sodium chloride (NaCl; purity 99.8%) supplied by AppliChem PANREAC (Barcelona, Spain); and chromium(III) sulphate basic ($Cr_4(SO_4)_5OH_2$; 26% Cr_2O_3) obtained from Fluka Analytical (Buchs SG, Switzerland). The chitosan (cs) used for the preparation of functional chitosan membranes was provided from Sigma-Aldrich (St. Louis, MO, USA). Acetic acid (CH_3COOH; purity 99.8%), potassium sulphate (K_2SO_4; purity > 99%), and sodium hydroxide (NaOH; purity > 93%) were supplied by Carlo Erba (Val de Reuil, France). Glutaraldehyde (GDA; 25% in H2O) and hydrochloric acid (HCl; purity 35–38%) were purchased from Sigma-Aldrich Chemicals (St. Louis, MO, USA).

2.2. Methods

2.2.1. Concentrates of Real and Synthetic Tannery Effluents Obtained from Reverse Osmosis (RO)

The concentrates of real tannery effluent was obtained by reverse osmosis (RO) treatment of a real tannery effluent supplied by TAMEG-Rouiba-SPA—a Leather Industry located in Rouiba, close to Algiers (Algeria), whereas the concentrate of a synthetic tannery effluent was obtained by RO treatment of a synthetic solution, prepared in the lab, mimicking the composition of the real effluent in terms of the inorganic content (inorganic salts). The treatment of these effluents were performed using an SW30 reverse osmosis (RO) membrane supplied from DOW Chemical Company (Midland, MI, USA). RO showed rejections higher than 95% for all of the inorganic salts (99.2% rejection was obtained for Cr), allowing for the production of a treated water permeate [12] meeting the requirements for a direct discharge of the permeate stream into natural environments, according to the Algerian Legislation [35], and a concentrate enriched in the non-permeable components present in the effluents. The chemical composition of the concentrate of the synthetic and the real tannery effluents obtained by processing with the SW30 RO membrane are summarized in Tables 1 and 2, respectively.

Table 1. Chemical composition of the concentrate obtained by processing of a synthetic effluent with an RO SW30 membrane [12], at pH 3.6 and T = 20 °C.

Parameter [1]	**Ca**	**Cr(III)**	**K**	**Mg**	**Na**	**S**	**Cl^-**	**NH_4^+**
Unit	g/L	g/L	mg/L	g/L	g/L	g/L	g/L	g/L
Value	0.64	0.18	0.76	0.33	2.18	0.88	5.01	0.15

[1] The electric charge of the elements determined by ICP-AES was omitted, as ICP-AES quantifies the total amount present in the solution independently of their electric charge.

Table 2. Chemical composition of the concentrate obtained by processing of a real effluent from TAMEG-Rouiba Tannery with an RO SW30 membrane [12], at pH 3.6 and T = 20 °C.

Parameter [1]	**Ca**	**Cr(III)**	**K**	**Mg**	**Na**	**S**	**Cl^-**	**NH_4^+**
Unit	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L
Value	0.14	0.12	2.77	2.80	1.17	2.09	28.67	0.30

[1] The electric charge of the elements determined by ICP-AES was omitted, as ICP-AES quantifies the total amount present in the solution independently of their electric charge.

2.2.2. Preparation of the Chitosan-Based Membranes (cs-PES MF022)

Functional chitosan membranes were prepared by coating a 2.5% (*w*/*w*) chitosan solution on a polyethersulfone microfiltration membrane (PES MF022, 0.22 µm) from Merck Millipore (Carrigtohill, Ireland) which was used as a support. The 2.5% (*w*/*w*) chitosan solution was prepared by dissolving chitosan in a 5% (*v*/*v*) acetic acid aqueous solution, at room temperature, and then casted on the top surface of the PES MF022 support. The casting was carried out using an Elcometer casting knife film applicator (E.U.), by setting an application air gap of 90 µm, to ensure the formation of a chitosan layer with an uniform and reproducible thickness of ca. 10 µm, as shown in Figure 1 [12]. The resulting membrane was kept and dried at room temperature in a fume hood until complete solvent evaporation.

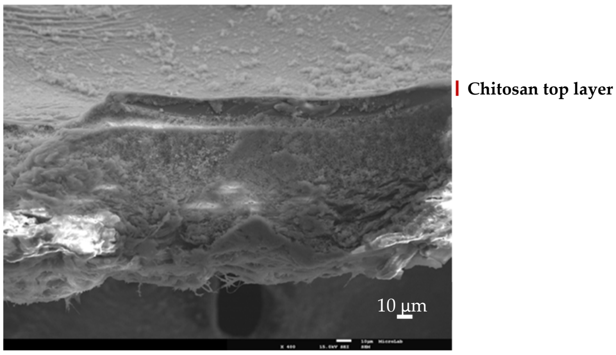


Figure 1. Scanning Electronic Microscopy (SEM) image of the cross-section of a chitosan modified membrane, cs-PES MF022, obtained after filtration of the synthetic tannery effluent (adapted from [12]).

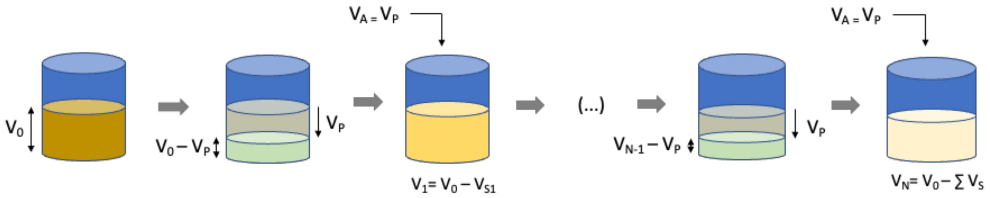
The membrane was then soaked in a 1 M NaOH solution for four hours, immersed in a glutaraldehyde solution (25% in H_2O) overnight, and then washed exhaustively with distilled water. The membrane washing efficiency was accessed by a periodic determination of the UV-Vis spectra (from 200 nm to 400 nm) using a spectrophotometer Thermo Scientific Evolution 201 (Madison, WI, USA), and by determination of the pH and conductivity of the washing solution (supernatant) for inspection of the complete release of the NaOH excess, and the possible release of loosely bound compounds, e.g., chitosan [12]. A pH-meter, type CRISON (Barcelona, Spain), was used to monitor the pH, whereas conductivity was measured by a Schott Lab960 conductivity meter (Mainz, Germany). The washing procedure was considered complete when the pH and conductivity registered for the washing solution were equal to the pH and conductivity values of the distilled water, and the absorbance of the washing was lower than 0.05 within the analysed wavelength range [26]. The membrane was kept in a closed petri dish with some drops of water to ensure the air humidity needed to prevent possible membrane structural alterations.

2.2.3. Diafiltration

Before the permeation experiments, the chitosan modified membrane cs-PES MF022 was mounted in a pressurized stirred filtration cell (MetCell, Greenford, UK), which was then filled with demineralized water acidified with HCl to a pH = 3.6 (acidic water). In the first stage, the cs-PES MF022 membrane was operated in stepwise mode, increasing pressures up to 40 bar for membrane structural compaction, to avoid the possibility of membrane structural changes along the process. In a second stage, the permeation cell was re-filled with acidic water (pH 3.6), and the permeation was conducted by the subsequent increase and decrease of the pressure from 7 bar to 20 bar, in a stepwise way to confirm the structural stability of the membrane. Each pressure step was kept for 10–20 min.

The permeate solution obtained was collected in a reservoir and weighted for a long time using a balance connected to a PC for data acquisition, and then used for determination of the membrane hydraulic permeability.

Each diafiltration experiment was conducted using 35 mL of feed solutions (SW30 concentrate of the synthetic and real tannery effluents). The cell was operated at a constant pressure of 20 bar in a dead-end diafiltration mode, and under a constant stirring speed of 400 rpm. The diafiltration was conducted by the intermittent addition of water (acidified at pH 3.6 with HCl) during the process [36]. As illustrated in Scheme 1, intermittent diafiltration consisted in a series of successive concentration mode filtration steps, interrupted after each 20 mL of permeate collected, for the addition of an identical volume of fresh solvent (20 mL) to the remaining retentate solution in order to restore the initial feed volume in each step. The retentate was sampled (0.5 mL) each time before re-initiation of the diafiltration. This procedure was repeated 7 times during the diafiltration process, leading to a final number of 4 diafiltration volumes (diavolumes).



Scheme 1. Schematic representation of the intermittent diafiltration strategy used in the present work. V_0, V_1 and V_N are the feed volumes at the beining of each diafiltration stage, V_P is the permeate volume collected and V_A is the volume of solvent added in each diafiltration stage. V_S corresponds to the volume of the retentate sampled for analysis at each diafiltration stage.

After collecting the final retentate solution, the filtration cell was rinsed with distilled water and pressurized from 20 to 40 bar in order to check the membrane hydraulic permeability after the process.

2.2.4. Data Treatment

Membrane Permeability

The permeate flux, J, L/(m^2·h) was calculated as:

$$J = \frac{Q_P}{A} \quad (1)$$

where Q_P is the volumetric permeate flow (L/h) and A is the surface area of the membrane (m^2). The membrane hydraulic permeability was calculated by registering the permeate flux and applying the Darcy equation:

$$J = L_P * (\Delta P - \Delta \pi) \quad (2)$$

where L_p is the membrane hydraulic permeability, ΔP is the applied pressure, and $\Delta \pi$ is the osmotic pressure difference between the concentrate and the permeate side. The osmotic pressure difference ($\Delta \pi$) was also considered, but given the good permeability of the membrane to most of the species and the reduced amount of species remaining in the retentate along the process, an average $\Delta \pi < 1$ bar was obtained, which was considered negligible compared to the applied operating pressure of 20 bar. Ionic speciation was accessed through the determination of chemical equilibrium diagrams obtained using Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA) software (version: Eq. calcs 32) [37].

Determination of the Compounds Retained in the Membrane and Cr Retention Selectivity

The amounts of each compound, i, retained in the membrane after diafiltration, were calculated by a global mass balance (M_i) to the process, using Equation (3):

$$M_{m,i} = C_{F,i} \times V_F - \sum C_{P,i} \times V_P - \sum C_{S,i} \times V_S - C_{R,i} \times V_R \quad (3)$$

where $M_{m,i}$ is the mass of compound i in the membrane; $C_{F,i}$, $C_{P,i}$, $C_{R.i}$, and $C_{S,i}$ are the concentration of the compound i in the feed, permeate, retentate, and sampling solutions; and V_F, V_P, V_R, and V_S correspond to the volumes of feed, permeate, final retentate, and sampling volume.

The chromium retention selectivity (S_{CR}) was calculated according to the equation:

$$S_{Cr} = R_{Cr}/R_i \quad (4)$$

where R_{Cr} and R_i are the mass of Cr and the mass of each compound i retained in the membrane, relative to that present in the feed, calculated according to Equation (5):

$$R_i = \frac{M_{m,i}}{M_{F,i}} \quad (5)$$

where $M_{m,i}$ and $M_{F,i}$ correspond to the mass of each compound i, retained in the membrane at the end of the process (N_D = 4) and that present in the feed solution at the beginning of the process, respectively.

2.2.5. pH Induced Desorption

The cs-PES MF022 membrane used for the diafiltration of the SW30 concentrate from synthetic tannery effluent was cut into identical pieces with an area of 15.9 cm^2. One piece was immerged in a beaker containing 10 mL of demineralized water (pH 5.8), and the other was immerged in an identical volume of demineralized water acidified with HCl to pH 2. The solutions were periodically sampled along 72 h, and the samples were analysed by ICP-AES as described below.

2.2.6. Analytical Methods

Quantification of the Compounds

An inductively coupled plasma atomic emission spectrophotometer, ICP–AES (Ultima model, Horiba Jobin-Yvon, France)—equipped with a radio-frequency (RF) generator of 40.68 MHz—a Czerny–Turner type monochromator with 1.00 m (sequential), an AS500 autosampler, and data acquisition software were employed to determine the concentration of target elements, i.e., Na, K, Ca, Mg, Cr, and S in the feed, permeate, and retentate solutions. Kits (LCK11) from Hach Lange GmbH (Düsseldorf, Germany) were used for chloride determination. The $NH_4{}^+$ content was determined colorimetrically using a Skalar SAN++ segmented flow analyser, Skalar Analytical B.V. (AA Breda, The Netherlands).

Characterization of Membrane Structure and Chemical Characterization

The structural characteristics of the cs-PES MF022 membranes were examined using a Field Emission Scanning Electronic Microscopy, FEG-SEM (Jeol JSM–7001F, Tokyo, Japan), upon coating the membrane with an AU/Pd film of 20 nm thickness using a sputter coater from Quorum Technologies (model Q150TES, West Sussex, UK), which were discussed in a previous paper [12]. An energy dispersive X-ray spectrometer (EDS) detector was also used for inspecting the presence of compounds at the membrane surface.

3. Results and Discussion

3.1. Diafiltration of the SW30 Concentrate Solution—Synthetic Tannery Effluent

The concentrate of a tannery synthetic effluent obtained by reverse osmosis (RO) was processed by diafiltration using the chitosan modified membranes (cs-PES MF022), aiming at a selective recovery of chromium.

Prior to filtration of the SW30 concentrate, the structural stability of the membrane was inferred, after its compaction, based on the determination of the membrane hydraulic permeability at increasing and decreasing pressures in a range from 7 bar to 20 bar. As shown in Figure 2, identical permeate fluxes were obtained at the same ΔP values during ascending and descending volumetric flux profiles, resulting in a practically identical hydraulic permeability, *Lp*, of about 0.5 L/(h·m^2·bar). This evidences that the cs-PES MF022 membrane has good structural stability, with an ability to support pressures within the considered ΔP range.

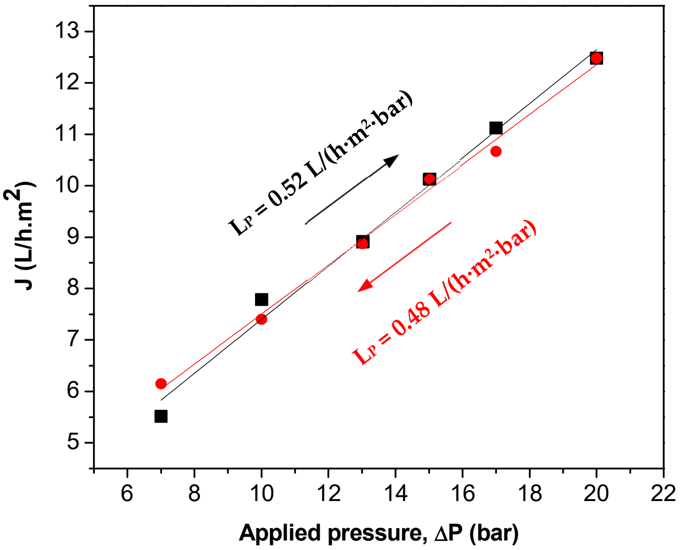


Figure 2. Permeate fluxes, *J*, obtained during filtration of acidic water (pH 3.6) at increasing (squares) and decreasing (circles) pressures using the cs-PES MF022 membrane before diafiltration. *Lp* represents the hydraulic permeability of the membrane determined at increasing and decreasing pressures.

The SW30 concentrate obtained from the RO treatment of a synthetic effluent with the chemical composition indicated in Table 1 was diafiltrated through the cs-PES MF022 membrane, at a ΔP of 20 bar, using a solvent (acidic water) stepwise addition strategy. The permeate flux profile observed during the diafiltration, depicted in Figure 3, shows a constant oscillating profile with an average value of 10.5 L/(h·m^2). A time dependent decline of the permeate flux was not observed, suggesting the absence of significant concentration polarization and fouling phenomena during the process. This may be explained by the attenuation of solutes' accumulation related effects at the membrane surface due to the intermittent addition of solvent and the fluid dynamic conditions established in the filtration cell.

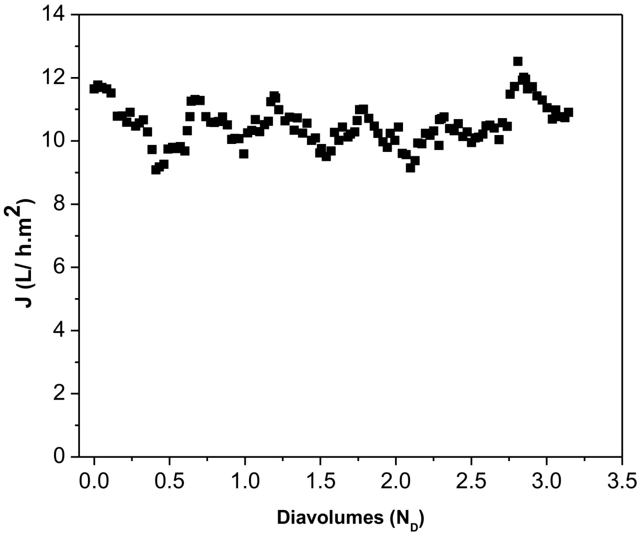


Figure 3. Permeate flux, *J*, obtained during diafiltration of the SW30 concentrate of the synthetic tannery effluent, using the cs-PES MF022 membrane at an applied pressure of 20 bar.

The efficiency of the diafiltration process was evaluated based on the membrane ability to selectively remove Cr(III) (the target compound) in reference to the other ionic species present in the SW30 concentrate, namely Na, K, Ca, Mg, S, Cl^- containing ionic species, and NH_4^+.

As shown in Figure 4, the removal of the different compounds from the SW30 concentrate by diafiltration shows an exponential decay reaching minimum values for most of the species, after permeation of at least 2.5 diavolumes. The mass removal of all the compounds tested fit a negative exponential function, as represented in Equation (6):

$$\frac{M_{Ret,\,i}}{M_{F,i}} = e^{-aN_D} \quad (6)$$

where $M_{Ret,i}$ corresponds to the mass of a given compound, *i*, in the diafiltration retentate at a specific diavolume number, N_D, whereas $M_{F,i}$ is the mass of compound *i* in the feed solution (N_D = 0). The exponential term *a* reflects the intensity of the mass decay of each compound *i* in the retentate solution during diafiltration, which is commonly interpreted as the sieving coefficient of a given molecular species at each time, t, of the process [38]. The $M_{Ret,i}/M_{F,i}$ reflects the apparent mass rejection of the target species, thus, it only accounts for the mass of each species in the retentate solution (excluding that retained in the membrane) at a given N_D. The fitting and exponential parameters obtained for the different compounds are listed in Table 3.

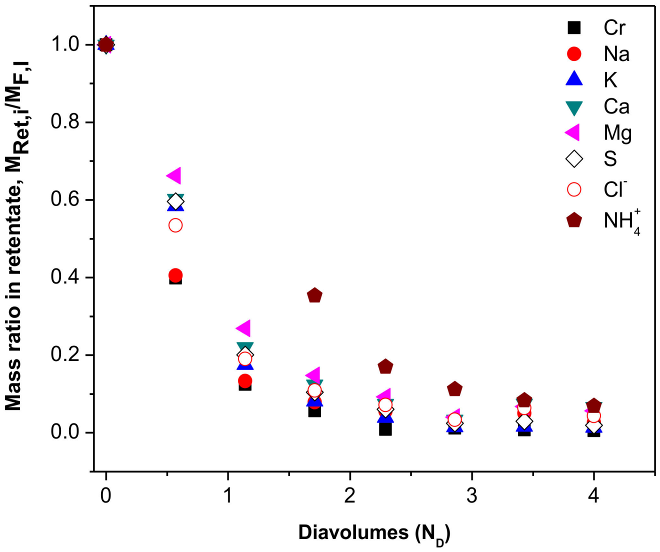


Figure 4. Mass ratio of each compound in retentate during diafiltration with a cs-PES MF022 membrane at 20 bar. Mass ratio was calculated in reference to the total mass of the same compound, $M_{i,x}$, in the SW30 concentrate of a synthetic tannery effluent before diafiltration (diafiltration feed solution). Note that the electric charge of the elements quantified by ICP-AES was omitted, as this technique quantifies the total amount of the element in the solution independently of its electric charge.

Table 3. Fitting parameters to the exponential decay of the mass removal for different compounds in the diafiltration retentate: *a* corresponds to the exponential term, whereas the fitting quality is expressed by the respective R^2.

Compounds [1]	*a*	R^2
Cr	1.69 ± 0.04	0.999
Na	1.60 ± 0.08	0.993
K	1.26 ± 0.10	0.984
Ca	1.11 ± 0.08	0.982
Mg	0.99 ± 0.07	0.982
S	1.18 ± 0.08	0.987
Cl^-	1.24 ± 0.07	0.990
NH_4^+	0.70 ± 0.03	0.993

[1] The electric charge of the elements determined by ICP-AES was omitted, as ICP-AES quantifies the total amount present in the solution independently of their electric charge.

A comparative analysis of the exponential function parameters shows that the removal of all compounds tested fit adequately to Equation (6) with $R^2 \geq 0.982$. The exponential term *a* showed similar values for most ionic species, being slightly higher for Cr and Na, reflecting a faster depletion of these elements (or the respective ion-containing species) from the retentate. On the other hand, a lower value was observed for NH_4^+, indicating a slower removal of this ionic compound from the retentate solution.

The depletion of these compounds from the retentate solution may be explained either by their permeation through cs-PES MF022 membrane or by their adsorption to the membrane, which depends on the chemical affinity of their ionic-containing species to the membrane material.

To elicit the removal mechanism of each compound, a comparative analysis of their permeation and adsorption profiles through/to the membrane was performed.

The permeation profiles (Figure 5A) clearly show that the permeability of the Cr(III)-containing species is significantly lower than that observed for the other species. The mass ratio of Cr(III) in the permeate solution reached only 19.2% after permeation of four diavolumes (N_D = 4), whereas mass ratios higher than 50% were observed for all of the other species tested. The highest mass ratios in the permeate were observed for Mg and K, showing mass ratios of 96.5% and 98.0%, respectively, whereas a mass ratio of 62.6% was observed for Ca, after N_D = 4.

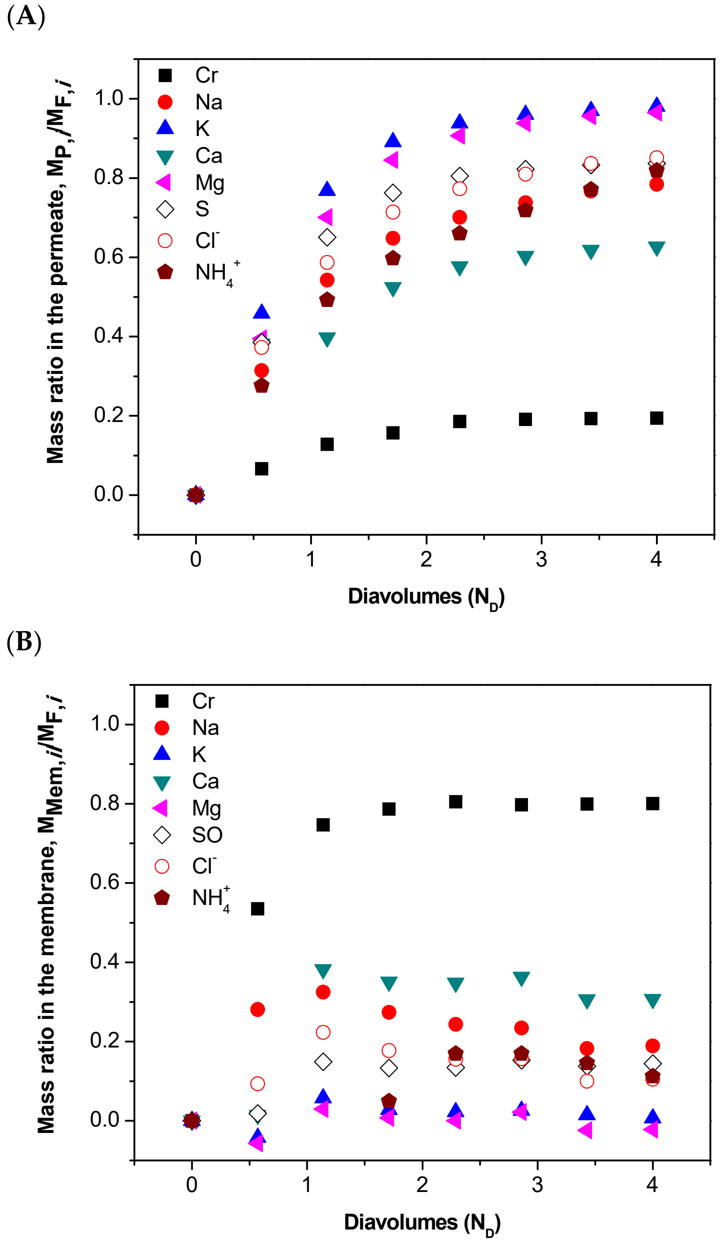


Figure 5. (**A**) Mass ratio of each compound permeated and (**B**) mass ratio of each compound retained in the cs-PES MF022 membrane during diafiltration with the cs-PES MF022 membrane at 20 bar. Mass ratio of each compound was calculated in reference to the total mass of the same compound, $M_{F,I}$, in the SW30 concentrate of a synthetic tannery effluent before diafiltration (diafiltration feed solution). Note that the electric charge of the elements quantified by ICP-AES was omitted, as this technique quantifies the total amount of the element in the solution independently of its electric charge.

The high transmission of these compounds to the permeate resulted in their low accumulation in the membrane, which was found to be inferior to 35% of their total mass, with K and Mg registering residual values close to zero, whereas the mass ratio of Ca in the membrane was equal to 30.7%, at $N_D = 4$. In contrast, the loss of Cr(III) from the retentate solution is mainly explained by the effective retention of Cr-containing compounds in the membrane. As shown in Figure 5 B, a maximum Cr(III) mass ratio of 80% was found in the membrane after permeation of two diavolumes ($N_D = 2$).

In a study developed by Vinodhini et al. [39], UF acetate cellulose and nanochitosan membranes showed Cr rejections varying between 78.5% (initial rejection) and 30.33% (rejection after 90 min of operation) when using feed solutions with 200 ppm of Cr(VI) at pH 5, which were explained by the adsorption of Cr to the amine groups of chitosan. Efficient Cr(VI) and Cr(III) rejections were also reported by Zhang et al. [40] using ultrafiltration membranes decorated with positively charged UiO-66-NH_2 compounds, from feed solutions containing 10.4 mg/L of these ions. The removal of Cr(VI) was explained by the electrostatic attraction to the positive charges in the membrane, whereas concentrations of Cr(III) lower than 1.5 mg/L in the effluent (stable during the operation time) were obtained with MOF@PVDF-0.02 and PEI/MOF@PVDF-0.02 membranes. However, and in contrast to that observed in the present work, the rejection of Cr(III) by these membranes was attributed to the electrostatic repulsion by the positively charged membrane.

The preferential accumulation of Cr-containing compounds at the surface of the chitosan modifying layer upon filtration of the tannery effluent was confirmed in the present study by SEM-EDS analysis. The SEM-EDS results obtained after analysis of chitosan modified membranes (Figure S1, in Supplementary Materials) after permeation of a synthetic tannery effluent (non-processed by reverse osmosis) in concentration mode, showed a significant relative intensity of Cr, in reference to elements such as C, O, and S, which are components of the membrane matrix, and to Au and Pd, which were used to coat the membrane surface, as required for the SEM-EDS analysis.

Despite the high Cr(III) rejection obtained through diafiltration, it was lower than that obtained with the same membrane operated in concentration mode (>99%) or with BW30 and SW30 reverse osmosis (RO) membranes, which led to Cr rejection values of 90% and 99.6%, respectively. However, diafiltration is advantageous if selective removal of Cr is required. Diafiltration produces a higher “cleaning effect”, which results in a more efficient removal of compounds non-size excluded by the membrane, in the presence of insignificant fouling effects which prevents the permeate flux decline [12].

Analysis of the Cr(III) retention selectivity in reference to the other compounds tested (Figure 6) shows a retention selectivity of Cr(III)-containing compounds of 2.6 and 4.2 in reference to Na and Ca-containing compounds, respectively; a retention selectivity of 5.5, 7.1, and 7.6 in reference to S-containing compounds, NH_4^+ and Cl^-, respectively; and a selectivity >100 in reference of K-containing compounds, whereas only a vestigial accumulation of Mg-containing compounds in the membrane was detected. The selective retention of Cr(III) in the cs-PES MF022 membrane may be explained by the high chemical affinity of chitosan to heavy metals, via coordination with the amine (NH_2) groups of chitosan [8]. The chemical characterization of cs-PES MF022 membranes by FTIR-ATR was performed and discussed in our previous paper [12]. The presence of chitosan was confirmed based on the detection of the NH_2 stretching band at 1586 cm^{-1}, whereas chitosan crosslinking was confirmed by the decreased intensity of the C=N signal at 1680–1620 cm^{-1} [12]. In particular, the preferential adsorption of Cr(III) to chitosan, in detriment of the other ionic species present in the SW30 concentrate, can be interpreted based on the ability of the NH_2 groups to coordinate heavy metals with f unsaturated orbitals, and its inability to form complexes with alkali and alkali earth metals, such as Na^+, K^+, or Mg^{2+}.

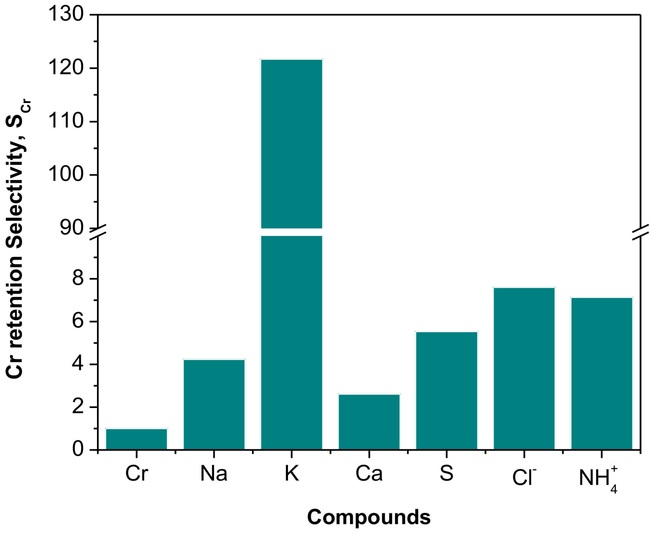


Figure 6. Selective retention of Cr(III), in reference to other species, in the cs-PES MF022 membrane, during diafiltration of the SW30 concentrate of a synthetic tannery effluent at 20 bar.

The selective adsorption of Cr(III) to the cs-PES MF022 membrane (as evidenced in Figure 5B) led to our hypothesis that it is possible to selectively recover the Cr(III) contained in the effluent by membrane desorption after diafiltration, taking advantage of the pH-responsiveness behaviour of chitosan.

3.2. *Diafiltration of the SW30 Concentrate Solution—Real Tannery Effluent*

The concentrate obtained by RO treatment of a real effluent from the TAMEG-Rouiba tannery with an RO SW30 membrane was also processed through a cs-PES MF022 membrane in a diafiltration mode. Identically to that observed for the diafiltration of the SW30 concentrate from a synthetic effluent, a relatively constant oscillating permeate flux was obtained through the whole process (Figure 7). These results are compatible with the absence of significant concentration polarization and fouling events, revealing that, contrarily to what might be initially expected, the organic content of this effluent (the chemical oxygen demand, COD, of the TAMEG-Rouiba tannery effluent is 92 mg O_2/L after pre-filtration with a microfiltration membrane with an average pore size of 0.45 µm [12]), did not affect the performance of the diafiltration process, at least considering the investigated operation time window.

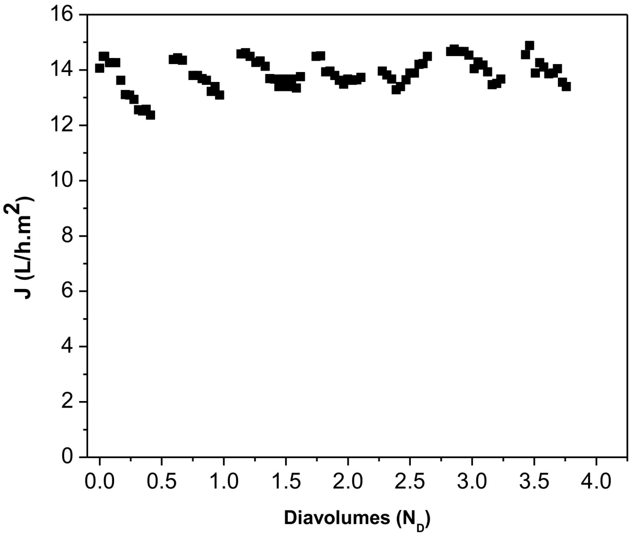


Figure 7. Permeate flux, *J*, obtained during the diafiltration of the SW30 concentrate of the real tannery effluent with the cs-PES MF022 membrane at an applied pressure of 20 bar.

As shown in Figure 8, the diafiltration process led to an exponential loss pattern of all the species studied. However, this exponential decay behaviour was clearly more accentuated for Cr(III), indicating a faster removal of Cr-containing compounds from the diafiltration retentate solutions. Similarly to that observed for the diafiltration of the SW30 concentrate from a synthetic effluent, the removal profiles fit very acceptably to the exponential function represented in Equation (6), as it can be confirmed by the respective R^2 values (Table 4).

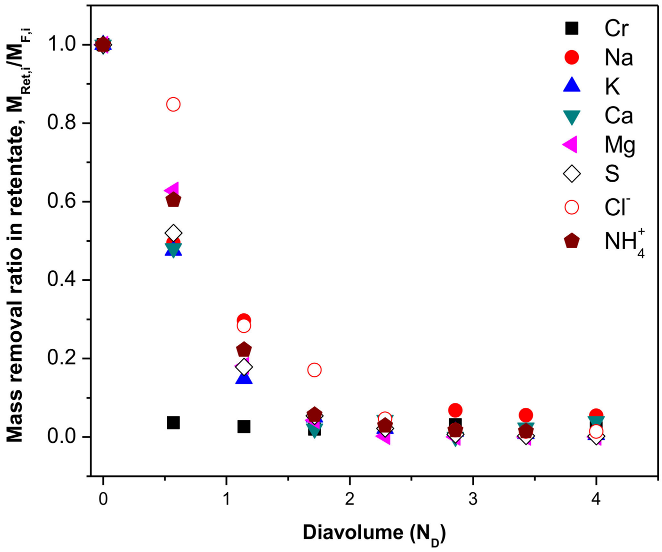


Figure 8. Mass ratio of each compound in the retentate solution during diafiltration with a cs-PES MF022 membrane at 20 bar. Mass ratios were calculated in reference to the total mass of the same compound, $M_{F,i}$, in the SW30 concentrate of the real tannery effluent before diafiltration (diafiltration feed solution).

A comparative analysis of the exponential term, *a*, obtained for the diafiltration of SW30 concentrates from synthetic and real tannery effluents, seems to indicate an identical removal efficiency of most of the compounds studied, with the exception of Cr(III)-containing compounds. The exponential term, *a*, corresponding to the loss of Cr(III)-containing compounds from the SW30 concentrate of the real tannery effluent was equal to 5.85, thus being much higher than that corresponding to the diafiltration of the SW30 concentrate from a synthetic effluent, which was equal to 1.69.

Table 4. Fitting parameters to the exponential decay of the different compounds in diafiltration retentate: *a* is the exponential term, whereas the fitting quality is expressed by the respective R^2.

Compounds [1]	*a*	R^2
Cr	5.85 ± 1.06	0.996
Na	1.13 ± 0.07	0.993
K	1.52 ± 0.07	0.995
Ca	1.45 ± 0.12	0.991
Mg	1.29 ± 0.15	0.968
S	1.41 ± 0.08	0.992
Cl^-	0.93 ± 0.15	0.923
NH_4^+	1.24± 0.11	0.980

[1] The electric charge of the elements determined by ICP-AES was omitted, as ICP-AES quantifies the total amount present in the solution independently of their electric charge.

Such an increase in the exponential term reflects an improved removal of Cr(III) species from the SW30 concentrate from a real tannery effluent, potentially associated to the adsorptive capacity of the organic matter present in real effluent, as discussed in detail below.

In order to understand the removal mechanisms associated with the depletion of each species from the diafiltration retentate, the mass ratio of each compound permeating across the cs-PES MF022 membrane, and that retained in the membrane during diafiltration were determined by respective mass balance calculations.

The profiles depicted in Figure 9A,B show that the cs-PES MF022 membrane exhibits a satisfactory permeability to most of the studied species. Mass ratios higher than 74% were obtained, with Mg and S-containing compounds showing the highest permeability and mass ratios in the permeate of 98% and 99%, respectively, for N_D = 4. Oppositely, the mass ratio profiles in the permeate indicate that the Cr-containing compounds are almost completely retained by the cs-PES MF022 membrane, with the Cr(III) mass ratio in the membrane reaching ca. 94% after the permeation of only 0.6 diavolumes. The Cr(III) retention efficiency obtained with the SW30 concentrate of a real tannery effluent was thus much higher than the 80% retention of Cr-containing species obtained by diafiltration of the SW30 concentrate of the synthetic effluent. These results suggest that organic matter present in real tannery effluents contributes positively to the retention of Cr-containing compounds in the membrane. Although the reason for this behaviour is not yet clearly understood, it suggests that the overall adsorption of Cr(III) results from a combined effect of the ability of chitosan to selectively adsorb Cr(III), as previously discussed, and the membrane ability to reject/adsorb organic matter, thus rejecting/adsorbing simultaneously the Cr(III) potentially bound to it.

(**A**)

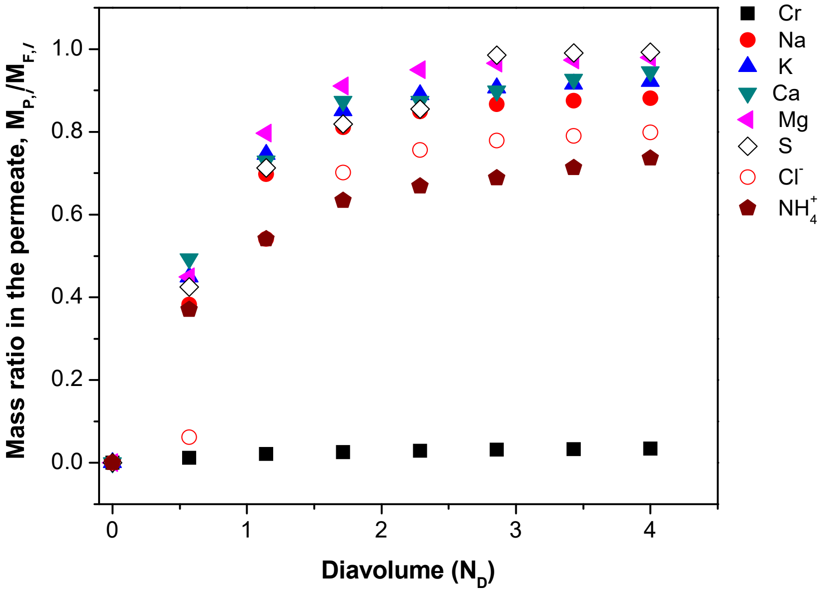


Figure 9. *Cont.*

(B)

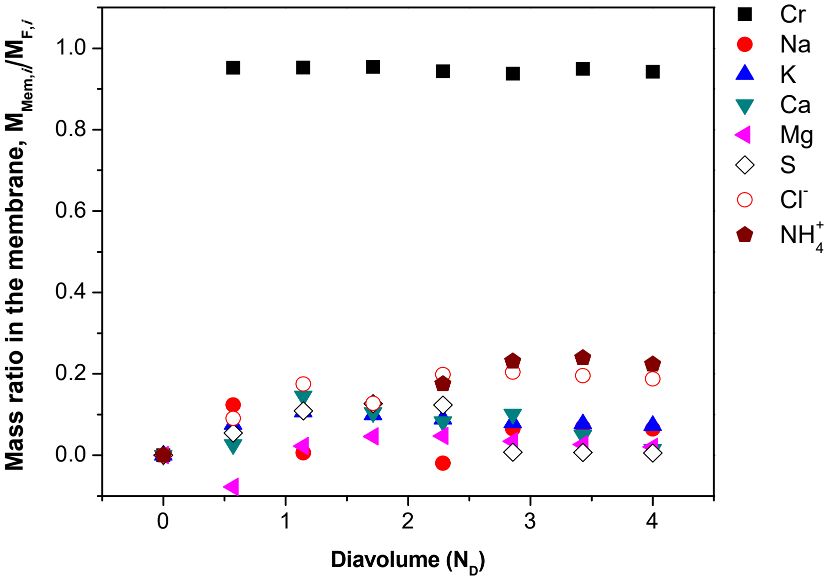


Figure 9. (**A**) Mass ratio of each compound *i* permeated and (**B**) mass ratio of each compound *i* retained in the cs-PES MF022 membrane during diafiltration at 20 bar. Mass ratio for each compound was calculated in reference to the total mass of the same compound, $M_{F,I}$, in the SW30 concentrate of a real tannery effluent before diafiltration (diafiltration feed solution).

The mass ratios of other compounds in the membrane showed maximum values of 18.7% and 22.4% for Cl^- and NH_4^+, respectively, whereas Mg, K, S, and Ca compounds showed mass ratios in the membrane inferior to 7.5%. These differences led to significantly high Cr(III) retention selectivity in the membrane, of 4.2 and 5 in respect to NH_4^+ and Cl^-; 12.9 and 14.6 in reference to K and Na-containing compounds, respectively; and higher than 45 in respect to Mg, Ca, and S -containing compounds, as shown in Figure 10. As shown in Figure S2, the Cr(III) retention selectivity relative to the divalent ions was higher during the diafiltration of the real tannery effluent than that found during the diafiltration of synthetic tannery wastewaters.

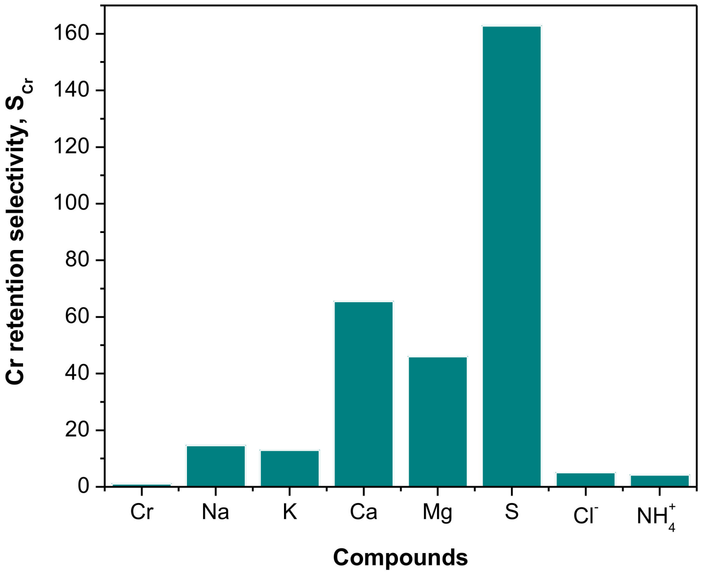
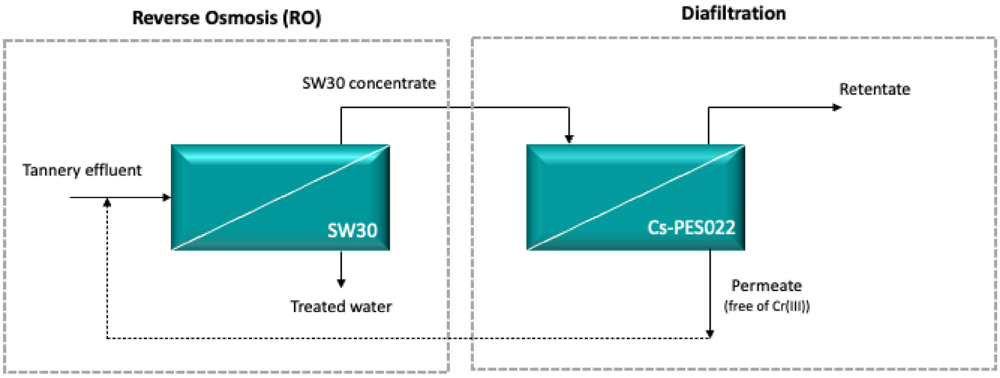


Figure 10. Selective retention of Cr(III) in the cs-PES MF022 membrane during the diafiltration of the SW30 concentrate of a real tannery effluent at 20 bar.

These results suggest the possibility of recovering Cr(III) from tannery effluents by desorption, taking advantage of the pH-responsiveness of chitosan, and thus allowing for Cr(III) reuse in the tannery industry. Moreover, a permeate solution with a residual amount of Cr(III) (only 3% of the Cr(III) mass content of the SW30 concentrate from a real tannery effluent permeate in the cs-PES MF022 membrane) and a retentate solution with a content in ionic species lower than that of the permeate solution are generated by the diafiltration process. Therefore, considering the overall treatment of the tannery effluent through an RO-diafiltration integrated process, illustrated in Scheme 2, the processing costs associated with the disposal of the effluent in the diafiltration could be reduced by recycling the permeate solution to the inlet of the reverse osmosis process.



Scheme 2. Schematic representation of the integrated RO-diafiltration process for purification of a real tannery effluent from TAMEG-Rouiba-SPA and selective recovery of Cr(III).

The retentate solution may also be recirculated to the RO inlet for water recovery; however, the low content of ionic species in this processing stream allows for its direct discharge into the ecosystem via Reghaia Lake, respecting the limits for discharge of liquid industrial effluents imposed by the norm No. 06-141 of Rabie El Aouel 1427 (19 April 2006) [35].

3.3. *pH Induced Desorption of Cr from the cs-PES MF022 Membrane*

The membranes used in the diafiltration of the SW30 concentrate from a synthetic effluent were then immersed in water solutions with pH 2 and pH 5.8 in order to demonstrate, as a proof of concept, the possibility to recover Cr(III) by desorption.

The desorption profiles obtained for the different compounds studied are shown in Figure 11.

As shown, a poor desorption of most of the compounds was observed at pH 5.8 (Figure 11A). The desorption of Cr(III) was negligible, while a higher desorption was found for chloride ions (Cl^-). In contrast, as shown in Figure 11B, the desorption of Cr(III) significantly increased at pH 2 in reference to most of the other compounds, except for Cl^- and Na^+ ions (considering that the Na content is all present in the form of Na^+). The mass fraction of Cr(III) equal to 10.7% in the membrane before desorption increased to 20.6% in the solution (leaching solution). Note that the mass fractions in the membrane that were determined only considered the studied compounds (Ca, Cr, Na, K, Mg, S, and Cl^-).

The adsorption of Cr(III) to chitosan is explained by the ability of amine groups (NH_2) to coordinate Cr(III), and also by possible interactions to the hydroxyl groups (OH^-). Amine and hydroxyl groups are mainly neutral at pH 6 (pKa = 6.3 for $R\text{-}NH_3^+$) and protonated at pH 2 ($R\text{-}NH_3^+$ and $R\text{-}OH_2^+$). Therefore, the adsorption ability of chitosan is ruled by pH induced protonation/deprotonation of amine and hydroxyl groups, promoting the desorption of cationic species at lower pH values. It particularly favours those with higher electronic valence, cationic Cr(III) species, such as $Cr(OH)^{2+}$ and $Cr(OH)_2^+$, which are the prevalent Cr(III)-containing species in an aqueous solution at pH 3.6 [6].

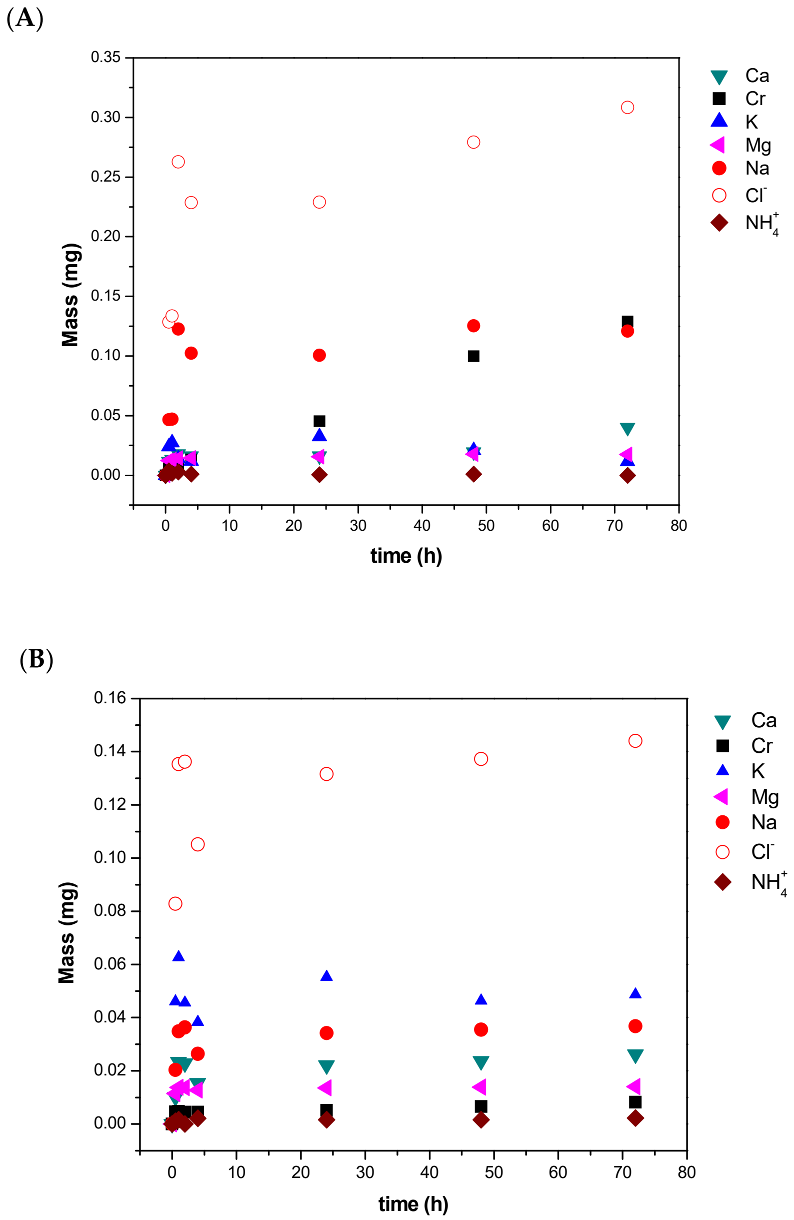


Figure 11. Mass of the compounds desorbed from the cs-PES MF 022 membrane at (**A**) pH 5.8 and (**B**) pH 2, after diafiltration of the SW30 concentrate obtained from filtration of a synthetic tannery effluent.

The high amount of Cl^- and Na^+ ions found in the leaching solution is due to their much higher amount compared to that of Cr(III) in the tannery effluents. Therefore, despite the much lower percentage retention of Na^+ and Cl^- in the membrane, this results in final amounts in the membrane of 6.17 mg and 7.91 mg for Na^+ and Cl^-, respectively, which were higher than the mass of Cr(III) retained in the membrane, equal to 2.91 mg.

As a preliminary proof of concept, the desorption of the target ions was evaluated. A moderate desorption extent (<25%) was obtained for three compounds, Cr(III), Na^+, and Cl^-, in these preliminary desorption assays. Optimization of the desorption process is thus required by the suitable adjustment of desorption parameters, such as temperature, stirring speed, and volume of the leaching solvent for enhanced desorption of these elements. Although desorption optimization is out of the scope of this work, a comparative analysis of the desorption profiles obtained at pH 2 and 5.8 on one hand evidences that Cr(III) desorption selectivity may be improved by conducting the process through successive desorption steps at variable pH values, i.e., a significant Cl^- and Na^+ removal might be attained in a first desorption step at pH 5.8, with good maintenance of the adsorbed Cr(III). This is then followed by a second desorption step at pH 2, for the selective removal of Cr(III) with minimal interference of Na^+ and Cl^-. On the other hand, the desorption profiles obtained for Cr(III), Na^+, and Cl^-, at pH 5.8, show that the Na^+ desorption was faster during the first 5 h of the process, tending to plateau after this period. In contrast, the Cr(III) desorption kinetics showed a more constant behaviour, crossing the Na^+ desorption curve after 72 h, suggesting that process optimization may render a final leaching solution with a more significant Cr(III) content relative to the amount of Na^+.

Nevertheless, if a complete separation of Cr(III) and Na^+ is required. This can be achieved either by an additional nanofiltration operation benefiting from the different size and valence of Cr(III)-containing compounds and Na+, or by using selective cation-exchange resins. The desorption of chloride ions is not actually regarded as a significant problem, as it may lead to the recovery of Cr(III) in the form of chromium chloride.

4. Conclusions

This work evaluates the performance of chitosan modified membranes (cs-PES MF022) for selective recovery of Cr(III) from synthetic and real tannery effluent concentrates obtained by reverse osmosis (RO) with an SW30 membrane, through a diafiltration process. The cs-PES MF022 membrane shows a high ability to retain Cr-containing compounds and a satisfactory permeability to the other compounds studied, which results in a selective removal of Cr-containing compounds of 81% and 97%, in synthetic and real tannery effluents, respectively. The removal of Cr(III)-containing species was mostly explained by Cr(III) retention in the membrane, as only an insignificant amount (<2% of the total amount of Cr in the feed solution) was found in the retentate solution after diafiltration of four diavolumes. The high retention of Cr(III) in the membrane was attributed to the chitosan capacity to adsorb heavy metals with unsaturated *f* orbitals, such as Cr(III), by coordination to the amine groups of chitosan.

It was noteworthy that the permeability of Cr(III)-containing species through the cs-PES MF022 membrane changed significantly during the filtration of real and synthetic tannery effluents. The mass transmission of Cr(III) contained in the real tannery effluent was significantly lower than that obtained by filtration of the synthetic tannery effluents, resulting in a higher and more selective membrane retention of Cr(III)-containing compounds in the former case. This demonstrates the role of the organic matter present in real effluents in the retention of metals.

Moreover, 2.5 diavolumes were found to be the optimal condition for achieving the maximum transmission of most of the compounds studied and the highest retention of Cr(III), without significant variation of permeate flux. This demonstrates the feasibility of a diafiltration strategy for attenuating concentration polarization and membrane fouling effects.

Proof of concept experiments were carried out to demonstrate the possibility to recover Cr(III) by its selective desorption based on the pH-responsive behaviour of chitosan. While a low desorption was obtained for most of the compounds, Cr(III) shows an increased desorption at more acidic pH values (pH = 2), confirming that Cr(III) adsorption to chitosan is mainly due to the coordination to the amine groups. A leaching solution enriched in Cr(III), but still with considerable amounts of Na^+ and Cl^-, was obtained. These results showed that the diafiltration of RO concentrates of tannery effluent with the cs-PES MF022 membrane followed by acidic desorption did not allow for a complete isolation of Cr(III)-containing species. Instead, it rendered a final solution of 92.5% enriched in Cr(III), relative to the tannery effluent RO concentrate (feed solution). Improved Cr(III) purification requires an optimization of the desorption process, or additional treatment of the effluent for separation of Cr(III) from Na^+, e.g., by nanofiltration or by selective Cr(III) adsorption by cation exchange resins. However, this decision depends on the required degree of Cr(III) purity, and should be taken upon a careful analysis of the economic viability of the integrated process.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/w13182598/s1, Figure S1: SEM-EDS analysis of the cs-PES MF022 membranes before (top spectrum) and after (bottom spectrum) filtration of the tannery effluent at 20 bar, in concentration mode. Figure S2: Comparative analysis between the selective retention of Cr(III), in reference to other species, by the cs-PES MF022 membrane, during diafiltration of the SW30 concentrate of a synthetic and real tannery effluent at 20 bar.

Author Contributions: Conceptualization, C.A.M.P., J.G.C., and S.V.; methodology, C.A.M.P., J.G.C., and S.V.; data curation, A.Z. and C.A.M.P.; writing—original draft preparation, A.Z. and C.A.M.P.; writing—review and editing, A.Z, F.S., C.A.M.P., J.G.C., and S.V.; supervision, C.A.M.P., J.G.C., and S.V.; funding acquisition, C.A.M.P., J.G.C., and S.V. All authors have read and agreed to the published version of the manuscript.

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