Effect of landfill leachate ageing on ultrafiltration performance and membrane fouling behaviour

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Abstract:

In this study, the effect of ageing on the performance and fouling mechanisms in the ultrafiltration of landfill leachates using titania-zirconia (ZrO_2-TiO_2) tubular membrane was thoroughly studied. Results revealed that the maturation of the leachate has a positive effect on its ultrafiltration, with a twofold higher final permeability compared with the young one. This is the result of the higher organic load, particularly that corresponding to proteins and carbohydrates, of the young leachate.

Resistance-in-series analysis demonstrated that the loss of permeability was mainly due to reversible fouling, caused by cake filtration. Either irrecoverable or irreversible fouling were scarce and not conditioned by the stage of maturation of the leachate. Chemical oxygen demand (COD) rejection for the mature leachate varied with volume concentration ratio (VCR) showing an approximately sigmoidal shape, from an initial value of 18.5% to a final one of 49.6%, with the faster increase at VCR ranging from 1.2 to 1.7, due to the permeation of fatty acids by the ultrafiltration (UF) membrane. On the other hand, COD rejection remained approximately constant at 48% during the ultrafiltration of the young leachate, which can be attributed to the presence of higher molecular weight compounds in its composition.

Keywords

Landfill leachate; Wastewater management; Ageing; Ultrafiltration; Fouling modelling

1. Introduction

The increasing solid waste landfilling has led to one of the major environmental challenges of today: the efficient management of the leachates generated. These aqueous wastes, which can be defined as the liquid that passes through a landfill and has extracted dissolved and suspended matter from it, are considered a significant threat to surface water, groundwater and soil [1]. Many factors have been reported that influence leachate composition, such as the age of the landfill, the local climate or season, the depth of the waste in the landfill and, mainly, the composition of the waste material [2–4]. This fact makes leachate matrices significantly complex and variable [5], which in turns means that the improvement and/ or development of a generalized treatment method for any leachate to meet the relevant quality standards is not possible [6]. In fact, leachate treatments are based on process schemes which generally comprise some combination of biological, physical and/or chemical treatment [7–10]. Biological treatments are used for removing the biodegradable organic matter content in the leachate; while chemical and physical treatments such as flotation, coagulation-flocculation, precipitation, adsorption or air stripping are employed as pre-treatments in order to improve the efficiency of a subsequent treatment, or when a biological oxidation process is hampered by the presence of bio-refractory materials, like non-biodegradable (humic and fulvic acids) and/or undesirable compounds (heavy metals, AOXs, PCBs…). Besides, these treatments can also be employed as post-treatments after a biological one with the aim of ensuring final polishing level by removing toxic metals and organic compounds [6,10]. Advanced oxidation processes (AOPs), such as ozonation (alone or in combination with UV) and UV/TiO_2 photocatalysis, which are a particular case of chemical treatment, can also be used as post-treatments after biodegradation processes for removing recalcitrant compounds [6]. In addition to the conventional treatments, physical treatments based on membrane technology have emerged as viable alternatives to reach the level of purification needed to fully reduce the negative impact of landfill leachates on the environment. Either as a main step in a landfill leachate treatment chain or as a single treatment step, the use of membrane technologies has shown to be an indispensable means of achieving a high degree of purification of this stream [10]. Among the various membrane technologies, ultrafiltration (UF) is used in separation and purification because of its high efficiency and lower energy consumption, thus reducing treatment costs [11].

UF is effective in eliminating macromolecules and particles; around 50% of organic matter can be separated from the leachate [12,13]. Although a study reported UF as a sufficient treatment to ensure the discharge standards for a leachate [13], this technique is not individually used, but in combination with others. Thus, UF can serve as a pre-treatment prior to reverse osmosis [14–17], nanofiltration [15], evaporation [18] or Fenton oxidation [19]; and as a post-treatment for biologically active carbon [20], adsorption [12,15,21], coagulation [15], lime addition [22], nanofiltration (for the concentrate generated) [23], air stripping and coagulation [24] or Fenton reaction and neutralization [25]. Particularly, this technique can also be effective as a pre-treatment for biological degradation of landfill leachate, since it helps reducing the content in humic acids, which can compromise the efficiency of the biological treatment.

At this point, it should be noted that, to the best of our knowledge, the effect of the landfill leachate age on the membrane performance has not been studied yet. This is surprising because, although there are many factors affecting the composition of such leachates, this varies greatly depending on the age of the landfill and, thus, the degree of solid waste stabilization [26]. In fact, two types of leachates have been defined according to landfill age: young and mature. Young leachates are those which come from landfills less than 1 year old, with chemical oxygen demand (COD) values above 15 g/L and the ratio between the biodegradable matter (as biological oxygen demand (BOD_5)) and the total organic one (as COD) higher than 0.5. On the other hand, mature leachates are those from facilities which are more than 5 years old (maturation phase) with COD values below 3 g/L and mainly composed of a refractory mixture of humic substances. Their BOD_5 to COD ratio is lower than 0.1 [7,10].

It should be noted that the results of ultrafiltration reported in the bibliography for leachates, either for the individual operation or coupled with other processes, are highly subjected to the age of the specific leachate selected for each experimentation, thus making the comparison between the findings of the different studies difficult.

In view of these considerations, the aim of this work was to study, for the first time ever, the effect of the landfill leachate age on the quality of the effluent treated by UF as a pre-treatment prior to a biological process, as well as modelling the fouling mechanism of the membrane.

2. Experimental

2.1. Landfill leachates

All the leachates used in this study were obtained from the sanitary landfill site La Zoreda and provided by COGERSA (Asturias, Spain). Two different leachates were employed during the experimentation: mature (M) and young (Y). The young leachate was obtained from a new area of the landfill which is in expansion. Regarding the mature leachate, it comes from an area of the landfill where wastes has not been deposited since 2010.

A description of the main physicochemical characteristics of the different leachates can be found in Table 1. Higher colour value in young leachate has already been reported [27], and can be explained by higher total organic carbon (TOC) and suspended solid concentrations. Leachates were pre-filtered with a metal mesh filter of 250 µm of pore size and 200 mm of diameter (Cisa, Spain) to remove coarse particles. Samples were stored at 5ºC before being used.

Parameter	**Type of landfill leachate**	
	Old leachate	**Young leachate**
pH	8.2 ± 0.4 [7.8]	8.8 ± 0.2 [8.7]
COD (mg O_2/L)	4005 ± 592 [3960]	7559 ± 2414 [5548]
TOC (mg/L)	n/a [641]	n/a [1784]
Humic acid (mg/L)	n/a [137]	n/a [90]
BOD_5 (mg O_2/L)	559 ± 280 [372]	2435 ± 974 [3077]
Colour Number	n/a [1.322]	n/a [1.573]
Suspended solids (mg/L)	29 ± 24 [30]	92 ± 65 [100]
NH_4^+ (mg/L)	2200 ± 368 [2323]	2959 ± 427 [3247]
Cl^- (mg/L)	n/a**(1)**	3329 ± 1182 [3136]
NO_3^- (mg/L)	5 ± 1 [4]	3 ± 2 [2]
NO_2^- (mg/L)	1.0 ± 0.5 [1]	2 ± 1 [2]
Alkalinity (mg $CaCO_3$/L)	212 ± 28 [221]	258 ± 36 [281]
Conductivity (µS/cm)	21089 ± 4557 [23800]	25737 ± 3323 [19990]

(1) n/a= not available

Table 1. Main characteristics of the mature and young leachates (average values from 2008 to 2018) and values determined in this study (in brackets).

2.2. Experimental setup

A scheme of the experimental set up is shown in Figure 1. All the ultrafiltration experiments were conducted using a locally house made and assembled system (Figure 1). This system consisted of a glass vessel of 3 L, where the corresponding leachate was stored and pumped towards the ultrafiltration module using a Masterflex I/P 7591-55 (Cole-Parmer, USA) peristaltic pump attached to an Easyload Masterflex I/P 77601-10 (Cole-Parmer, USA) pump head. Ultrafiltration cell was composed by a tubular ZrO_2-TiO_2 membrane (600 × 6mm) (TAMI Industries) with an area of 1.14 10^{-2} m^2 and a molecular weight cut-off (MWCO) of 150 kDa. Ceramic membranes are more resistant to mechanical, chemical, thermal or biological stresses than polymeric membranes, and they have been already implemented for wastewater treatment [28]. Also, the use of ZrO_2-TiO_2 in form of particles [29] or membrane additives [30] has been reported to be efficient in reducing the fouling caused by humic acid. As for pore size, membrane MWCO was selected in order to minimize humic acid-caused fouling. In this sense, Yan et al. [31] have reported that, when ultrafiltrating humic acids, maximum fluxes can be obtained using membranes within a MWCO range between 100 and 300 kDa. Pressure gauges and valves were placed in the flow line before and after the ultrafiltration module in order to measure and set the value of the transmembrane pressure (TMP). All experiments were carried out at a flow rate of 5.4 L/min and cross flow velocity of 3.2 m/s over the membrane. In order to select the temperature of work, a previous study of ultrafiltration performance at temperatures from 50ºC to 70ºC was performed. Lower fouling rates and higher fluxes were obtained when higher temperatures were used, thus all experiments were carried out at a steady temperature of 70ºC. The permeate flux was determined by weighing of permeate under a TMP of 1.6 bar. Temperature was kept at the desired value using a water bath.

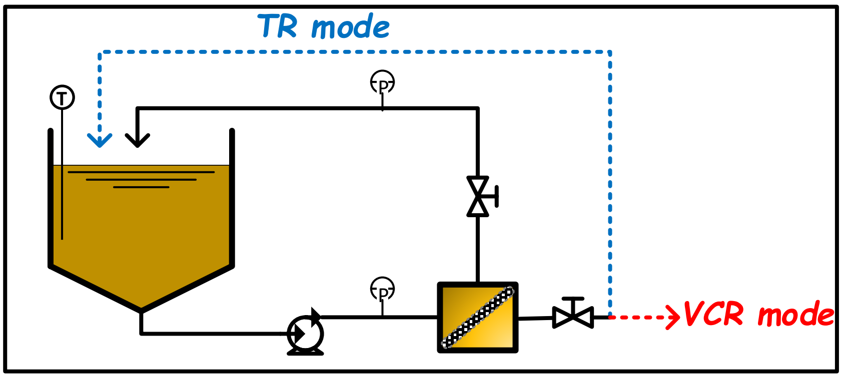


Figure 1. Experimental setup scheme.

Two different kinds of experiments were carried out using this experimental setup (see Figure 1): i) Total recycle (TR) mode and ii) volume concentration ratio (VCR) mode. The first one is necessary in order to determine the evolution of membrane fouling with time, while the second one is needed to evaluate the effect of concentration on the permeate flux and fouling resistances.

Regarding TR mode experiment, retentate and permeate were both completely recirculated to the supply tank and permeate flux was periodically measured until achieving a constant value. Afterwards, membrane was washed with distilled water until the permeate flux did not change with time, and then cleaned at 70ºC with 0.5% aqueous solution of basic detergent (Divos 124 VM5 provided by Diversey) until the final flux was higher than 90% of the initial permeate flux [32].

In the case of the VCR mode experiment, retentate was also continuously recirculated to the supply tank, but permeate was discarded. Samples of permeate were periodically withdrawn to measure COD, TOC, colour number (CN) and humic acid retentions, as well as permeate fluxes. Leachate filtration was maintained up to a final VCR of 3. Afterwards, the UF membrane was washed and cleaned in the same way than that used in the TR mode test.

Both TR and VCR mode experiments were performed at least in duplicate, and in all cases the experimental error was below 5%.

2.3. Fouling modelling

In order to define the fouling during the ultrafiltration of both leachates in terms of permeability recovery, the next equation was employed (eq. 1):

$$J = \frac{TMP}{\mu R_T} = \frac{TMP}{\mu(R_M + R_{rev.} + R_{irrev.} + R_{irrecov})} \qquad (1)$$

Where J is the permeate flux (m·s^{-1}), TMP is the transmembrane pressure (kg·m^{-1}·s^{-2}) μ is the dynamic viscosity (kg·m·s^{-1}), R_T is the total fouling resistance, R_M is the intrinsic membrane resistance and $R_{rev.}$, $R_{irrev.}$ and $R_{irrecov.}$ are the reversible, irreversible and irrecoverable fouling resistances, respectively (all resistances in m^{-1}). In a practical way, reversible fouling is removed by physical cleaning, irreversible fouling is eliminated by chemical cleaning and irrecoverable fouling refers to those foulants that cannot be removed by any cleaning step [33]. By measuring the initial tap water flux through the membrane (J_0), and the permeate fluxes achieved at the end of the ultrafiltration (J_S) and after the physical (rinsing with distilled water) (J_{pc}) and chemical (J_{cc}) cleanings, the values of each resistance can be calculated according to the methodology included in the Appendix [34].

In addition to this resistance-in-series model based on permeability recovery, fouling evolution was also modelled by the Hermia's model [35] with the aim of obtaining an in-depth knowledge of the fouling mechanisms involved (eq. 2).

$$\frac{dJ}{dt} = -K \cdot (J - J_0) \cdot J^{2-n} \tag{2}$$

Where K is a constant, J_0 is the limiting flux ($m \cdot s^{-1}$), and n is a constant with different values for the four simple mechanisms of fouling proposed by Hermia: complete blocking ($n=2$, K in min^{-1}), standard blocking ($n=1.5$, K in m^{-1}) intermediate pore blocking ($n=1$, K in m^{-1}) and cake filtration ($n=0$, K in $min \cdot m^{-2}$) [36]. The choice of the best model was based on the sum of squared residuals (SSR), where each residual was equal to the difference between the experimental data and the value predicted by the model.

2.4. Analytical methods

Humic acids were extracted from leachate according the method proposed by Thurman and Malcolm [37]. Stated briefly, 10 mL of the corresponding sample were acidified with HCl 1 mol/L to pH 1.0, in order to precipitate the humic acids. Then, the sample was filtrated, and the solid fraction was redissolved in a 7 g/L NaOH solution until the initial volume is reached. Absorbance values at 465 nm and 665 nm were measured using a Helios Alpha UV-Vis spectrophotometer (Thermo Fisher Scientific, USA). A calibration curve was constructed by dissolving different amounts of commercial humic acid (Sigma Aldrich) in a 7 g/L NaOH solution. COD was obtained by the dichromate method using a HACH DR/2500 spectrophotometer (Hach Company, USA) [38]. TOC was determined using a TOC analyzer (Shimadzu TOC-V_{CSH}). The CN, which is defined in equation 3 [39], was used to monitor changes in the colour of the leachate during the ultrafiltration process. Spectral absorbance coefficients (SAC) are defined as the ratio of the values of the respective absorbance over the cell thickness. Both CN and SAC have units of cm^{-1}. This parameter was measured at 436, 525 and 620 nm using a UV/Vis spectrophotometer (Thermo Scientific, Heλios γ).

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \tag{3}$$

Rejection coefficients were defined as follow (eq. 4):

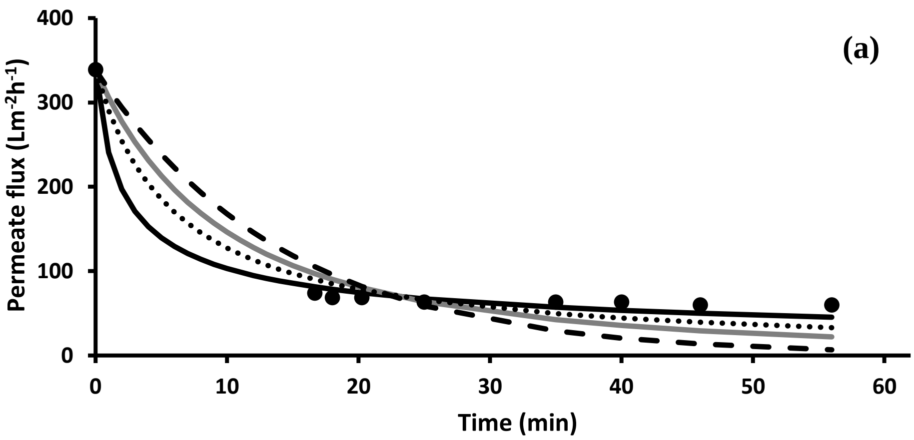
$$R_i = 1 - \frac{C_{P,i}}{C_{R,i}} \tag{4}$$

Where $C_{P,i}$ and $C_{R,i}$ the concentration of the analyte *i* in permeate and retentate, respectively.

3. Results and discussion

3.1. Total Recycle mode

Figure 2 shows the evolution of the permeate flux with time during the ultrafiltration of the mature leachate (2a) or the young one (2b) in a TR mode. The initial water permeability of the membrane was 211.5 L/m^2 h bar. Once the filtration of the leachate started, this permeability decreased rapidly for both assayed leachates, finally reaching constant values of around 37.5 and 17.6 L/m^2 h bar for the mature and the young leachate, respectively, after less than 15 min of filtration. These results correspond to reductions in permeability at the end of the experiment of 82.3 and 91.7%. According to several authors, these drastic flux declines, observed during the first minutes of filtration, may be due to the fast accumulation on the membrane surface of a first layer of fouling, which is thin but very resistant to mass transfer due to its low porosity. After that, the structure of the newly formed layers is less compact, indicating the existence of a porosity gradient through the cake thickness [34,40].



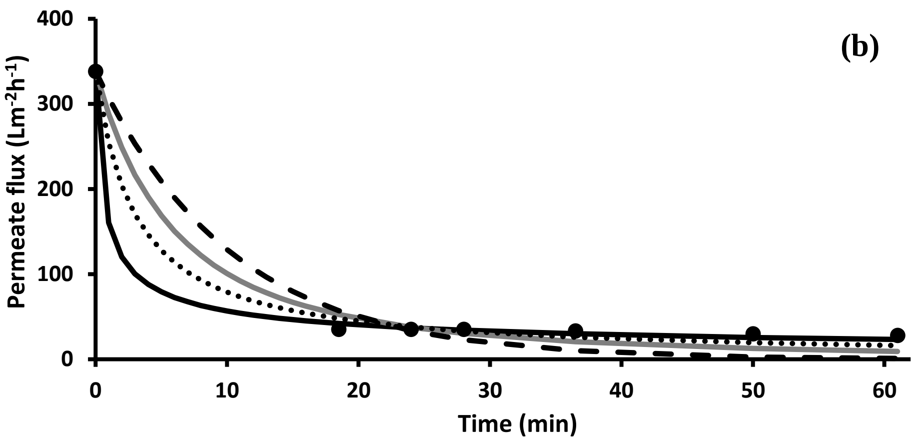


Figure 2. Evolution of the permeate flux (●) during the ultrafiltration of the mature (a) or young (b) leachate under TR mode. Cake model (solid black line), standard model (solid grey line), complete model (dashed black line) and intermediate model (dotted line) predictions for each of them. In all cases: 1.6 bar, 70 ºC, flow rate of 5.4 L/min and cross flow velocity of 3.2 m/s.

Therefore, the maturation of the leachate has a positive effect on its ultrafiltration, with a twofold higher final permeability than that obtained with a young leachate. As it was previously explained, the ageing of the leachate involves a reduction in either its COD or BOD_5/COD ratio. This fact, together with the higher concentration of proteins and carbohydrates in the young leachate explain why the old leachate are more easily ultra-filtered than the young one [41,42].

Figure 3 shows the fouling resistances obtained for either the mature or young leachate under TR mode ultrafiltration.

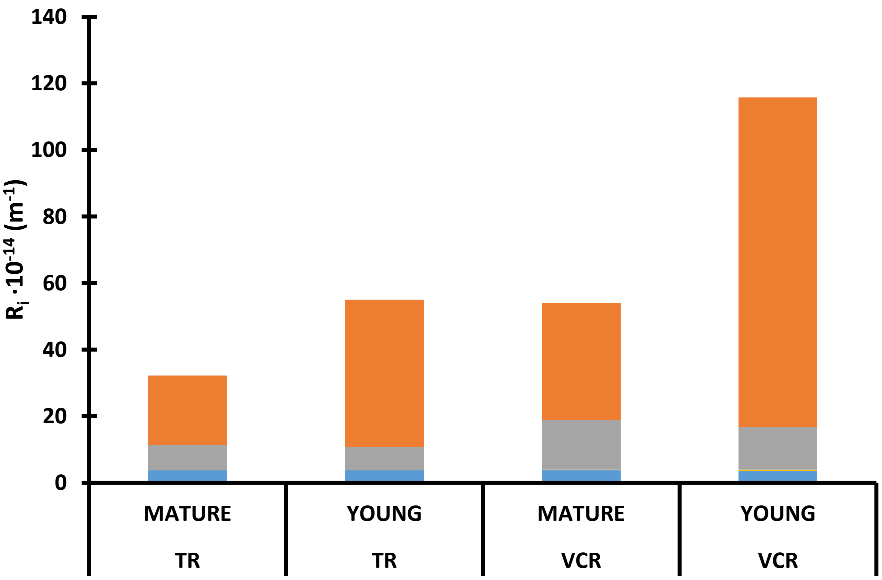


Figure 3. Fouling resistances obtained during the ultrafiltration of the mature (a) or young (b) leachate under TR or VCR mode: R_M (■), $R_{rev.}$ (■), $R_{irrev.}$(■) and $R_{irrecov}$ (■). In all cases: 1.6 bar, 70 ºC, flow rate of 5.4 L/min and cross flow velocity of 3.2 m/s.

As expected from the permeability data previously commented, total resistance (R_T) for the young leachate ($4.4 \cdot 10^{15}\ m^{-1}$) is higher than that obtained for the mature one ($2.1 \cdot 10^{15}\ m^{-1}$). Nevertheless, these results also revealed that the flux decline due to irreversible fouling is significantly lower than that caused by the reversible one. Thus, calculating the ${R_{rev.}}/{R_{irrev}}$ ratio for both leachates, the values obtained are 2.8 and 6.3 for the mature and young one, respectively. In this regard, it is also interesting to point out that the resistances due to irreversible fouling for both experiments are somewhat similar, indicating that the internal fouling is scarce and not conditioned by the stage of maturation of the leachate. Considering that reversible fouling is widely associated with the cake layer resistance (also known as external fouling), whereas the irreversible one has to do with pore fouling resistance (or internal fouling), results show that the main reason for the permeability decrease during the ultrafiltration of leachates is the external fouling, this being higher for younger leachates. This fact also implies that the initial membrane permeability can be easily recoverable in a high proportion after leachate ultrafiltration by means of membrane relaxation, backflushing or other physical cleaning techniques (standard rising) [43]. In addition, leachate age had a negligible effect on both the irreversible or irrecoverable fouling. Finally, low values of $R_{irrecov.}$ indicated that more than 99.5% of the initial permeability is recovered after cleaning, thus suggesting a long lifespan of the membrane in plant operation, either for mature or young leachates, although a higher number of physical cleaning cycles would be required during the ultrafiltration of the latter. If the filtration sequence (filtration followed by physical cleaning) does not result in complete recovery of membrane fouling status, a chemical cleaning phase is needed, which should be optimized in order to maximize as much as possible the cost-efficiency of the operation.

Figure 2 shows the results of permeate flux and their fittings to the four simple mechanisms of fouling proposed by Hermia. Additionally, Table 2 provides the values of the main fitting parameters for each model as well as goodness of fit of the data to the curve.

Blocking			**Complete (C)**	**Standard (S)**	**Intermediate (I)**	**Cake (G)**
Figure						
Description			Particles seal off pore entrances	Particles accumulate inside membrane on the walls of straight cylindrical pores	A portion of the particles seal off pores and the rest accumulate on the top of other deposited particles	Particles accumulate on the membrane surface
Mode	**Leachate***	**n**	**2**	**1.5**	**1**	**0**
TR	**ML**	**K_i**	$(7.0\pm0.6)10^{-2}$	$(2.8\pm0.3)10^{-3}$	$(4.9\pm0.8)10^{-4}$	$(8\pm2)10^{-6}$
		r^2	0.93	0.97	0.98	0.995
		SRR	660	4726	9947	2333
	YL	**K_i**	$(9.6\pm0.9)10^{-2}$	$(4.5\pm0.6)10^{-3}$	$(9.7\pm0.1)10^{-4}$	$(3\pm1)10^{-5}$
		r^2	0.97	0.990	0.995	0.9991
		SRR	2188	850	329	59
VCR	**ML**	**K_i**	$(5.2\pm0.8)10^{-2}$	$(2.1\pm0.4)10^{-3}$	$(3.8\pm0.9)10^{-4}$	$(9\pm3)10^{-6}$
		r^2	0.92	0.95	0.97	0.990
		SRR	9461	6231	3484	1230
	YL	**K_i**	$(1.2\pm0.2)10^{-1}$	$(4.7\pm0.8)10^{-3}$	$(8\pm2)10^{-4}$	$(2.2\pm0.7)10^{-5}$
		r^2	0.94	0.95	0.97	0.995
		SRR	7004	5113	2587	372
		Units for K_i:	*1/min*	*1/m*	*1/m*	*min/m²*

*ML: mature leachate; YL: young leachate

Table 2. Main fouling mechanisms: brief description, fitted parameters and SRR obtained using the experimental data for ultrafiltration of mature and young leachates under TR or VCR modes.

Based on the results obtained, the prevailing fouling model during the ultrafiltration of leachate under TR mode corresponds to cake formation, indicating that the accumulation of leachate particles occurred on the surface of the membrane in a permeable cake of increasing thickness until a limit value is reached. According to this mechanism, the evolution of the permeate fluxes showed in Figure 2 could be explained as follows: the first phase of flux decline observed during the first few seconds or minutes of operation is primarily due to concentration polarization. The second phase of flux decline is slower and is attributed to the formation of a complete surface layer over the initial mono-layer. The third phase represents a quasi-steady-state period, wherein the flux decline occurs slowly, and may be due to the consolidation of the fouling layer due to a balance between the deposition of foulants on the cake and their removal due to the shear stress caused by the cross flow [20]. The final achievement of a final cake with an almost constant thickness is consistent with the prevalence of an external fouling observed from the analysis of the resistance-in-series mode. Ma et al. [44] also found that cake filtration was the main fouling mechanism involved during the ultrafiltration of humic acid with and without addition of inorganic salts. Syzdek and Ahlert [14] reported some results during the ultrafiltration of a high-strength industrial landfill leachate which suggested the predominance of cake formation as main fouling mechanism as well. For example, the fouling layer did not block the passage of organic carbon across the membrane, but only created a pressure drop that resulted in a lower flux. The occurrence of this fouling mechanism poses operational implications. When working with a non-foulant stream, a linear relationship between applied TMP and flux is assumed. Nonetheless, if fouling particles present in the stream are larger than the membrane pore size, a fouling cake will eventually deposit on the membrane surface. This phenomenon occurs more drastically when higher pressures are applied, compressing the fouling cake and minimizing membrane flux [45]. It has been reported that, in these cases, Reynolds number happens to be more relevant for flux improving that applied pressure [46], making it possible to minimize the fouling layer by increasing the shear at the membrane surface.

Several authors reported that fouling of the majority of membrane processes applied to leachate treatment was mainly due to the presence of humic substances in the leachate organic fraction [22,47]. If the formation of an external fouling layer, as suggested by previous fouling models, is assumed, then it is also reasonable to suppose that humic acids are mainly retained on the membrane surface. It should be highlighted that interactions between humic acids (as well as other natural organic matter) and the membrane are of hydrophobic nature [48], and thus a high ionic strength of the stream fosters membrane fouling caused by humic acid [31].

As the concentrations of humic acids are quite similar in both leachates because the biodegradability of these compounds is almost null, the lower permeability of the young leachate should be associated with the species which are biologically degraded during its maturation. Considering that the fouling associated with humic substances is approximately the same, the leachates which are degraded during the landfill maturation are responsible for the 75% (calculation based on K_i) of the fouling observed during the ultrafiltration of the leachate in TR mode.

3.2. Volume Concentration Ratio mode

In order to gather information about the influence of solute concentration on the permeability and membrane rejection during the ultrafiltration of either the young or mature leachates, a set of experiments without permeate recirculation to the feed tank were also carried out. It is worth noting here that, whereas the TR mode simulates a continuous filtration, the aim of these experiments, named as VCR mode, is to study the batch filtration and decide the most convenient solute concentration in a continuous filtration.

Figure 4 shows the evolution with time of the permeate flux during the VCR mode ultrafiltration of a mature (a) or a young leachate (b). As in the case of TR, the decline in the permeate flux for the young leachate was stronger than that obtained for the mature one. Again, the reduction in the permeability mainly occurred during the first minutes of filtration. Nevertheless, the permeability losses were more noticeable for the VCR mode filtration than for the TR mode operations, as expected due to the gradual increase in the concentration of the feed. So, the final permeate fluxes for VCR mode experiments with mature or young leachates were a 41 and 55% lower than those obtained during the ultrafiltration inTR mode.

These results indicate that the fouling resistance, $(R_T - R_M)$, during the batch ultrafiltration (VCR mode) is approximately twofold higher than that of the continuous one (TR mode) under the same time of filtration (60 min). More specifically, the fouling resistances obtained during TR and VCR mode experiments were 2.8 10^{15} and 5.0 10^{15} m^{-1} for the mature leachate and 5.1 10^{15} and 11.2 10^{15} m^{-1} for the young one, respectively. Using the resistance-in-series model (see Figure 3), it can be deduced that the main contribution to this resistance is due to reversible fouling, which represented 70% and 88% of the total fouling for the mature and young leachates, respectively. These percentages were pretty similar to those obtained under TR mode. Nevertheless, the irreversible fouling during the batch ultrafiltration increased substantially in comparison to the continuous one, although no significant differences were found between young and mature leachates (Figure 3). Regarding the irrecoverable fouling, its contribution to the total fouling was negligible for both leachates.

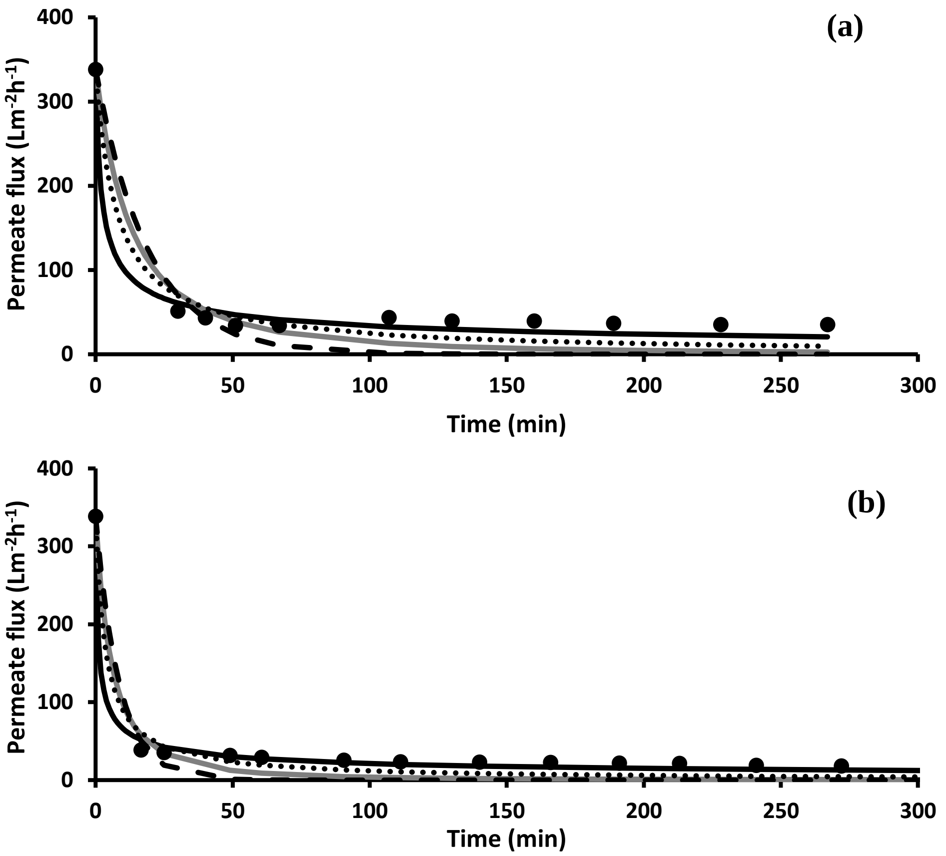
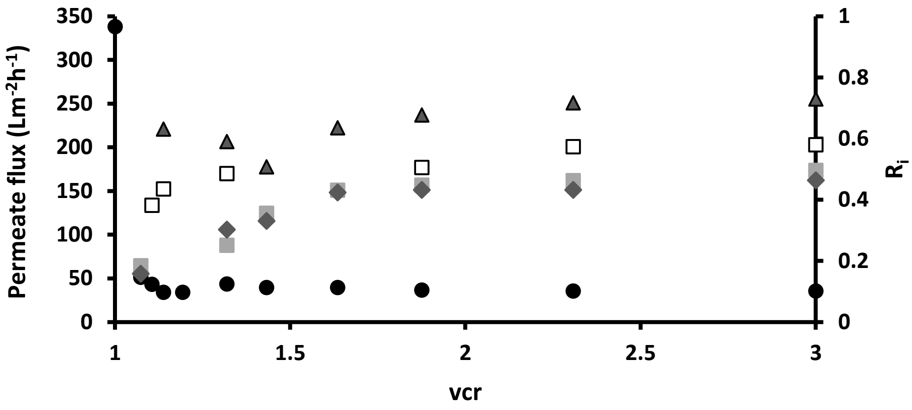


Figure 4. Evolution of the permeate flux (●) during the ultrafiltration of the mature (a) or young (b) leachate under VCR mode. Cake model (solid black line), standard model (solid grey line), complete model (dashed black line) and intermediate model (dotted line) predictions for each of them. In all cases: 1.6 bar, 70 ºC, flow rate of 5.4 L/min and cross flow velocity of 3.2 m/s.

Using again the individual fouling models proposed by Hermia [35] (Figure 4 and Table 2), the loss of permeability during the batch ultrafiltration of either the mature or young leachate was mainly attributed to the cake formation mechanism, as with the continuous one. The predominance of this fouling model is consistent with the high proportion of reversible fouling [49].

Figure 5 shows the evolution of the rejection coefficients for COD (R_{COD}), TOC (R_{TOC}), colour (R_{CN}) and humic acids (R_{HA}) as well as the permeate flux with the VCR mode during the ultrafiltration of either a mature or young leachate.

(a)



(b)

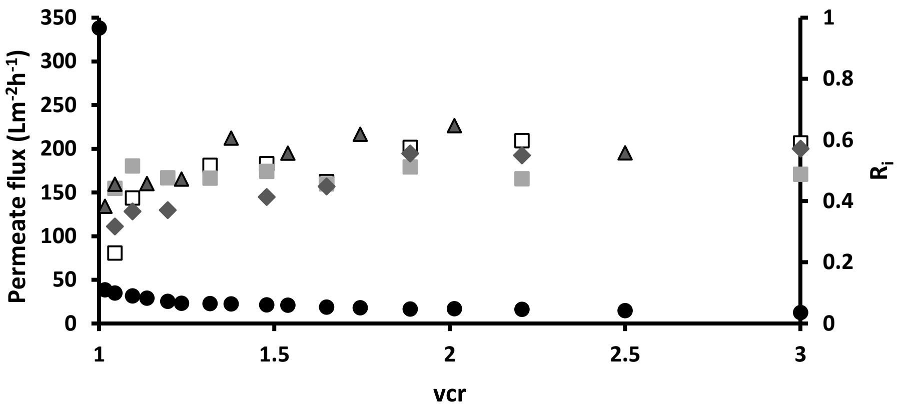


Figure 5. Evolution of the rejection coefficients for COD (■), TOC (◆), colour (▲) and humic acids (□) and permeate flux (●) with the VCR mode during the ultrafiltration of either a mature (a) or a young leachate (b). In all cases: 1.6 bar, 70 ºC, flow rate of 5.4 L/min and cross flow velocity of 3.2 m/s.

Dealing first with permeate fluxes, the evolutions of these with VCR are the expected ones for both leachates, differentiating three periods. Thus, a rapid flux drop was observed initially, which was mainly attributed to concentration polarization, followed by a less marked decrease in the flux due to irreversible fouling and a final period corresponding to a small flux decrease. As can be seen in Figure 5, the short duration of the second period suggests that internal fouling is not significant, as it was deduced from the analysis of resistances. Regarding the latter period, it is usually associated with the foulant deposition on the membrane surface, that is to say, the reversible fouling [50]. During this stage, approximately constant fouling rates of $4.3\ 10^{-3}$ or $7.9\ 10^{-3}$ $m^{-1}h^{-1}$ were observed for the mature or the young leachate, respectively.

Regarding the rejection coefficients, their evolutions differed between leachates. For instance, the COD rejection for the mature leachate showed an approximately sigmoidal shape, from an initial value of 18.5% to a final one of 49.6%, with the faster increase at VCR ranging from 1.2 to 1.7. Nevertheless, this parameter seemed to remain approximately constant during the ultrafiltration of the young leachate, although a slight increase was perceived at the beginning of the filtration. Concerning R_{TOC}, it showed similar values to R_{COD} throughout the filtration experiment. Nevertheless, in the case of the young one, the R_{COD} values were slightly higher than that of the R_{TOC} at the beginning of the ultrafiltration. In regard to CN, the rejections were significantly higher for the mature leachate, although a decrease in the R_{CN} for mature leachate during the early stages of the operation could be seen. These differences in the evolution of the COD, TOC and CN rejections for both leachates can be explained on the basis of their composition. A more in-depth and detailed discussion of this statement will be carried out in the next section.

3.3. Fouling mechanism

The previous observations on permeate fluxes and rejection coefficients seem to suggest that there is clear connection between ultrafiltration performance and the changes in the leachate composition due to landfill ageing.

In this regard and before developing this relationship, it is interesting to mention that landfills undergo at least four stages of decomposition during their ageing: an initial aerobic phase, an anaerobic acid phase, an initial methanogenic phase and, finally, a stable methanogenic phase, thus existing a strong relationship between the state of refuse decomposition and its corresponding leachate characteristics [51]. On the basis of size exclusion chromatography results, Aftab and Hur [52] proposed that leachates are composed by five different fractions: biopolymers (>10 kDa), humic substances (approx. 1 kDa), building blocks (300–500 Da), and low molecular neutrals and acids (<350 Da). As the landfill is becoming older, biopolymers are broken up into building blocks and these are decomposed and transformed into simple molecules, such as fatty acids, carbon dioxide and methane, whereas humic substances are hardly modified due to their recalcitrant character [17,53] (see Figure 6). Therefore, a high relative abundance of low molecular weight compounds in the mature leachate but not in the young one is accepted. In this sense, Mohammadzadeh and Clark (2008) reported that leachates generated in an area of old wastes were mainly composed of humic substances and simple fatty acids (mostly acetic and propionic) [53]. Taking into account that COD and TOC measurements include all the organic compounds, the small fatty acids easily passed through the membrane during the first minutes of ultrafiltration of the mature leachate, thus increasing the permeate COD and TOC and reducing the initial R_{COD} and R_{TOC}, as it is observed in Figure 5. Meanwhile, the proportion of compounds with higher molecular weight in the retentate increased. Once most of the fatty acids had already been removed, the COD and TOC values in the permeate mainly depended on the presence of humic substances on it. Obviously, this causes a progressive increase in the COD and TOC rejection, thereby the rejection coefficients of the compounds tend to approximate to that of the higher molecular size, that is to say, to the humic acids one (R_{HA}), thus explaining the sigmoidal evolution of R_{COD} and R_{TOC} observed in Figure 5. At this point, it should be pointed out that the increase in the humic acids rejection during the first minutes of filtration was probably due to the rapid development of a fouling layer on the membrane surface, as explained above. This external fouling layer is mainly made up of humic acids and acts as a dynamic membrane, reducing the permeability and increasing R_{HA} [44,54]. The additional barrier would not have influence on the pass of small molecules, such as the fatty acids, so its reject coefficient would not be affected. Once the cake was formed, its compaction and/or the consolidation of irreversible fouling are likely the main reasons why the R_{HA} slightly increased after the external fouling layer was formed (Figure 5) [50,55]. With regard to the high values of R_{CN}, it should be taken into account that mature leachate is mainly composed of humic acids, which are highly coloured, and simple fatty acids, which are colourless. Therefore, permeate results in an almost colourless stream, thus achieving a high colour retention due to humic acid retention.

On the other hand, the composition of a young leachate is more complex. When compared with mature leachates, the lower relative content in small molecules of the young ones can also explain the results depicted in Figure 5. Thus, the small variation in R_{COD} with VCR observed for the young leachate, instead of the sigmoidal tendency of the mature one, can be attributed to the higher abundance of high molecular weight compounds and their cohesive interactions facilitated by the higher ionic strength of the young leachate [56]. Taking into account that the molecular weight cut-off of the membrane is 150 kDa and the predominance of biopolymers (>10 kDa) and humic acids (approx. 1 kDa) in the young leachate, COD and humic acids rejections should be pretty similar to each other, as was experimentally proved (Figure 5) [4,52].

As for R_{CN}, lower values were observed in comparison to that of the mature leachate. This can be explained considering the chemical nature of the young leachate. This stream is highly complex, as opposed to the mature leachate which, as it was previously mentioned, is mainly made up of humic acids and simple fatty acids. Thus, both retentate and permeate will be richer in coloured species, therefore, reducing colour differences between these streams.

Finally, the experimental evidence that total resistance for the young leachate is higher than that of the mature one can be also linked to the leachate composition. Young leachate has a high proportion of biopolymers (>10 kDa), while organic matter in mature leachate consists basically of humic substances. Renou et al. (2009) reported that the major cause of ceramic membrane fouling during the ultrafiltration of landfill leachate was the formation of precipitated humic acid on the surface of the membrane, fostered by the presence of calcium ions [22]. Nevertheless, during the filtration of young leachate, interactions between the deposited humic acid and biopolymers present in the stream are expected, generating a thicker, less permeable fouling cake (Figure 2). In this sense, Jermann et al. (2007) observed that humic acids could act as a bridge between alginate and membrane, resulting in a more stable and less reversible fouling layer [41]. In a similar way, Xiao et al. (2013) also reported the interaction proneness between humic acids, polysaccharides and proteins [42].

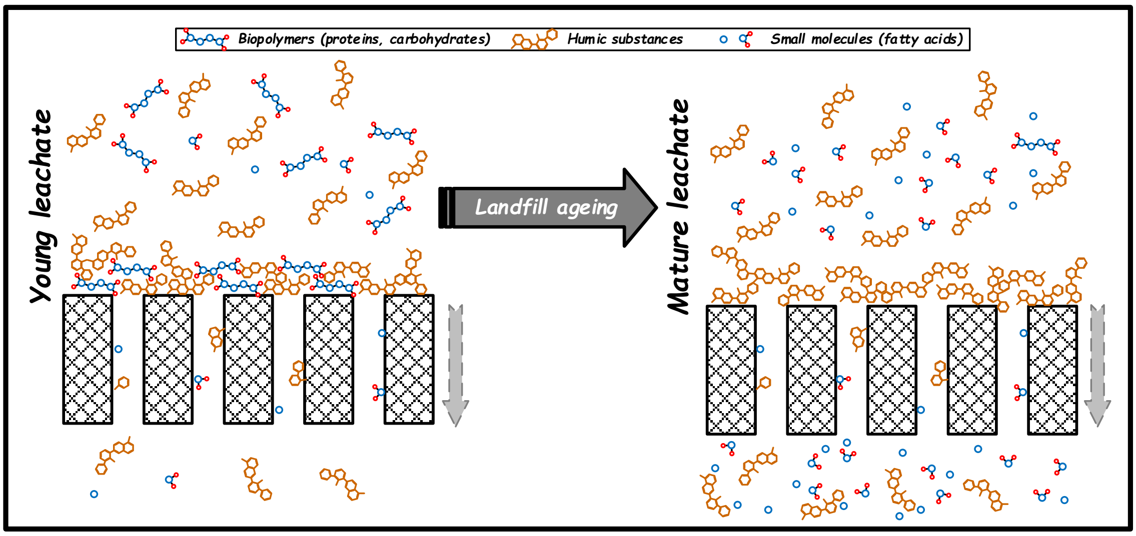


Figure 6. Proposed effect of the landfill age on the ultrafiltration of the leachate generated.

Conclusions

Results suggest that there is a clear connection between ultrafiltration performance and the changes in the leachate composition due to landfill ageing. Both young and mature leachates cause a very steep permeate flux decline, during the first minutes of filtration, probably due to the fast accumulation on the membrane surface of a first layer of fouling. In a second stage, the flux declines slower, caused by the consolidation of the fouling layer due to a balance between the deposition of foulants on the cake and their removal produced by the shear stress of the cross flow.

The maturation of the leachate has a positive effect on the permeability, with a twofold higher final permeability than that obtained with a young leachate. This finding is likely related to the higher concentration of proteins and carbohydrates in the young leachate. The main reason for the decrease of permeability during the ultrafiltration of leachates is the external fouling, this being higher for younger leachates. Resistance-in-series analysis demonstrated that the loss of permeability was mainly due to reversible fouling. Either irrecoverable or internal fouling were scarce and not determined by the stage of maturation of the leachate. This leads to suggest a long lifespan of the membrane in plant operation, since more than 99.5% of the initial permeability can be recovered after cleaning.

The prevailing fouling model during the ultrafiltration of both leachates is the corresponding to cake formation, either under TR or VCR modes. COD rejection for the mature leachate showed an approximately sigmoidal shape, from an initial value of 18.5% to a final one of 49.6%, with the faster increase for VCR ranging from 1.2 to 1.7. The main reason for this behaviour is due to the fatty acids are not retained by the UF membrane. On the other hand, COD rejection remains approximately constant during the ultrafiltration of the young leachate (48%), which can be attributed to the presence of higher molecular weight compounds in its composition.

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Appendix

Determination of R_m, R_{rev}, R_{irrev} and $R_{irrecov}$

Figure A.1 illustrates the evolution of J throughout the experiments. Initial flux (J_o), flux after leachate ultrafiltration and before cleaning (J_s), flux after physical cleaning with water (J_{pc}) and flux after chemical cleaning (J_{cc}) are measured to calculate the resistances model.

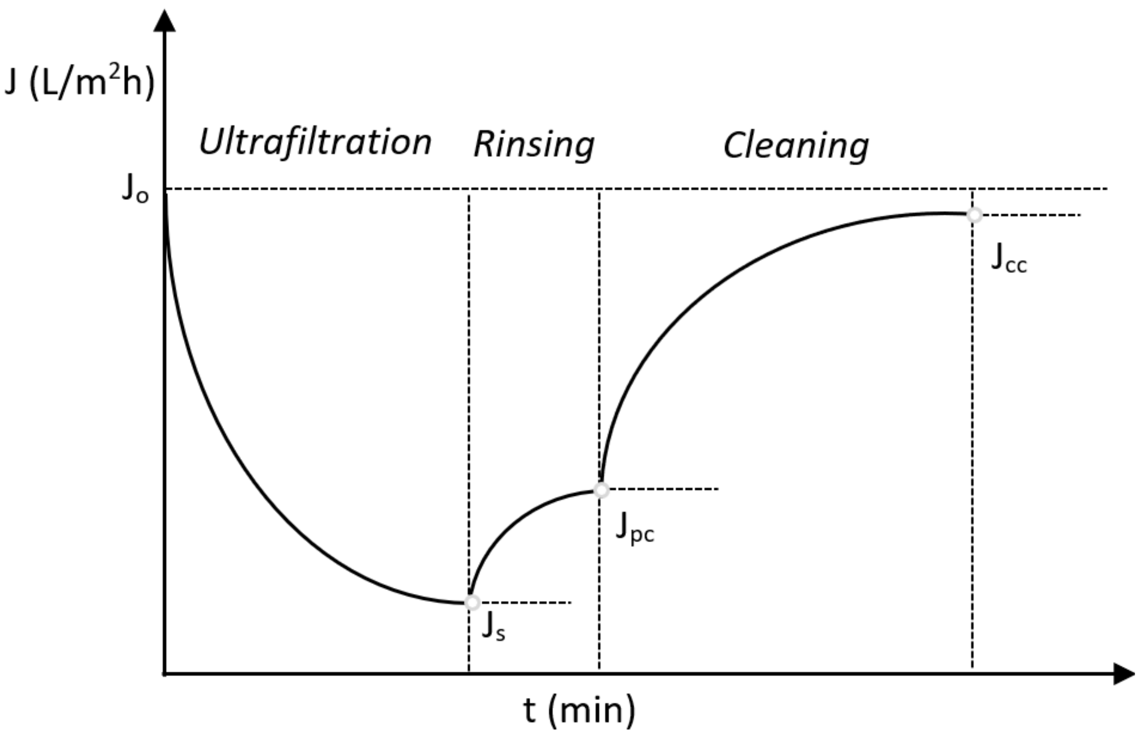

Figure A1. Evolution of flux during ultrafiltration, rinsing and cleaning.

According to Darcy's law:

$$R = \frac{\Delta P}{\mu J}$$

Where R is the hydraulic resistance of the membrane, ΔP is the TMP, μ is the viscosity, and J is the permeate flux. Also, according to the resistances-in-series model, total resistance can be expressed as a sum of different resistances (eq. A.1):

$$R_s = R_m + R_{rev} + R_{irrev} + R_{irrecov} \tag{A.1}$$

Where R_s is total resistance after operation, R_m is the intrinsecal membrane resistance, R_{rev} is the resistance corresponding to reversible fouling, R_{irrev} is the resistance caused by irreversible fouling, and $R_{irrecov}$ is the resistance referable to irrecoverable fouling.

Through simple operations (eqs. A.2-A.4), we can obtain R_{rev}, R_{irrev} and $R_{irrecov}$ with the resistances calculated with J_s (R_s), J_o (R_m), J_{pc} (R_{pc}) and J_{cc} (R_{cc}) (Figure A.2) [57].

$$R_{rev}=R_s-R_{pc} \tag{A.2}$$

$$R_{irrev}=R_{pc}-R_{cc} \tag{A.3}$$

$$R_{irrecov}=R_{cc}-R_m \tag{A.4}$$

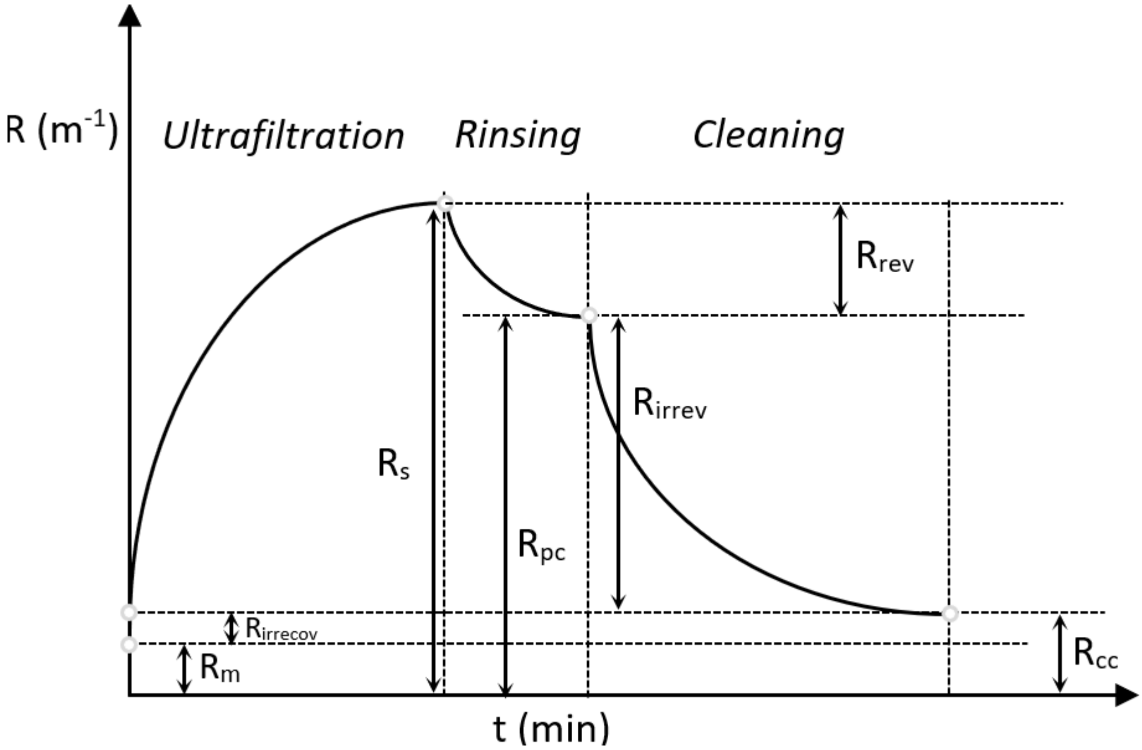

Figure A2. Evolution of resistances during ultrafiltration, rinsing and cleaning. Adapted from [51].