
Aromas potentiality of tuna cooking juice concentrated by nanofiltration

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Abstract:

Tuna cooking juices contain high organic load preventing the rejection in the environment without treatment. But the effluents present an interesting fishy odour and it is worth recovering aroma compounds. In this work, two industrial tuna cooking juices were concentrated by nanofiltration. Nanofiltration performance was discussed in terms of permeation fluxes, organic matter retention and impact on the aromatic properties of juices.

NF sharply decreases the global intensity of juices and modifies their aromatic equilibrium. However, the main characteristics and the marine nature of juices were kept. A pre-treatment by microfiltration (MF) induces a marked increase in permeation fluxes during NF concentration while it slightly affects the aromatic properties of juice.

Keywords: Tuna cooking juice; Aromas concentration; Membrane separation; Nanofiltration; Sensory analysis

1. Introduction

Tuna is among the largest commercial canned fishery products in Tunisia. Tuna cooking juices have high organic and salt contents and cannot be rejected in the environment without treatment. As cooking juices are rich in aromas and proteins interesting food or feed sectors [Cros, Lignot, Razafintsalama, Jaouen & Bourseau (2004), Jao & Ko (2002)], processes that both reduce pollution load and recover valuable compounds are worth to be investigated.

Membrane processes have been claimed to have a good potential of development to recover valuable compounds in seafood processing industries [Massé, Vandanjon, Jaouen, Dumay, Kechaou & Bourseau (2008); Bourseau et al. (2008)]. Recovered compounds include biopolymers such proteins [Jaouen & Quéméneur (1992)] or chondroïtine sulfate [Lignot, Lahogue, & Bourseau, (2003)] and smaller organic compounds such as peptides [Bourseau et al. (2009), Chabeaud, Vandanjon, Bourseau, Jaouen, Chaplain-Derouiniot & Guérard (2009), Vandanjon, Grignon, Courois, Bourseau & Jaouen (2009)] or aromas [Vandanjon, Cros, Bourseau & Jaouen, (2002), Walha, Ben Amar, Bourseau & Jaouen (2009)]. Regarding aroma recovery, reverse osmosis RO membranes have been the most widely investigated although some studies mention the use of nanofiltration (NF) and electrodialysis (ED) [Lin & Chiang (1993), Vandanjon et al. (2002), Cros, Lignot, Bourseau, Jaouen & Prost (2005)]. RO has the advantage to retain aromas better than NF but required generally a desalination step prior to concentration [Cros et al. (2004)] that will increase significantly the production cost of the aromatic concentrate [Cros, Lignot Jaouen, Bourseau (2006)]. Indeed, juices usually contain a great amount of salts that are almost totally retained by RO membrane leading to a large increase of osmotic pressure that limit the concentration extent.

In this work, aromas were concentrated from highly salted tuna cooking juices by NF. Concentration was discussed in terms of permeation fluxes and organic matter retention and NF concentrates characterized by sensory analysis. The impact of a pretreatment by microfiltration (MF) on NF permeation fluxes and on the aromatic quality of the concentrate was studied for one juice.

2. Material and Methods

2-1- Cooking juices

Juices used in this work were provided by tow Tunisian companies (Sultan Company, Sfax, and Ecofish Company, Médénine). Juices were filtered on a 50 μm -mesh in order to remove large suspended matter and stored at -20°C within 30 days until use. Before experiments, filtered juices were thawed at 4°C overnight.

2-2- Experimental set-up

Juices were concentrated with a Microlab 40 pilot plant (VMA, Industries, Meung sur Loire, France) equipped with a NF tubular membrane made in Polyamide coated on Polyethersulfone (PCI, Ltd, ref. AFC 30, 30% retention in NaCl, length 0.8 m, inside diameter 12 mm and surface area 0.033 m^2).

MF pre-treatment of Sultan cooking juice was carried out with a Rhodia filtration unit equipped with a multi-channel (7 channels) TiO_2 , $0.1\ \mu\text{m}$ membrane (Orelis, Kerasep K01). Membrane length was 1.2 m, the inside diameter 25 mm and useful surface 0.155 m^2 .

2-3- Membrane experiments

The same MF and NF (new) membranes were used for all runs. Membranes were completely regenerated by basic and acid washings performed before each run.

MF experiments were conducted at 25°C, $2 \cdot 10^5$ Pa and $3.1 \text{ m}\cdot\text{s}^{-1}$ and NF ones at 40°C, $35 \cdot 10^5$ Pa and $2.5 \text{ m}\cdot\text{s}^{-1}$. A 4 L volume of non-microfiltered or microfiltered tuna cooking juices was nanofiltered until a VRF of 5 was reached, after a 2 h stabilization step where concentrate and permeate were recycled in the feed tank. Samples of permeate and retentate (50 mL) were recovered at the beginning and at the end of filtration to estimate initial and final retention factors. Filtration experiments were made twice for which fluxes and retention factor variations were lower than 4% and $\pm 0.5\%$ respectively. Values given in this paper are the average of values obtained in the two experiments.

2-4- Analyses

Dry matter (DM) contents were evaluated on a 5 mL sample with an infra-red dessicator SMO 01 (SCALTEC Instruments, Heiligenstadt, Germany). Mineral matter (MM) was measured by drying 20 mL of solution for 2h at $525 \pm 25^\circ\text{C}$. Organic matter OM content computed as the difference between dry and mineral matters contents was found to be correlated to Chemical Oxygen Demand (COD) contents through a linear relation:

$$\text{OM} [\text{g}\cdot\text{L}^{-1}] = 1.1657 \times \text{COD} [\text{g}\cdot\text{L}^{-1}]$$

Turbidity was measured with a turbidimeter Turb 550 IR (MTW, Weilheim, Germany). Chemical Oxygen Demand, suspended solids, Kjeldahl nitrogen (NK) and conductivity were measured according to the French association of norms (AFNOR) protocols: T90-101 (1988), T90-105-1 (1996) and T90-110-(1994), T90-111 (1975).

Sensory analyses

Samples were sniffed by a trained panel of 12 persons (between 30 to 59 years old), 6 females and 6 males, selected among the internal jury of IFREMER (Institut Français de Recherche pour l'Exploitation de la Mer). Six samples P_1 , P_2 , P_3 , P_4 , P_5 and P_6 , received in double, were stored at -80°C before analysis. The day of sensory session, distilled water and NaCl were added to the defrosted samples in order to obtain for all juices the same contents in organic ($10.1 \text{ g}\cdot\text{L}^{-1}$) and mineral ($106.6 \text{ g}\cdot\text{L}^{-1}$) matter as the microfiltered Ecofish one (sample P_1) which had the lowest content in organic matter. Indeed, sodium chloride is known to heighten flavour by its activity and to influence the flavour of the final aromatic concentrate [Freger, Arnot & Howell (2000)].

In a first sensory session, panellists were invited to describe the odour characteristics of each sample. A discussion with the panellists allowed to reach a consensus on attribute selection and their definition. Eight descriptors of odour were chosen: global intensity, fat fish, dried fish, marine/iodine like, vegetable, fruity (lemon type), rancid, sulphur odour (mud like). In a second sensory session of profiling test, panellists were required to score each descriptor on an unstructured scale anchored by the term low intensity (0) and high intensity (10). 15ml of each sample were poured in a plastic flask assigned 3 digit numbers. Samples were let one hour at 18°C before to be served and then randomized to the panellists. The tests were realized in individual booths equipped with a micro-computer using a data acquisition software (Fizz, Biosystems, Couternon, France). Analysis of variance was performed by ANOVA procedures in two factors (judges, products) on data provided by judges. Significant differences between means were determined using Duncan's multiple range test ($P < 0.05$) [Meilgaard, Civille & Carr (1991)].

2.1. 2-5- Calculation of performance indicators for NF concentration

Volume reduction factor (VRF), concentration factor (CF) in chemical oxygen demand (COD), observed retention factors (RF) at the beginning (initial), the end (final) and on average over the filtration (mean) were calculated as:

$$\text{VRF} = V_0 / (V_0 - (V_p + V_{pf})) \quad (1)$$

$$\text{CF} = C_R / C_0 \quad (2)$$

$$\text{RF}_i = 1 - C_{pi} / C_0, \text{RF}_m = \text{Ln CF} / \text{Ln VRF}, \text{RF}_f = 1 - C_{pf} / C_R \quad (3, 4, 5)$$

where V_0 , V_p and V_{pf} were respectively the volumes of the filtered (feed) solution, the sample of average permeate over the filtration and the final permeate; C_0 , C_{pi} , C_{pf} and C_R were the mass concentrations (in COD) of the feed solution, the initial permeate, the final permeate sample and the concentrate recovered after filtration. VRF, CF and RF_m are global indicators on the whole extent of the separation; the comparison of the initial, mean and final retention factors gives information on the drift in COD retention during the filtration. Precisions of mass balances on each solute were quantified by the relative error ε expressed as:

$$\varepsilon (\%) = (V_0 \cdot C_0 - (V_p \cdot C_p + V_{pf} \cdot C_{pf} + V_R \cdot C_R) / V_0 \cdot C_0) \times 100 \quad (6)$$

3. Results and discussion

3-1- Characterization of tuna cooking juices and effect of the microfiltration pretreatment.

Physico-chemical characteristics of the two juices (before sieving) are presented in table 1. Juices had different contents in COD (23.5 and 12.1 g.L⁻¹ for Sultan and Ecofish juices respectively). Their salt concentration, mainly due to sodium chloride NaCl, were very high (MM > 100 g.L⁻¹). High juices turbidity was significantly reduced by the 50 μm -mesh sieve filtration by (e.g. the turbidity of the filtered Sultan juice was lowered by about 60 % from 496 to 185 NTU).

Processing the filtered Sultan cooking juice by MF results again in a strong decrease in turbidity (from 185 to 2.7 NTU) proving that the MF step clarified juices efficiently.

3-2- Concentration by nanofiltration

NF concentration was carried out on the three juices (non micro-filtered Sultan juice, microfiltered Sultan and Ecofish juices). For all juices, results are encouraging insofar the permeation flux decreased only smoothly with VRF and kept satisfactory value until a VRF of 5 (see Fig. 1). Final permeation fluxes for microfiltered and non-microfiltered Sultan juices were respectively 80 and 30 L.h⁻¹.m⁻², indicating again that the MF pretreatment was effective.

MM contents in permeates, retentates and raw juices are close together for the three juices as monovalents salts are weakly retained by the AFC 30 membrane (see Table 2). The high COD contents in permeates indicates that a significant amount of organic matter permeated through the NF membrane. These results are in agreement with those of [Lin & Chiang (1993)] who showed that shrimp flavours were not retained by loose RO, i.e. NF membrane.

Mass balances for dry, mineral, organic matters and COD were fulfilled for the three juices within a maximum error of 6.6 % so that performances indicators computed can be considered as accurate (see Table 2). For the three juices, similar concentration factors (CF) were obtained and retention factors RF seems to increase very regularly. Rise in RF can be attributed either to membrane fouling or to the development of a concentration polarization

layer (CPL) at the membrane surface. As the mean value over the concentration RF_m was systematically closer to the initial factor RF_i than to the final one RF_f , it can be supposed that membrane fouling or CPL establishment was more important at the end of filtration than at the beginning.

3-3- Sensory evaluation

Table 3 gives the panel average score of each sample for each smelling feature. The samples were significantly distinguished each others by the four following criteria: the global intensity and the marine/iodized, fruity and rancid smells. The samples P_5 , P_1 and P_3 had a global intensity stronger than the others whereas P_5 and P_6 developed the strongest marine smell, P_5 having also a rancid associated smell. P_1 was rather particular because it presented a marked, qualified smell of fruity (lemon type). Principal component analysis (PCA) was performed on the means of the sensory scores to bring out the main features of each sample and allow a synthetic representation of what the panel perceived. The first axis is mainly defined by the descriptors "fat fish", "dried fish", "rancid" and "global intensity" and the criteria "marine / iodine", "fruity" and "vegetable" mostly involved in the creation of the second axis. This first plane accounts for 71.7% of inertia.

The most intense products in smell, the Sultan juices (P_3 , P_5) were grouped on the right hand side of Figure 2. Sultan juices exhibited also rancid notes probably connected to their fat content. The Ecofish juice P_1 that presented very characteristic fruity (lemon type) notes was located in the zone defined by the fruity smell. Nanofiltrate samples (P_2 , P_4 and P_6) were characterized by a weaker smell intensity and a little more perceptible marine smell were located on the left hand side of Fig.2.

Regarding the impact of the prefiltration processes on the aromatic properties, the most significant fact is that NF decreased sharply the global intensity of juices (at same contents in salts and in organic matter), what can be attributed to the fact that NF eliminate volatile, small-sized molecules (under 400 daltons) responsible of the pungent odour. The decrease in global intensity of odour modified deeply the odour characteristic of juices. Certain notes which were masked by deeply odours can be revealed in this way, the marine note in particular. However, the global characteristics and the marine nature in particular are preserved. Finally, it seems that the NF decreased also the rancid note.

4. Conclusion

This paper dealt with the concentration of aromas in highly salted tuna cooking juices by a one-or two steps nanofiltration (NF) process. The concentration was performed by direct nanofiltration- until a significant VRF (5) by keeping reasonable permeation fluxes and with retention factors in inorganic matters ranging from 70 to 76 %. The global intensity of juices was found to sharply decrease by NF concentration. Consequently, the aroma properties of juices were modified, but global characteristics and the marine note in particular was preserved.

In addition, a pretreatment by a 0.1 μm microfiltration has allowed increasing markedly NF permeation fluxes, final flux at VRF 5 ranging from 90 to 100 $\text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ($35\cdot 10^5$ Pa, 2.5 ms^{-1} and 40 °C).

These results are encouraging as for the concentration of marine aromas contained in highly salted seafood cooking juices at industrial level, either by a one-step NF process or a two-steps process including in a MF pretreatment before NF concentration. The interest of the MF pretreatment should however be evaluated through an economic evaluation balancing the gain in permeation fluxes (and thus in NF membrane area) and the presence of this additional operation.

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Symbols and abbreviations

CF: concentration factor

C_0 : mass concentration (in COD, DM, OM or MM) of the solution filtered

C_{Pf} : mass concentration (in COD, DM, OM or MM) of the final permeate sample

C_{Pi} : mass concentration (in COD, DM, OM or MM) of the initial permeate sample

C_R : mass concentration ((in COD, DM, OM or MM) of the concentrate recovered after filtration

NK: Nitrogen content

NF: nanofiltration

P_1 : microfiltered Ecofish juice

P_2 : concentrate Ecofish

P_3 : microfiltered sultan juice

P_4 : concentrate Sultan

P_5 : Sultan juice

P_6 : concentrate Sultan juice

RF_i , RF_m , RF_f : initial, mean and final retention factor

SS: suspended solids

V_0 : volume of the solution filtered

V_p : volume of the average permeate

V_{pf} : volume of the final permeate sample

V_R : volume of the concentrate

VRF: volume reduction factor

ΔP : transmembrane pressure

Tables

Table 1. Physico-chemical properties of raw tuna cooking juices (before sieving) produced by Tuna Sultan and Ecofish Companies.

	Sultan juice	Ecofish juice
pH	5.91	6.05
Turbidity (NTU)	496 ± 7	280 ± 5
Suspended solids SS (g.L ⁻¹)	2.1 ± 0.1	1.3 ± 0.1
Chemical oxygen demand COD (g.L ⁻¹)	23.5 ± 0.7	12.1 ± 0.5
Kjeldahl nitrogen NK (g.L ⁻¹)	4.0 ± 0.7	2.3 ± 0.4
Dry matter DM (g.L ⁻¹)	147.7 ± 3	121 ± 2
Mineral matter MM (g.L ⁻¹)	120.3 ± 0.5	107 ± 0.4

Table 3. Odour characteristics of Tuna cooking juices; P₁ : microfiltered Ecofish juice; P₂ : concentrate Ecofish; P₃ : microfiltered Sultan juice; P₄ : concentrate Sultan; P₅ : Sultan juice; P₆ : concentrate Sultan juice.

Odor criteria	P ₁ ⁽¹⁾	P ₂ ⁽¹⁾	P ₃ ⁽¹⁾	P ₄ ⁽¹⁾	P ₅ ⁽¹⁾	P ₆ ⁽¹⁾	F ⁽²⁾	Probability ⁽³⁾
Global intensity	6.41a	4.52b	5.86a	4.55b	6.39a	4.34b	8.01	< 0.0001***
Fat fish	2.55	2.45	3.04	2.73	3.29	2.89	0.45	NS
Dried fish	1.51	1.57	2.44	2.14	2.38	1.36	0.85	NS
Marine/iodized	1.43ab	1.68ab	0.63b	1.90ab	2.07a	2.82a	2.59	0.0358*
Vegetable	1.75	1.77	2.05	0.78	0.96	0.99	1.89	NS
Fruity (lemon type)	2.71a	0.89b	0.78b	0.30b	0.23b	0.40b	6.43	< 0.0001***
Rancid	1.26bc	0.35c	1.90ab	0.38c	2.38a	0.75c	5.81	0.0002***
Sulphur odour (mud)	0.33	0.47	0.46	0.58	0.32	0.30	0.48	NS

⁽¹⁾ Mean score (scale from 0 to 10) of sensory panel (12 persons between 30 to 59 years old, 6 females and 6 males) for each sample; different letters indicate significant differences (Duncan's multiple range test, $p < 0.05$).

⁽²⁾ Value of Fisher Test for product effect.

⁽³⁾ Significant level : NS = non significant, * = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$

Figures

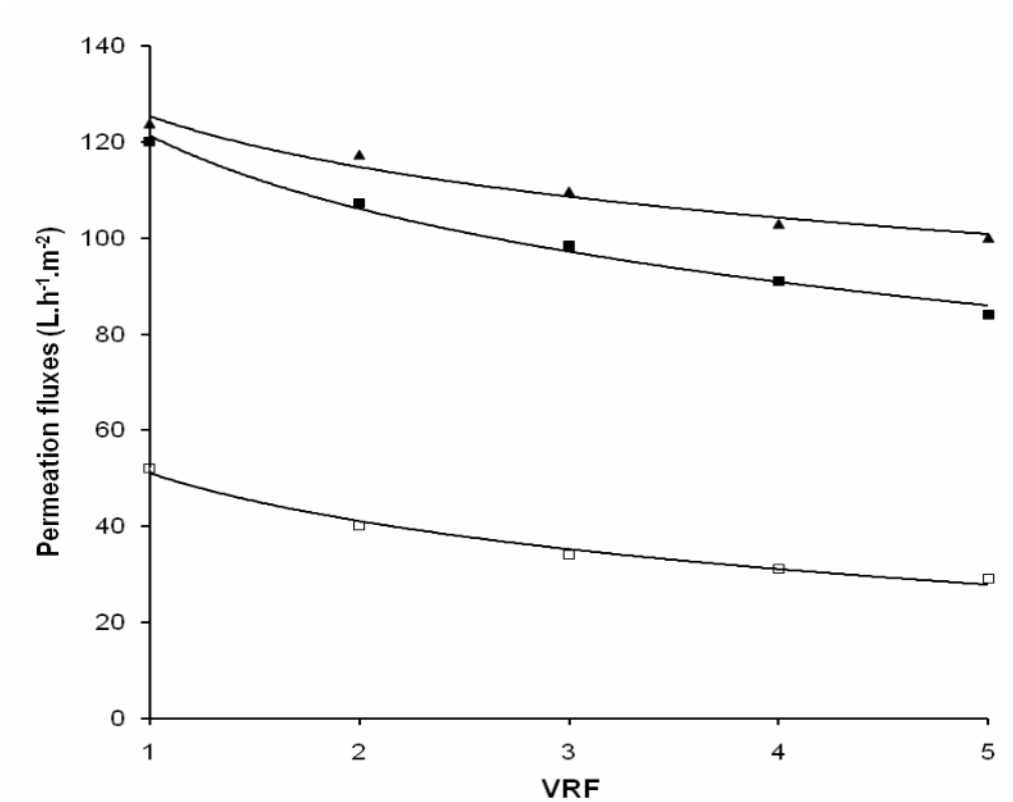


Fig.1. Evolution of flux (NF membrane AFC 30, 35.10^5 Pa, 40°C , 2.5 m.s^{-1}) versus VRF (Volume Reduction Factor). ▲: microfiltered Ecofish juice; ■: microfiltered Sultan juice; □: non microfiltered sultan juice.

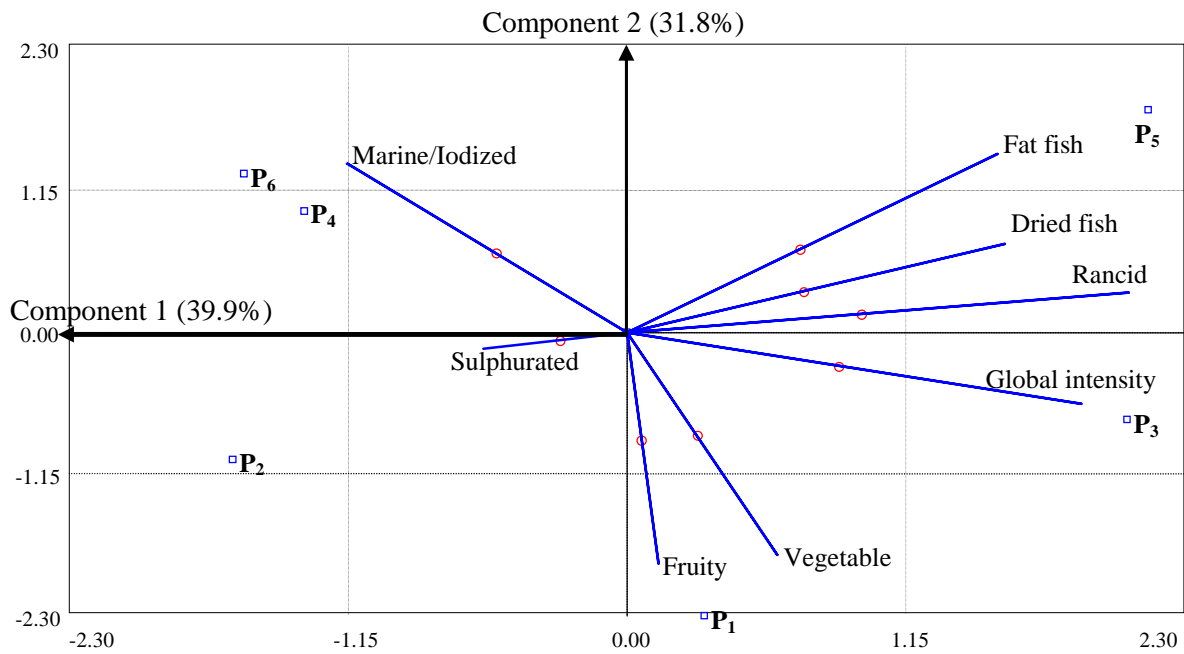


Fig.2: Simultaneous representation of products and sensory variables in the plan 1-2 of the principal component analysis. P₁ : microfiltered Ecofish juice; P₂ : concentrate Ecofish; P₃: microfiltered Sultan juice; P₄ : concentrate Sultan; P₅: Sultan juice; P₆: concentrate Sultan juice.