

Technical–economic evaluation of chromium recovery from tannery wastewater streams by means of membrane processes

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ABSTRACT

Leather tanning processing and manufacturing industry uses high large amounts of water in the range of 40–45 L kg⁻¹ during processing. As a result, tannery wastewater rises by the same amount, is characterized by a large inorganic load (chlorides, with concentration ranging from several hundred to over 10,000 mg L⁻¹ Cl⁻; sulphate (VI), ammonium ions and sulphide ions, exhibiting concentration that ranges from tens to several hundred mg L⁻¹) and together with organic pollution (the chemical oxygen demand value is usually several thousand mg L⁻¹ O₂). The use of conventional treatment processes to treat wastewater streams from the tannery industry resulted to bear not satisfactory. In the case of biological treatment methods, the treatment results are incomplete and complicated by an excessive sludge production at the end. On contrary, physical and chemical methods are too expensive in terms of energy and chemicals. Therefore, the only partially treated tannery wastewater is given passed to the industrial sewer system or, in the worst case, directly to the environment, representing therefore a threat to the environment. In this work, a nanofiltration membrane operation was used, developed to treat tannery wastewater after an initial sedimentation process. To avoid severe membrane fouling operating conditions, the determination of the boundary flux was determined. In the second step, experimental work was carried out to permit the validation of the adopted approach. The purification target of the here proposed process for tannery wastewaters was reached, that is the legal discharge to municipal sewer system according to Italian law of 90% of the initial volume. Since discharge costs to municipal sewer system are approx. 1/3 compared with the industrial one, the practice allows immediate cost saving of 26%. Moreover, an additional benefit is achieved by the by-production of chromium rich concentrate streams in amount equal to 5% of the initial volume, suitable to tannery process recycle and reuse. In total, cost saving rates may exceed 30%. At the end, scale-up of the proposed process will be discussed from technical and economic point of view.

Keywords: Chromium; Tannery wastewater; Reuse; Recovery

1. Introduction

Tannery industries operate worldwide, located mostly in China, India, Northern Africa, Europe (Italy) and United States. Tanning is the process of treating skins and hides of

animals to obtain a final product leather. The tanning is necessary to alter the structure of skin, making it more durable and less susceptible to decomposition. During the process it is possible to colour the leather by using dyes. In the past, tanning used tannin, an acidic chemical compound, as main chemical to process the skins. At the beginning of the 19th

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century, tannin was substituted by a Cr(III) solution, since it results to be sensibly more efficient.

At the end of the process, almost the same amount of water used during processing results as wastewater (WW). Tannery WW is characterized by high inorganic (chlorides, with concentration ranging from several hundred to over 10,000 mg L⁻¹ Cl⁻; sulphate (VI), ammonium ions and sulphide ions, exhibiting concentration that ranges from tens to several hundred mg L⁻¹) and moderate organic (the chemical oxygen demand (COD) value is usually several thousand mg L⁻¹ O₂) pollution. This WW, containing mostly Cr(III), represents a serious threat to environment and human health. Moreover, in particular conditions such as sun drying of stagnant puddles, even the stable Cr(III), found in the tannery WW, can be converted back into carcinogenic Cr(VI), making environmental pollution even worse. Therefore, this WW stream should not be introduced to the environment untreated.

Unfortunately, many conventional processes have been carried out to treat this WW stream, such as biological process [1], oxidation process [2] and chemical process [3]. Among these, physical and chemical methods are considered very expensive in terms of energy and reagents consumption [4]. Moreover, the generation of excessive sludges makes biological treatment tedious [5]. As a result, especially in those countries where WW regulations are not strictly followed, and municipal (industrial) sewer systems are not widely developed, the tannery WW is given to the environment partially treated, leading to high impact situations to the environment and human health.

Therefore, the treatment of this WW needs technical reorganization, by combining and integrating alternative systems to the conventional ones. On the other hand, the developed treatment process should result economically feasible.

In particular, the use of membrane technologies applied to the leather industry represents an economic advantage, especially in the recovery of chromium from residual waters of leather tanning.

Several studies showed that crossflow microfiltration, ultrafiltration, nanofiltration (NF), reverse osmosis (RO) and supported liquid membranes can be applied in leather industry for the recovery of chromium from spent liquors. RO with a plate-and-frame membrane has been used as post-treatment to remove refractory organic compounds (chloride and sulphate) [6]. The high quality of the permeate stream produced by the RO system with a plane membrane allowed the reuse of the tannery effluent within the production cycle, thus reducing groundwater consumption.

In this work, the tannery feedstock, after primary conventional treatment, was driven to an NF membrane process for purification, by the production of a permeate stream compatible to municipal sewer systems, and reuse purposes, by the production of Cr rich concentrates.

Moreover, economic feasibility for the use of efficient membrane processes in the tannery industry was checked. A major phenomenon that limits the economic feasibility for this kind of processes is membrane fouling. The exceptional performances of membranes, exhibited by the new membranes, may be quickly lost due to fouling. Moreover, irreversible pore occlusion will occur on the membrane; therefore, the

longevity will result sensibly decreased, leading to periodic and costly membrane module substitutions.

Membrane fouling, expressed as a permeate flux reduction as a function of time given by some phenomena different than polarization and/or aging of the membrane, can be subdivided into three main typologies as follows:

- A reversible fouling: this kind of fouling strictly follows the driving force amplitude, for example, operating pressure values. As soon as the pressure over the membrane is reduced, this fouling is eliminated after a certain (short) period of time by the same quota.
- A semi-reversible fouling: this kind of fouling accumulates over the membrane surface and cannot be easily eliminated. The only way to eliminate this kind of fouling is to stop the separation process and clean or wash the membranes, with water or aqueous solution of chemicals, respectively. Although this kind of fouling is after the cleaning/washing procedure almost eliminated, it represents a problem in the continuous process operation since it forces to process shut-down at timed intervals.
- An irreversible fouling: once formed, this kind of fouling cannot be eliminated by any procedure. It is the main cause of membrane failure concerning productivity.

In all cases, during operation of tangential cross flow separation by membranes, all three fouling types will unavoidably appear and form. The existence of different fouling typologies affecting membranes were previously explained by Bacchin et al. [7] and Ognier et al. [8], and are based on the assumption of possible local conditions triggering different liquid/gel phases over the membrane and in the membrane pores due to the concentration profiles by polarization.

Field et al. [9,10] introduced the critical and boundary flux concepts. Summarizing, both critical and threshold fluxes divide the operation of membranes in two regions: a lower one, where no or a small, constant amount of fouling (mostly reversible and/or semi-reversible) triggers, and a higher one, where (irreversible) fouling builds up very quickly.

In the second step, Stoller and Ochando-Pulido [11] suggested to merge the critical and threshold flux equations in one set by introducing a new flux, that is the boundary flux J_b ; the relevant equations are as follows:

$$\frac{dm}{dt} = -\alpha; J_p(t) \leq J_b(t) \quad (1)$$

$$\frac{dm}{dt} = -\alpha - \beta [J_p(t) - J_b(t)]; J_p(t) > J_b(t) \quad (2)$$

where:

- α , expressed in L h⁻² m⁻² bar⁻¹, represents the constant permeability reduction rate suffered by the system and will be hereafter called the sub-boundary fouling rate index. α is a constant, valid for all flux values.
- β , expressed in h⁻¹ m⁻² bar⁻¹, represents the fouling behaviour in the exponential fouling regime of the system, and will be hereafter called superboundary fouling rate index. β appears to not be a constant, and changes with the transmembrane pressure (TMP).

Eq. (1) is the most relevant one, since only reversible fouling triggers and therefore the membrane longevity results maximized. In this respect, operating below the J_b value is sufficient to guarantee long-term performances. In the second step, the value of α determines how long the membrane may operate without cleaning procedures. Cleaning membranes represent a cost and an operation stop which is certainly not desired to certain extent. Therefore, low α value membranes are preferred to high α value ones.

Therefore, for a membrane-based tannery WW process to be economically feasible it is essential that operation be sub-boundary. Indeed, the same indication was observed in many cases where the treatment of water, which is a low added value product, is involved [12]. In these cases, frequent membrane substitution operations represent an unsustainable OPEX that must be avoided at all costs.

Consequently, the determination of the J_b value of the examined system must be determined experimentally. After this, it is possible to feed the data as an input to a simulation model, that is capable to predict membrane performances over a long period of time. The same can be used for the evaluation of scale-up processing of the proposed purification process. At the end, economic feasibility can be evaluated for an industrial plant.

2. Experimental setup

The pilot plant used is shown schematically in Fig. 1.

The plant consisted of a 100 L feed tank, FT1, in which the pretreated feedstock was charged. The centrifugal booster pump, P1, and the volumetric pump, P2, drove the WW stream over the used spiral wounded NF (NF model DK supplied by Osmonics) or RO (RO model SC supplied by Osmonics) membrane, fitted in the housing, M1, at an average flow rate equal to 600 L h⁻¹. The active membrane area of both the modules was equal to 0.51 m². The maximum allowable operating pressure was equal to 32 and 64 bar for NF and RO, respectively.

Acting on the regulation valves, V1 and V2, it is possible to set the desired operating pressure over the membrane with a precision of 0.5 bar, maintaining the feed flow rate constant.

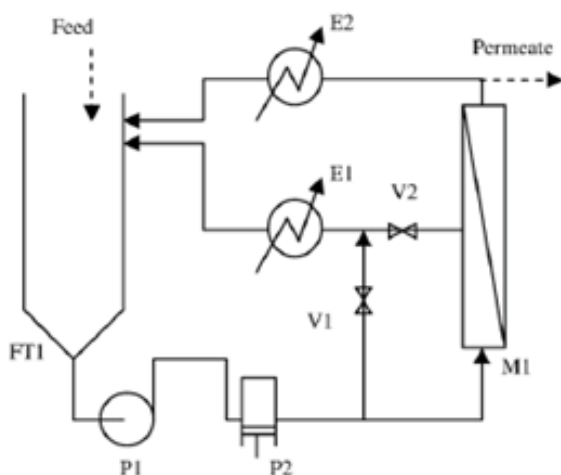


Fig. 1. Scheme of the experimental setup.

Permeate and concentrate streams was cooled down to the fixed feedstock temperature, mixed together and recycled back to the feedstock. In this way, the feedstock composition was kept constant during each experimental batch run. The temperature was controlled for all experiments at the value of 20°C ± 1°C.

After each experiment, the membrane was rinsed with tap water for at least 30 min.

3. Results and discussion

The first objective of this work was to identify optimal operating conditions for the two different membrane modules.

The boundary flux was measured for the NF membrane only, since RO did not show significant fouling issues in the adopted pressure range. The measurements were performed by applying the pressure cycle step method and successive evaluation method, described in detail elsewhere, starting from a value of 2 bar [13–15].

Below boundary flux condition, no fouling was observed; therefore, a constant contribution to the fouling phenomena was absent ($\alpha = 0$). This is not the case below the threshold flux value, where fouling was immediately observed ($\alpha \neq 0$). Above boundary flux values, the fouling behaviour sensibly increased, and fouling quickly occurred ($\beta \neq 0$).

Of interest is Eq. (1), since operation should occur with no or a small amount of fouling. Eq. (1) can be discretized between t_1 and t_2 , equal to one pressure cycling period, Δt , and the following linear equation, hereafter marked by an asterisk, can be derived as follows:

$$\left(-\frac{\Delta m}{\Delta t}\right)^* = \alpha; J_p(t) \leq J_b(t) \quad (3)$$

As long as the adopted TMP values remain below the boundary one, no effect on the changes of the permeability loss rate should be observed, thus resulting in a constant $(-\Delta m/\Delta t)^*$ value. This value is the expected permeate reduction if Eq. (3) holds, that is, at sub-boundary flux regimes, and must be compared with the measured one, hereafter reported as $(-\Delta m/\Delta t)^\circ$.

The application of Eq. (3) implies the knowledge of the ' α ' parameter value: in this work, this value was calculated at the lowest available TMP value, where chances to work at subthreshold operating conditions are highest.

Finally, by the application of the pressure cycling method, following conditions on the measured $(-\Delta m/\Delta t)^\circ$ values are met, that is [16]:

$$\left(-\frac{\Delta m}{\Delta t}\right)^* > \left(-\frac{\Delta m}{\Delta t}\right)^\circ \quad (4)$$

Pretreatment processes sensibly affect the boundary flux of the system [16,17]. In this case study, the tannery WW was only treated by conventional primary WW treatment processes.

The obtained results from the analysis are reported in Table 1.

From the obtained results, the value of the ' α ' parameter in Eq. (1) at 2 bar was successfully calculated, since the

Table 1
Boundary flux determination (in bold)

TMP (bar)	Δt (h)	$(-\Delta m/\Delta t)^\circ$ ($10^{-5} \text{ L h}^{-2} \text{ m}^{-2} \text{ bar}^{-1}$)	$(-\Delta m/\Delta t)^*$ ($10^{-5} \text{ L h}^{-2} \text{ m}^{-2} \text{ bar}^{-1}$)
2	1	14.124	14.124
3	2	5.817	14.124
4	3	6.394	14.124
5	4	12.191	14.124
6	5	16.130	14.124
7	6	16.847	14.124

permeability decline was within the measured limits, even at higher TMP values, thus confirming that the reference was taken at subthreshold flux operating conditions.

A boundary flux exists in correspondence to 6 bar, where $(-\Delta m/\Delta t)^\circ$ started to become higher than $(-\Delta m/\Delta t)^*$, equal to $4.4 \text{ L h}^{-1} \text{ m}^{-2}$ at operation start and characterized by an α value equal to $14.124 \times 10^{-5} \text{ L h}^{-2} \text{ m}^{-2} \text{ bar}^{-1}$.

The NF permeate had a final COD value of 102 mg L^{-1} , corresponding to an overall rejection value of 95%. The permeate characteristics are reported in Table 2. Although reclaim of chromium appears adequate, the remaining concentration of Cr and possibly other heavy metals in the permeate stream does not allow legal sewer discharge. Therefore, RO must be applied to meet the purification and treatment targets of all parameters.

The osmotic pressure of RO was equal to 9.71 bar and permeability equal to $0.364 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. No J_b value was observed in the range of the allowable operating pressure values of this membrane, which is 90 bar. Therefore, the choice of the operating pressure for RO relies only on economics. By adopting higher pressure values, the investment costs in terms of required membrane area of RO is reduced, but higher operating costs in terms of electricity consumption must be considered. Moreover, the capacity of RO should equal the permeate stream arriving from NF. At the end, an operating value for RO equal to 22 bar was fixed in this work.

In Fig. 2, the obtained permeate flux profiles, with a target of 95% of recovery, were plotted at 6 and 22 bar for NF and RO, respectively. The characteristics of the obtained membrane permeate streams are reported in Table 2. After RO, all purification targets were reached, thus confirming possibility to discharge the WW directly into the municipal sewer systems in compliance with environmental regulations and at reduced costs.

Table 2
Composition of the streams

	COD (mg L^{-1})	TTS (mg L^{-1})	NH_4 (mg L^{-1})	P (mg L^{-1})	S (mg L^{-1})	Cr (mg L^{-1})
Feed (raw WW)	2,200	266	69	2.5	0.09	195
Discharge limits	160	80	15	10	1	2
NF permeate	102	0	5.89	<2.5	0.09	7.92
RO permeate	86	0	–	–	–	0.04

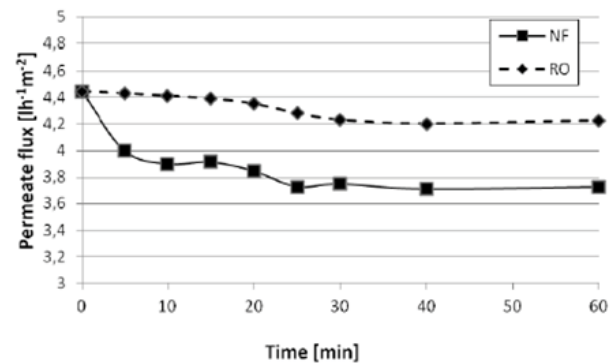


Fig. 2. Plot of the NF and RO permeate flux as a function of operating time.

From Fig. 2 it is possible to observe how polarization during the first minutes and the increase of the concentration of pollutants in the feedstock during the batch operation afterwards affects the boundary flux values. A precise relationship between boundary flux and pollutant concentration is not yet known. On the other hand, at the end of operation, boundary flux values of 3.7 and $4.2 \text{ L h}^{-1} \text{ m}^{-2}$ for NF and RO were experimentally found, respectively. Considering that after 1 h of operation the boundary flux reduces about the small α value, in the range of $10^{-4} \text{ L h}^{-1} \text{ m}^{-2}$, this aspect was neglected, and the observed values in Fig. 2 were adopted directly by the model.

In the second step, the experimental dataset was given as an input to a simulation model, capable to predict the performances of the membrane process over long period of time, reported and validated elsewhere [18]. The proposed membrane plant is therefore composed of NF and RO membrane processes in series. To check the economic feasibility of the membrane process, a rough cost estimation of the proposed treatment was carried out, by adopting the procedure suggested by Stoller and Ochando-Pulido [18]. The considered plant capacity was equal to $646 \text{ m}^3 \text{ d}^{-1}$, that is the capacity required by a medium-large tannery site.

The results are reported in Table 3.

It is interesting to notice how the presence of a boundary flux (with $\alpha \neq 0$) and aging directly affects the required membrane area (NF, Table 4).

In critical flux conditions and no aging for both NF and RO, a membrane surface area equal to $25,390 \text{ m}^2$ would be sufficient. On contrary, an overdesign of about 12% is required to consider (1) the presence of a boundary flux (only NF) and (2) aging, to permit to control the process at a fixed

Table 3
Results of the simulation model after technical process optimization

Feedstock	Key parameter	COD	COD
	Value in feed stream	2.0 g L ⁻¹	0.1 g L ⁻¹
	Pretreatments	Primary treatment	Primary treatment + NF
Membrane properties	Membrane type	NF	RO
	Membrane model	SW	SW
	Membrane ID	DK	SC
	Membrane supplier	Osmonics	Osmonics
	Pore size	0.5 nm	–
	mw (L h ⁻¹ m ⁻² bar ⁻¹)	2.500	0.364
Process properties	T (°C)	20	20
	v _F (L h ⁻¹)	600	600
	π (bar)	0.0	9.7
	Operation time (h)	4	4
	Operation cycles (–)	450	450
	R (%)	95.0	95.0
Boundary flux data	Boundary flux type	Threshold	Threshold
	α (L h ⁻² m ⁻² bar ⁻¹)	0.00014	0.00000
	Δw% (% h ⁻¹)	0.001	0.001
	J _b (L h ⁻¹ m ⁻²)	3.7	4.2
	TMP _b (bar)	6.0	22.0
Results	Plant capacity (m ³ d ⁻¹)	646	
	Total membrane area (m ²)	28,506	
	CAPEX (€ m ⁻³) ^a	1.64	
	OPEX (€ m ⁻³) ^b	0.34	
	Total costs (€ m ⁻³)	1.98	
Note	Cr is recovered back in the concentrate and might be used again in the tannery process. Cr concentration equal to 3 g L ⁻¹ , chemical savings equal to 6% of the total requirements.		

^aThe investment costs includes 7% of yearly depreciation of the technology and substitution of hardware (pumps, valves) at programmed intervals. Piping 15%. Engineering 10%.

^bOperating costs includes electricity and membrane substitution at 1/3 yearly (membrane duration estimated 3 years of operation).

Table 4
Details of the evaluation of the required membrane area

	Units	NF		RO	
		If α = 0, Δw% = 0	By simulation	If α = 0, Δw% = 0	By simulation
Target permeate capacity	L h ⁻¹	51,142		48,584	
Membrane area at J _b		13,822	13,859	11,041	11,041
Aging	%	0.0%	–10.8%	0.0%	–10.8%
Membrane area	m ²	13,822	15,538	11,041	12,378

permeate value up to the end of plant life. The required total membrane area to guarantee the performances within 3 years of the duty of the membrane modules before substitution is therefore 28,506 m². This corresponds to a plant composed of 891 standard SW modules, 32 m² each.

In this case study, aging is the main factor to membrane area increase to maintain the operation sub-boundary during the overall membrane plant life. It might appear that this factor may be neglected, but it should not: as soon as operation is performed in superboundary conditions,

Table 5
Cost saving estimation per year

Item	Unity costs	Without treatment plant		With treatment plant	
		Amount	Costs (€ year ⁻¹)	Amount	Costs (€ year ⁻¹)
CAPEX of plant	1.64 € m ⁻³	0.00 m ³ year ⁻¹	0 k€	193 × 10 ³ m ³ year ⁻¹	371 k€
OPEX of plant	0.34 € m ⁻³	0.00 m ³ year ⁻¹	0 k€	193 × 10 ³ m ³ year ⁻¹	83 k€
Personnel	50 € d ⁻¹	0 d year ⁻¹	0 k€	1,200 h year ⁻¹	60 k€
Soil occupation ^a	–	–	0 k€		5 k€
Wastewater disposal ^b	10 € m ⁻³	193 × 10 ³ m ³ year ⁻¹	1,930 k€	9.6 × 10 ³ m ³ year ⁻¹	96 k€
Wastewater disposal ^b	3 € m ⁻³	0 m ³ year ⁻¹	0 k€	174 × 10 ³ m ³ year ⁻¹	522 k€
Supply of Cr salts ^c	900 € t ⁻³	1,158 t year ⁻¹	1,042 k€	1,088 t year ⁻¹	980 k€
Costs of selected items (€ year ⁻¹)		2,972 k€		2,117 k€	
Total cost savings (€ year ⁻¹)		–855 k€ (–28.7%)			

^aConsisting of: storage of the wastewater for maximum 10 d capacity, and in addition to this, plant space occupancy. Storage basins were considered at an equivalent cost on the considered scale.

^bDisposal costs varies as: 10 € m⁻³ to industrial sewer system and 3 € m⁻³ to civil sewer system.

^cMean values for 1 t of raw material are: use of 175 kg of Cr salts and production of 30 t wastewater.

β -regimes of fouling (Eq. (2)) would apply with formation of irreversible fouling. In this case, the productivity of the membrane process drops severely to low values, such to not guarantee the required capacities within the life time of the modules fixed by design. On contrary, probably some additional overdesign of 10%–15% must be suggested to the process designer, to safely operate the plant below the boundary fluxes.

To estimate the total cost saving of the tanning process, without considering the treatment of the WW alone, the data resulting from Table 3 was used in Table 4. The obtained results are compared with legal disposal of the WW without treatment available to the tannery industry considering the case study plant per year (capacity equal to 646 m³ d⁻¹ for 1 year; operation equal to 12 h d⁻¹ for 300 d year⁻¹). Scale-up was obtained by considering the modularity of membrane processes, thus at a ratio equal to 1:1.

All other facilities remain; therefore, they do not contribute to process cost reductions, analysis was therefore performed only concerning the cost differences among process changes.

From Table 5, the use of a treatment plant based on membrane technology appears of great interest from a technical and economical point of view. Indeed, it is possible to sensibly reduce the environmental threat the WW represents, and at the same time, it is possible to achieve costs savings as high as 28% yearly.

4. Conclusions

The treatment of tannery WW streams by membrane technologies appears to be a practice of great interest and benefit, if irreversible fouling of the membranes is avoided. In this case, OPEX costs of the treatment plant are kept very low, and economic feasibility of the proposed process was therefore reached.

In particular, the use of a treatment plant of medium-large capacity may achieve a total cost saving of 28%. Concerning the NF section, a boundary flux value J_b equal to 4.4 L h⁻² m⁻² was

found. Moreover, the sub-boundary fouling parameter α was estimated to be equal to 0.14 10⁻³ L h⁻² m⁻² bar⁻¹. By adopting 28,506 m² of membranes, it is possible to operate the plant for 3 years before membrane substitution and permit the recovery of 90% of Cr free water. Therefore, the environmental impact of the tannery industry would result sensibly reduced. The residue is sent back to the process, for an almost complete Cr reuse. Only 5% of the initial volume raises as industrial waste.

List of symbols

J_b	–	Boundary flux, L h ⁻¹ m ⁻²
J_p	–	Permeate flux, L h ⁻¹ m ⁻²
m	–	Permeability, L h ⁻¹ m ⁻² bar ⁻¹
TMP	–	Transmembrane pressure, bar
t	–	Operating time, h
α	–	Sub-boundary fouling rate index, L h ⁻² m ⁻² bar ⁻¹
β	–	Superboundary fouling rate index, h ⁻¹ m ⁻² bar ⁻¹
Δm	–	Permeability gain/loss after one pressure cycle for J_b measurement, L h ⁻¹ m ⁻² bar ⁻¹
Δt	–	Time of one pressure cycle for J_b measurement, h

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