

## Hybrid Process for Potable Water Denitrification

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As fresh water scarcity is a growing problem, sustainable development of water reuse require maximal attention. Until now, the treatment of polluted water by membrane technology has not resolved entirely this problem. In this work, we investigate the feasibility of a hybrid system to treat polluted potable water with nitrates. We compare, the efficiency of well known technologies as Reverse Osmosis (RO), Ionic Exchange (IX) and Electrodialysis (ED) for denitrification, as well as, the coupling of RO-IX and RO-ED for the same purpose. The strategy of coupling is to further treat the RO reject by IX or ED in order to: remove nitrates from water, and to obtain the maximum water recovery keeping the desirable minerals at an acceptable level for drinking water. Results show that nitrate removal efficiencies range from 83 to 97 % and in some cases a water recovery of 100 %. In addition, nitrate removal fastness and power consumption of the different systems were also evaluated.

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**Keywords:** Nitrate pollution, RO rejects, Hybrid system, Recovered water,

### 1. INTRODUCTION

Excessive use of nitrate based fertilizers has lead to an increase in nitrate concentration in ground water in many regions around the world giving raise to environmental and public health concerns [1-3]. Research in denitrification by ED [4-10], RO [11-12], IX [13-15], heterogeneous catalytic denitrification [16-18], Electrochemical reduction [19-20], biological denitrification [21-26], and combination of two or more of these processes [27-38], have been conducted by many researchers. Even if these processes have shown good results they have their own disadvantages as low efficiency or selectivity, large amount of wastes, chemical treatment demand and possible contamination with

germs and organic residues that could lead to an additional treatment for final water conditioning among others.

In the present work, seeking for potable water denitrification, we compare the performance of IE, RO and ED separately and two combination of these processes. We have used the RO-IE and RO-ED combinations to find an alternative process for potable water denitrification. We have set the initial nitrate concentration as 250 mg/L  $\text{NO}_3^-$  as can be polluted well potable water. We are looking to reach a concentration below 45  $\text{mgL}^{-1}$  as Mexican regulatory standard demands, together with maximum water recuperation. Indeed, electrical conductivity, total dissolved solids (TDS),  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and pH were analyzed in the affluent, permeate and reject in RO; affluent, diluted and concentrate in ED and affluent with its respective permeate in IE processes. Nitrate was effectively removed and 100 % of water recovery has been reached with the RO-ED combination. Advantages and disadvantages of each process are discussed.

## 2. EXPERIMENTAL PART

### 2.1 Analysis techniques

The feed water used in all experiments was prepared with distilled water and dissolving an industrial grade  $\text{NaNO}_3$  fertilizer containing 5 % of  $\text{Na}_2\text{SO}_4$ . The analysis of feed water is shown in table I and would correspond to a well water polluted with  $\text{NO}_3^-$  at a concentration of 250 mg/L as found in many rural places.

**Table 1.** Feed water composition (mg/L)

$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{Na}^+$	pH
250	6.7	1.7	80	7.5

Temperature and pH measurements have been performed with a potentiometer HANNA HI 8424. Conductivity and Total Dissolved Solid (TDS) have been tested with a conductivity analyzer OAKTON after Mexican standard NOM-AA-93-2000.

Chlorides were determined by the Mohr method; Sulphates were measured by turbidimetry, the absorption of solutions was obtained in a spectrophotometer Agilent 8453; Nitrates were determined in a spectrophotometer HP 8452A and sodium was analyzed by Inductive Coupled Plasma spectroscopy (ICP-OES) in a Perkin Elmer model3300DV.

### 2.2 Reverse Osmosis (RO)

Reverse Osmosis experiments were performed in an Inversa Aquatica equipment model 601700 with three prefilters: Two polypropylene filters, 1 and 5 microns respectively and one activated carbon filter. Two pumps feed the water, the first one feeds the water to prefilters at a pressure of ca. 5

bar, the second pump feeds the water to the spiral-wounded membrane Osmonics Desal model TFM-50 at a pressure of ca. 9 bar. 20 liters of test dissolution were passed through column.

### 2.3 Ionic Exchange (IX)

Ionic Exchange experiments were performed in an in house made column 10 cm in diameter and 50 cm height filled with 1 L of Purolite A-500 anionic resin. 20 liters of test dissolution were passed through column.

### 2.4 Electrodialysis

Electrodialysis test were performed in an Asahi Glass electro dialyzer type filter press model DS-O, which hydrodynamic characterization was the object of a previous work [39]. A three compartment mode (Salt splitting) was used with three independent pumps. CMV cationic membrane and AMV anionic membrane, both from Asahi Glass, were used, as defined in previous works [10, 40]. The effective membrane area is of ca. 172 cm<sup>2</sup>. The anode was a Pt-coated Ti plate and the cathode was a plate of stainless steel 316 L. Both electrodes had the same area as the membranes. Limiting current was previously defined and set for a NO<sub>3</sub><sup>-</sup> concentration below 45 mg/L to avoid polarization concentration. Limiting current density was obtained from R vs. 1/I plots as described by Sorensen [41].

### 2.5 Reverse Osmosis-Ionic Exchange (RO-IX)

Experiments combining RO and IX were performed as outlined in the next section. Feed water is treated first in the RO system. RO reject is then treated in the IX column and finally mixed with the RO permeate.

### 2.6 Reverse Osmosis-Electrodialysis (RO-ED)

Experiments combining RO and ED were performed as outlined in the next section. Feed water is first treated in the RO systems then RO reject was treated in ED system with further mixing of RO permeate and ED dilute.

## 3. RESULTS AND DISCUSSION

An evaluation of efficiency, water quality with desirable ions, volume recovery, process fastness and power consumption for five processes was performed under the operation conditions listed in table 2. It is evident that, as expected, the nitrate concentration diminishes as a function of time for all the processes. Additionally, the results show marked differences in the volume water

recovery and power consumption even though all the processes produce the water quality demanded in the Mexican regulatory standard for drinking water, (NOM-127-SSAI,1994). The following section present the data for produced water quality against this standard after treatment by the five processes tested.

**Table 2.** Operation conditions

Parameter	Unit	RO	IX	ED	RO-IX	RO-ED
Pressure prefilter	Bar	5	---	---	5	5
Pressure membrane	Bar	9	---	---	9	9
Area membrane	cm <sup>2</sup>	598	---	178	598	598
Flow	mL/min	250	833	360	250-175*	538-363*
Volume treated	L	20	20	3	20	3
Resin capacity	Eq/L	---	1.15	---	---	---
Current density	A/m <sup>2</sup>	---	---	0.9	---	0.9

\* First number is the flow in RO, second number is the flow in the second process i.e. IX or ED

### 3.1 Ions

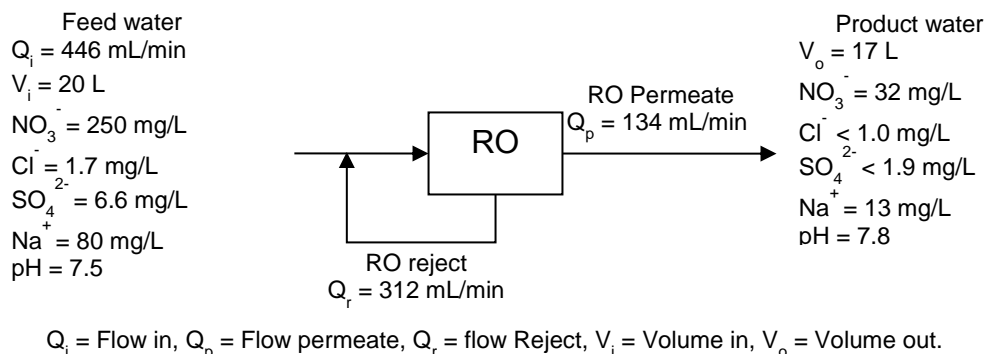
Three anions were analyzed: (NO<sub>3</sub><sup>-</sup>), (Cl<sup>-</sup>), (SO<sub>4</sub><sup>2-</sup>). The anion removal was performed under the operation conditions that can be seen in table 2. The nitrates were the only anion to be higher than permissible limits set by the Mexican standard in the feed water to the different processes. After treatment, as expected, nitrates were below the limits.

The only cation present in the feed water was Na<sup>+</sup>, it is present as counter ion for all the anions. Indeed, Na<sup>+</sup>, is below the limits set by the Mexican standard used as regulatory.

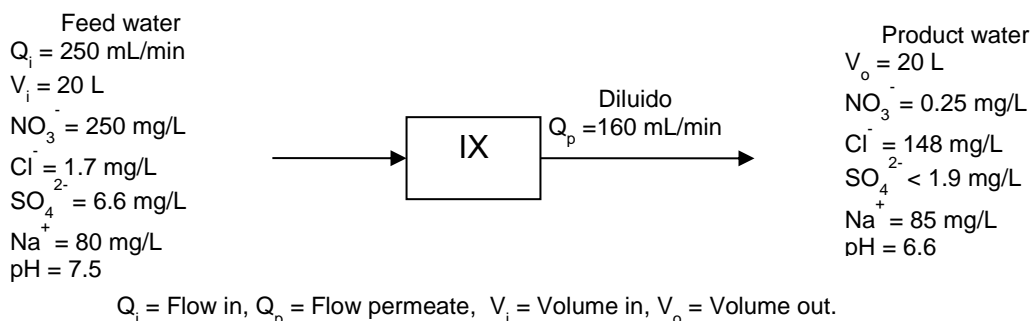
### 3.2 Process efficiency

Figure 1 outline the treatment scheme for each one of the processes tested as well as the feed and produced water quality. The concentration of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, as expected, diminish as a function of time in the five processes tested but this is not the case for Cl<sup>-</sup> and Na<sup>+</sup> (fig. 2 A, B). Both Cl<sup>-</sup> and Na<sup>+</sup> diminish in RO, ED and RO-ED processes, nevertheless Na<sup>+</sup> remains constant in IX and rises in RO-IX. This behavior is explained by the fact that in IX process there is no cationic resin to trap the ion sodium that is why it passes through IX column without change in concentration. In the case of RO-IX, sodium rises because it is first concentrated in the RO reject and then the RO reject is passed through anionic resin where there it is not trapped (see treatment scheme in figure 1a to 1e) and plots of concentration vs. time in figure 2). Same explanation is valid for Cl<sup>-</sup>. Cl<sup>-</sup> diminishes in RO, ED and RO-ED processes. Indeed, Cl<sup>-</sup> rises upon passage through IX column because NO<sub>3</sub><sup>-</sup> is simply exchanged by Cl<sup>-</sup>. A more noticeable increase in Cl<sup>-</sup> concentration after RO-IX treatment is due to the

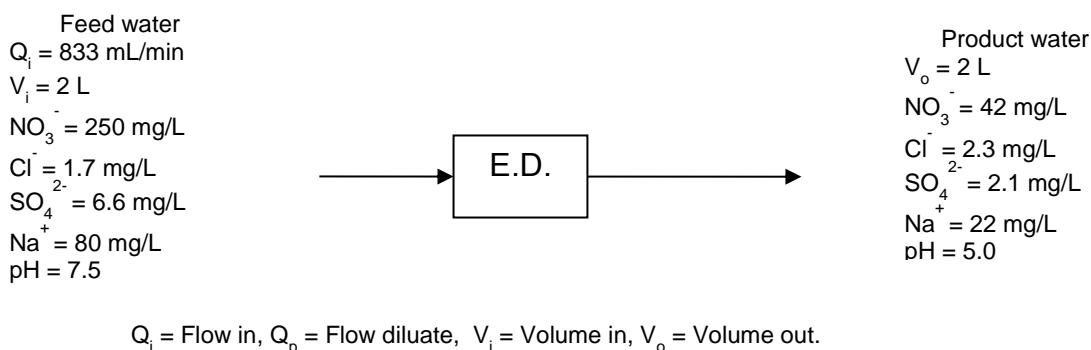
first concentration in RO reject followed by a second concentration upon passage through the IX column.



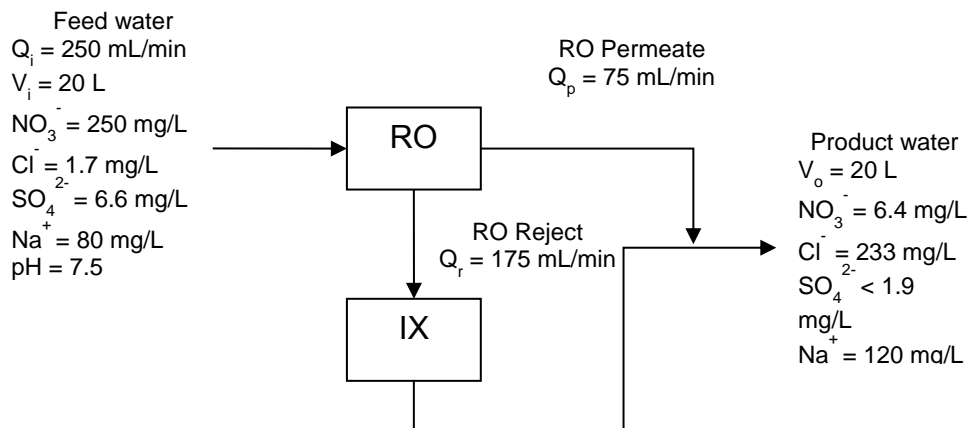
**Figure 1a.** Operation conditions for RO



**Figure 1b.** Operation conditions for IX

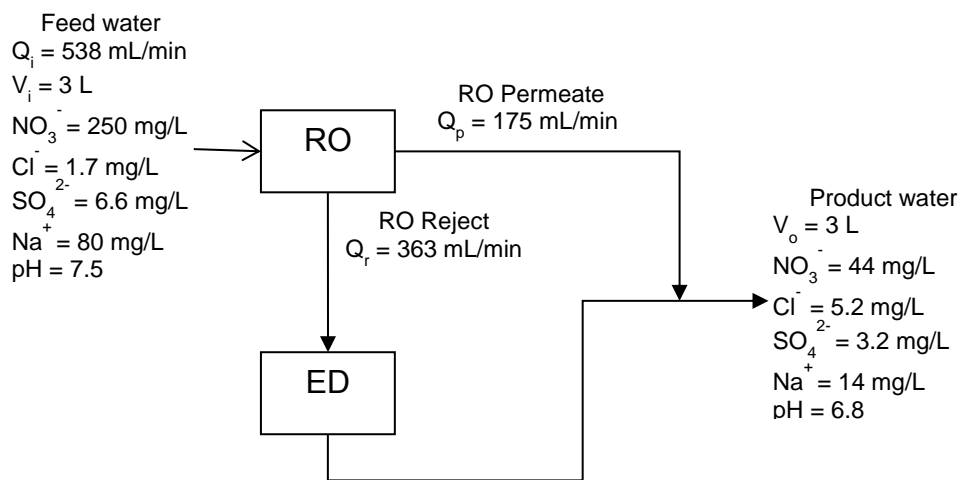


**Figure 1c.** Operation conditions for ED



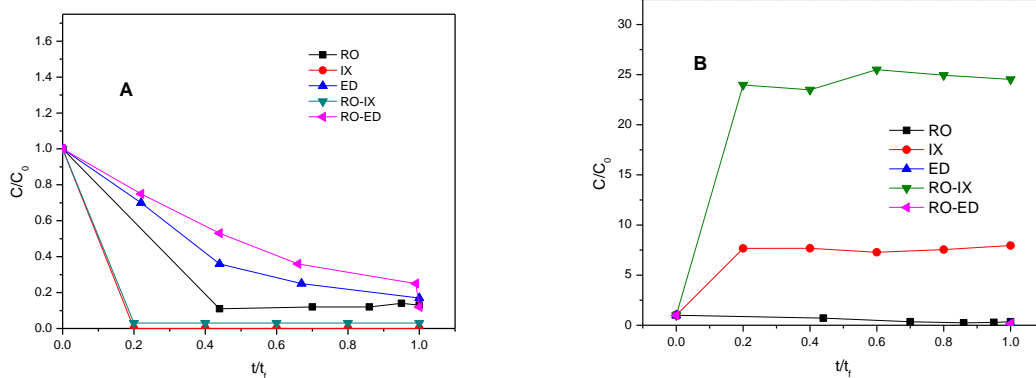
$Q_i$  = Flow in,  $Q_p$  = Flow permeate,  $Q_r$  = flow Reject,  $V_i$  = Volume in,  $V_o$  = Volume out.

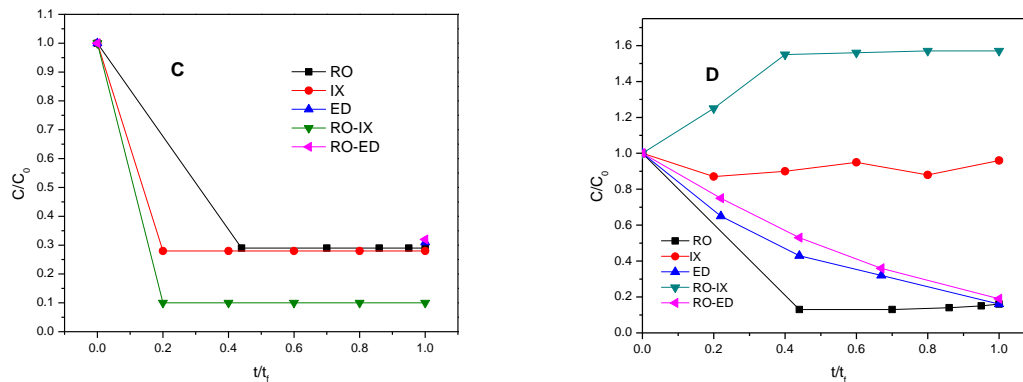
Figure 1d. Operation conditions for RO-IX



$Q_i$  = Flow in,  $Q_p$  = Flow permeate,  $Q_r$  = flow Reject,  $V_i$  = Volume in,  $V_o$  = Volume out.

Figure 1e. Operation conditions for RO-ED





**Figure 2.** Adimensional plots of concentrations Vs demineralization time: A)  $\text{NO}_3^-$ , B)  $\text{Cl}^-$ , C)  $\text{SO}_4^{2-}$ , D)  $\text{Na}^+$

**Table 3.** Characteristics of feed and product water

Parameter	Unit	Feed water	RO water	IX water	ED water	RO-IX water	RO-ED water	NOM-127-SSAI,1994
<b>Anions</b>								
$\text{NO}_3^-$	mg/L	250	32	0.25	42	6.4	44	45
$\text{Cl}^-$	mg/L	1.7	<1.0	148	2.3	233	5.2	250
$\text{SO}_4^{2-}$	mg/L	6.6	<1.9	<1.9	2.1	<1.9	3.2	400
<b>Cations</b>								
$\text{Na}^+$	mg/L	80	13	85	22	120	14	200
<b>Physicochemical parameters</b>								
TDS	mg/L	220	26.1	231	73.2	210.5	81.8	1000
pH		7.5	7.8	6.6	5.0	6.6	6.6	6.5-8.5

The characteristics of feed and product water as well as the efficiencies of each process are shown in table 3. For the operations conditions (table 2) we can notice that the order for nitrate removal is (table 4),  $\text{IX} > \text{RO-IX} > \text{RO} > \text{ED} < \text{RO-ED}$ .

3.3. Percentage of recovered water.

**Table 4.** Percentage of water recovery and Power consumption

Process	RO	IX	ED	RO-IX	RO-ED
<b>Water recovery (%)</b>	87	100	100	100	100
<b>Nitrate removal</b>	89	99	83	97	82
<b>Power consumption (KWh)</b>	0.11	0.08	0.2	0.15	0.29

The water recovery reported in literature varies depending on the investigation needs, it can be as low as 30-40% [42] and high as 91 % [43] or 100% as is our case. Indeed, under our operation conditions we found that the water recovery order is RO < IX < ED < RO-IX < RO-ED (Table 4).

Our results are in agreement with recent literature concerning nitrate removal, energy consumption and water recovery, indeed, the figures reported depend upon operating conditions. Some authors report that nitrate concentration diminish from 161 to less than 1.2 mg/L using an ED-IX hybrid system [44], the difference with our work is that they first feed the ED stack and then treat the ED dilute in a IX column, while we first treat feed water in RO then treat the RO reject by ED or IX, seeking to maximize water recovery. Indeed, Thampy et al; first feed the ED stack in an ED-RO hybrid system and report a decrease in TDS from 2000-4000 to 500 mg/L, in this case, as expected, the water recovery is only 50% due to the high TDS in feed water [45]. Our reported figures for denitrification by RO or ED individually, also agree with those reported in recent literature [46, 47].

### 3.4 Power consumption

The power consumption figures are in agreement with those reported in the specialized literature [43, 47]. The power consumption order found was IX < RO < RO-IX < ED < RO-ED (table 4).

### 3.5 Physicochemical parameters

Three parameters were followed before, during and after each process, namely: pH, total dissolved solid and temperature. The produced water pH was found to be within the Mexican allowable range of 6.5-8.5. ED was the only case with a pH bellow the standard (table 3 and fig. 3).

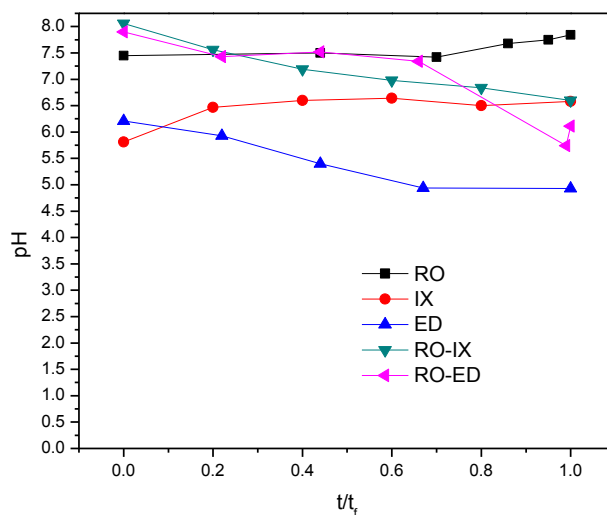
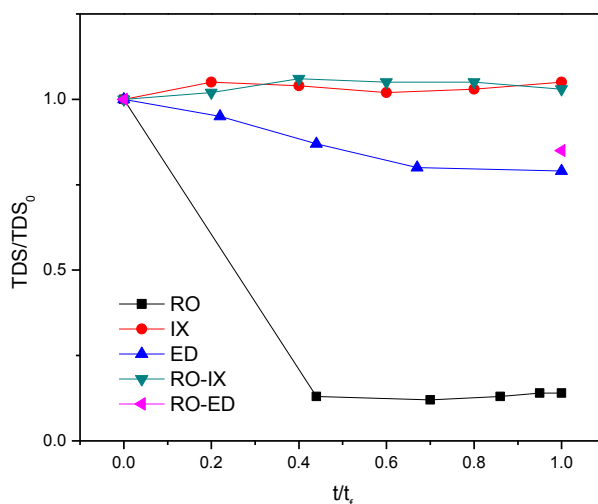


Figure 3. pH behavior for the processes tested.



Indeed, temperature remains unchanged during denitrification processes (data not shown).

Last parameter taken into account, total dissolved solids (TDS), remains almost at the initial level for IX, ED, RO-IX and RO-ED. The fact that TDS could be maintained at the same level means that we can adjust the operation parameters in order to produce water with a desirable quality. The only process, seeking for maximum water recovery, leading to a low TDS level was RO, showing an excessive demineralization that allow the production of water not suitable for human consumption (table 3 and fig. 4).



**Figure 4.** Adimensional plot of total dissolved solids behavior as function of time for the processes tested

#### 4 CONCLUSIONS

In this work, only nitrates have been left above of maximum allowed by the Mexican regulatory standard, this fact allowed us to assess the denitrification efficiency of each one of the technologies tested and to assess the behavior of the others ions presents in the water used.. The results show that we can remove the nitrates keeping the others ions at a controlled level. The level of others ions can be controlled via operations conditions.

Even if all the technologies tested remove nitrates from polluted water it is necessary to remark that we were seeking to maximize water recovery in this sense RO have well performed for denitrification nevertheless the recovery water attains only 87%. Indeed, in this case the demineralization was excessive leading to water not suitable for human consumption.

It was shown too that, at maximum water recovery, we can obtain water with desirable ions or TDS at an acceptable level of TDS for human consumption. Denitrification of water from polluted wells with the other ions below the regulatory standard is on the way.

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