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OSMOTIC DEHYDRATION OF CATFISH (*Hypophthalmus edentatus*) AS A PRETREATMENT, USING TERNARY SOLUTIONS

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ABSTRACT

A central composite rotatable design was used to evaluate the osmotic dehydration process of catfish (*Hypophthalmus edentatus*) using three factors: temperature (23-57°C), NaCl concentration (11.3 – 14.7% w/w) in aqueous solutions containing 30% sucrose and immersion times from (4-14h). Five levels of each variable were chosen for the study, including the center point and two axial points. Seventeen combinations were performed, including three replications of the center point. The best processing conditions were determined using Response Surface Methodology (RSM) to maximize water loss, minimize solids gain and TBA in the use of osmotic dehydration as a pretreatment for drying. It was observed that the concentration linear term and cross products: temperature – concentration and concentration – immersion time were not significant with respect to maximizing water loss and minimizing solids gain, but all the variables and cross products were significant for TBA. The results showed that the variables had a significant influence on the responses at a confidence interval of 95%.

INTRODUCTION

Catfish is a fish, found in the Amazon region, of increasing importance in Brazil due to its low cost making it available to the low-income group. Fish is one of the most perishable foods partly because of its high moisture content. In Brazil one of the commonest methods of preserving fish is dry salting followed by sun drying, with neither control of the osmotic agent nor of the temperature, leading to problems with microbial contamination and oxidation.

These traditional processes (salting, smoking, marinating, etc.) often have a common step in which the product (meat or fish pieces) is placed in contact with a solution concentrated with solutes (salt, sugars, acids, seasonings, etc.). This unit operation is termed osmotic treatment (Collignan *et al.*, 2001)

The two most common solute types used for osmotic treatments are sugar (mainly with fruits) and salts (with vegetables, fish, meat and cheese), with relevance for sucrose and sodium chloride which show advantages already described by several authors (Lenard & Flink, 1984; Collignan *et al.*, 1994; Medina, 1998, Bohuon *et al.*, 1998 e Araujo, 2000).

Previous works have also pointed out the effectiveness in combining both solutes to obtain a maximum water loss with low solid gain by the product without significantly affecting product taste (Lenart & Flink, 1984).

The absence of an experimental plan is usually the cause of the non success in an investigation, rare are the researchers whom think about statistics before they make their experiments. Through experimentation plans, which are based on statistical principles, one can extract from the system on study the maximum of useful information, making a minimum of experiments.

The experimental design evaluate quantitatively both the variables influence on the interest responses, and their possible interactions. When the main objective of the researcher is to optimize the system, that is, to maximize or to minimize some kind of response, it is used the response surface methodology (Barros Neto *et al.*, 2001)

The objective of this work was optimize osmotic dehydration process of mapará catfish as a function of salt concentration, temperature and immersion time, using experimental design for determining the best dehydration conditions through maximum water loss with minimum solid gain et TBA, prior to drying process.

MATERIALS AND METHODS

Raw Material

It was used specie mapará catfish (*Hypophthamus edentatus*) given by EDIFRIGO localized in Santarém city in Pará state. The animals, native from rivers in the Pará state, was carried to Campinas city; previously rinsed (with chlorinated water), eviscerated, packaged and frozen at -18°C.

Osmotic Dehydration

Filets were cut, in the frozen state, in flat slab geometry (0.5cm thick and 5cm length). After cut the samples were thawed under refrigeration at 10°C for 10 hours, according Beraquet and Mori (1984). Each sample was individually weighed and placed in beakers with dehydration solution kept at process temperature. The ratio product / solution, equal to 1/5, was chosen in order to avoid significant dilution of the solution during the osmotic treatment. The whole beaker-sample was placed in a shaker TECNAL (model 421), with agitation and temperature controls. The slices were then taken out after predetermined times, quickly rinsed and dryied in absorbent paper and weighed. Moisture content was determined in vacuum oven at 70°C for 24 hours.

According with studies about temperature and solute concentration effect in the dehydration osmotic kinetic, water and solute transportation may be monitored through water loss and solid gain degree (Lerici *et al.*, 1985) which may be calculated according to Equations (1) and (2), respectively (Hawkes and Flink, 1978).

Water Loss

$$WL(\%) = \frac{MA_O - (M_t - MS_t)}{MA_0 + MS_0} \times 100 \quad (1)$$

Solid Gain

$$SG(\%) = \frac{MS_t - MS_O}{MA_O + MS_O} \times 100 \quad (2)$$

Notation:
MA_o= initial water mass (g); MS_o = initial solid mass (g);
M_t = sample mass in time t (g); MS_t = solid mass in time t (g)

TBA (Number of Thiobarbituric Acid)

The TBA values of the samples, which were dehydrated, were determined according to Talardgis and others (1960), through the distillation extraction method. The distillation was submitted to the color reaction with 2 – thiobarbituric acid and read in spectrophotometer at 532 nm.

Experimental Design

The optimum processing conditions were considered maximized water loss and minimized solids gain and TBA and were determined by using response surface methodology (RSM). A central composite rotatable design (Khuri and Cornell, 1996) was used for designing the experiments for osmotic dehydration of catfish using three factors temperature, NaCl concentration in aqueous solutions containing 30% sucrose (concentration was determined through preliminary tests) and immersion time. Five levels of each variable were chosen for study, including the center point and two axial points (Khuri and Cornell, 1996), and 17 combinations were performed, including three replications of the center point (Table 1).

Table 1 – Levels of studied variables on experimental design.

Factors	-1.68	-1	0	+1	+1.68
Temperature (°C) –X1	23	30	40	50	57
Concentration solution (%) – X2	11.3	12	13	14	14.7
Immersion time (h) – X3	4	6	9	12	14

RESULTS AND DISCUSSION

At Table 2 are shown the water loss, solids gain and TBA, obtained experimentally in the osmotic dehydration of the mapará fillet using ternary solutions of NaCl+Sucrose, also is shown the ratio SG/PA. The experimental data were obtained according to 17 combinations of the experimental plan between the independent variables: temperature, NaCl concentration and immersion time, with sucrose concentration constant at 30%.

Table 2 - Experimental data for water loss (WL) and solids gain (SG) and TBA under different treatment conditions of temperature (T), salt concentration (NaCl) and immersion time (t).

	Codified			*Real*			*Answer*			
	X1	X2	X3	T (°C)	NaCl (%)	t (h)	PA (%)	SG (%)	TBA (mg Mal. /1000 g)	SG/PA
1	-1	-1	-1	30	12	6	12.9917	15.2146	0.0295	1.1711
2	+1	-1	-1	50	12	6	26.9553	13.8908	0.1324	0.5153
3	-1	+1	-1	30	14	6	14.2121	11.2162	0.1148	0.7892
4	+1	+1	-1	50	14	6	31.7322	10.3341	0.2332	0.3257
5	-1	-1	+1	30	12	12	25.3199	13.8444	0.1800	0.5468
6	+1	-1	+1	50	12	12	35.6687	9.9684	0.7700	0.2795
7	-1	+1	+1	30	14	12	22.7791	27.9970	0.2294	1.2290
8	+1	+1	+1	50	14	12	35.3321	14.7393	0.8844	0.4172
9	$-\alpha$	0	0	23	13	9	18.1446	19.5807	0.1085	1.0791
10	$+\alpha$	0	0	57	13	9	38.8231	9.1299	0.7960	0.2352
11	0	$-\alpha$	0	40	11.3	9	23.2694	11.1189	0.2300	0.4778
12	0	$+\alpha$	0	40	14.7	9	24.9771	14.1227	0.4900	0.5654
13	0	0	$-\alpha$	40	13	4	15.7834	14.5964	0.0100	0.9248
14	0	0	$+\alpha$	40	13	14	29.7409	17.2326	0.6100	0.5794
15	0	0	0	40	13	9	28.5638	10.0398	0.4100	0.3515
16	0	0	0	40	13	9	28.6492	11.7237	0.4300	0.4092
17	0	0	0	40	13	9	28.7863	10.4453	0.4427	0.3629

Comparisons between the real and the codified plans were made and observed that there was no difference between them about the significant factors, so it was opted to work with the codified plan.

The effects of the linear and quadratic factors and of the interactions in the water loss and solids gain, also the error, the statistical significance (p), can be observed at Tables 3 and 4. These values were determined through the pure error and by the SS residual, respectively. The values in bold type present significant values at $p \leq 0.05$.

Table 3 – Estimate effects for water loss and solid gain obtained through error

	WL			SG			TBA		
	Effect	**Pure error**	**P**	**Effect**	**Pure error**	**p**	**Effect**	**Pure error**	**P**
Main effect									
Temperature (L)	**13.0636**	**0.0608**	**0.0000**	**-5.4082**	**0.4758**	**0.0077**	**0.3842**	**0.0089**	**0.0005**
Temperature (Q)	0.1936	0.0670	0.1017	**2.6223**	**0.5242**	**0.0377**	-0.0044	0.0098	0.6998
Concentration (L)	**0.8778**	**0.0608**	**0.0048**	**2.4060**	**0.4758**	**0.0370**	**0.1153**	**0.0089**	**0.0059**
Concentration (Q)	**-2.8964**	**0.0608**	**0.0005**	1.3933	0.5242	0.1171	**-0.0697**	**0.0098**	**0.0193**
Time (L)	**8.3046**	**0.0670**	**0.0000**	**2.9788**	**0.4758**	**0.0246**	**0.3755**	**0.0089**	**0.0006**
Time (Q)	**-3.8609**	**0.0680**	**0.0003**	**2.7273**	**0.5242**	**0.0192**	**-0.1052**	**0.0098**	**0.0086**
Cross product									
Temp-Conc	**1.4402**	**0.0794**	**0.0030**	-2.2350	0.6214	0.0694	0.0201	0.0117	0.2264
Temp-Time	**-2.1455**	**0.0794**	**0.0014**	**-3.7320**	**0.6214**	**0.0266**	**0.2559**	**0.0117**	**0.0021**
Conc-Time	**-2.2187**	**0.0794**	**0.0013**	**-6.6197**	**0.6214**	**0.0087**	-0.0056	0.0117	0.6796

L: linear; Q: quadratic

Table 4 – Estimate effects for water loss and solid gain obtained through SS residual

	WL			SG			TBA		
	Effect	**SS residual**	**p**	**Effect**	**SS residual**	**P**	**Effect**	**SS residual**	**p**
Main effect									
Temperature (L)	**13.0636**	**0.3738**	**0.0000**	**-5.4082**	**0.9367**	**0.0007**	**0.3842**	**0.0247**	**0.0000**
Temperature (Q)	0.1936	0.4119	0.6526	**2.6223**	**1.0319**	**0.0386**	-0.0044	0.0272	0.8767
Concentration (L)	**0.8778**	0.3738	0.0512	**2.4060**	**0.9367**	**0.0371**	**0.1153**	**0.0247**	**0.0023**
Concentration (Q)	**-2.8964**	**0.4119**	**0.0002**	1.3933	1.0319	0.2190	**-0.0697**	**0.0272**	**0.0373**
Time (L)	**8.3046**	**0.3738**	**0.0000**	**2.9788**	**0.9367**	**0.0155**	**0.3755**	**0.0247**	**0.0000**
Time (Q)	**-3.8609**	**0.4119**	**0.0000**	**2.7273**	**1.0319**	**0.0086**	**-0.1052**	**0.0272**	**0.0061**
Cross product									
Temp-Conc	**1.4402**	**0.4882**	**0.0214**	-2.2350	1.2233	0.1104	0.0201	0.0322	0.5522
Temp-Time	**-2.1455**	**0.4882**	**0.0032**	**-3.7320**	**1.2233**	**0.0186**	**0.2559**	**0.0322**	**0.0001**
Conc-Time	**-2.2187**	**0.4882**	**0.0027**	**-6.6197**	**1.2233**	**0.0010**	-0.0056	0.0322	0.8676

L: linear; Q: quadratic

Analyzing Tables 3 and 4 for water loss, it can be seen that the parameter temperature (L) has the greatest effect between all variables and significant interactions. The significant parameters temperature (L), concentration (L) and time (L) and the interaction temperature × concentration present a positive effect by the water loss, that is, an increase in anyone of these factors carries an increase in water loss; and is verified that an increase in the effects of the parameters: concentration (Q), time (Q), the interactions temperature x time, and concentration x time, means a decrease in the water loss.The effect of the temperature (Q) was not significant, both by the pure error and by the residual error.

For the responses to the solids gain, the significant effects at 95% of trust, both for the pure error as for the SS residual are: temperature (L), temperature (Q), concentration (L), time (L), time (Q), and the interactions temperature × time, and concentration × time.

It is observed that the parameters temperature (L), temperature × concentration, and temperature × time present a negative effect in the solids gain, that is, an increase in anyone of these factors carries a decrease in the solids gain, while the parameters temperature (Q), concentration (L) and (Q), time (L) and (Q), and the interaction concentration × time present a positive effect, that is, an increase in these factors results an increase in the solids gain. It is also observed that the interaction concentration × time is the one which presents the greatest effect on the solids gain.

For the TBA responses the significant factors at 95% of trust, both by the pure error and for the SS residual, are the temperature (L), concentration (L), concentration (Q), time (L), time (Q), and the interaction temperature × time. Now, the temperature (Q), the interactions: temperature × concentration, and concentration × time present values for p much high ($p \geq 0.20$), therefore, they are not considered as significant. It was also verified that the factors which have more effect on the answer are the temperature (L) and time (L), and that along with concentration (L) and interaction temperature × time, have a positive effect on the responses, that is, the oxidation is as high as the variables effects, while that the others effects of the significant variables, concentration (Q), and time (Q), have a negative effect on the answer, that is, with an increase in anyone of these factors, lower the number of thiobarbituric acid (TBA).

It was also noticed trough tables 3 and 4 that the concentration (L), for the water loss, which has significant effect by the pure error and not significant in level at 95% of trust by the residual error, but which is significant at 94.88% of trust, as well as the interaction temperature × concentration for the solids gain (SG), analyzed by the pure error and by the SS residual, presented a p equal to 0.07, and 0.11 respectively, meaning that p is inside the trust limit of 93% when analyzed by the pure error and of 89% by the SS residual, for this reason would not be convenient discard them.

Table 5 – Variance Analysis of the codified model fitted for the TBA in osmotic dehydration of the mapará fillets without NaCl solution.

	Water Loss				*Solid gain*				*Ftab*	*TBA*				
Variation Source	**FD**	**SM**	**Fcal**	**R^2**	**FD**	**SM**	**Fcal**	**R^2**	***WL-SG***	**FD**	**SM**	**Fcal**	**Ftab**	**R^2**
Regression	8	113.03	262.67	0.99	8	39.50	11.97	0.92	3.44	6	0.1851	123.4	3.22	0.98
Residue	8	0.43			8	3.30				10	0.0015			
Lack of fit	6	0.57	45.20		6	4.13	5.35		19.33	8	0.0019	7.6	19.37	
Pure error	2	0.01			2	0.77				2	0.0003			
Total	16				16					16				

In agreement with table 5 for the water loss, the correlate coefficient (R^2) was 0.99 pointing that the model explained 99% of the variation of the data observed. The model computed an F 76.36 times superior to the table of F and an significant lack of fit in the same level of trust (F computed superior to the table of F), due to the good repetition of the central points.

For the solids gain it is observed that the model presented significant regression with R^2 equal to 0.92, pointing that the model explained 92% of the variation of experimental data. The lack of fit was not significant (Fcal fewer than the Ftab), however the model can not be considered predictable, as the Fcalculated (Fcal) from the regression was 3.5 times greater than the F in the table (Ftab). According to Box e Wetz (1973), for a regression to be significant not only statistically, but also to be useful for predictive purposes, the value of the Fcal for the regression must be, at least, four to five times greater than Ftab and the F of the lack of fit about the pure error, on the contrary, should present the minimum possible value, for a high F points that there is a great lack of fit of the data to the model.
The result of the analysis for the variance for TBA presented a significant regression. The value of the rate Fcal was 123.4. Comparing to Ftab (3.22), this value pointed out a significant regression and also useful for predictive ends, supported by the obtained F from the lack of fit been lower than Ftab.

The codified models, codified, proposed to represent the water loss, solids gain, and TBA in the osmotic dehydration of the mapará fillets in NaCl + sucrose solutions are the following:

$$PA(\%): 28{,}7416 + 6{,}5318T + 0{,}4389C - 1{,}4767C^2 + 4{,}1523t - 1{,}9589t^2 + 0{,}7201TC - 1{,}0727Tt - 1{,}1093Ct \quad (1)$$

$$GS(\%) = 11{,}616 - 2{,}704T + 1{,}106T^2 + 1{,}203C + 1{,}489t + 1{,}659t^2 - 1{,}118TC - 1{,}866Tt + 3{,}310Ct \quad (2)$$

$$TBA\,(\frac{mg\ malon.}{1000g}) = 0{,}428 + 0{,}192T + 0{,}058C - 0{,}034C^2 + 0{,}188t - 0{,}052t^2 + 0{,}128Tt \quad (3)$$

Notation:
T : temperature (°C)
C : concentration(%)
t : time (h)

OPTIMISATION

The Optimisation of the osmotic process of the mapará fillets had as objective to keep the features of the fish *"in natura"*, using temperature, concentration, and time which did not cause many alteration in the structure of the material, through the maximize of the water loss and minimize of the solids gain. The rate solids gain/water loss (SG/WL) is a good indicator of the degree that the process reaches, for fewer the value of this relation greater is the water loss and fewer is the solids gain (Lazarides et al. (1995); Ravindra e Chattopadhyay, 2000).

It was observed that at high temperatures, concentration of NaCl, and dehydration time, the samples presented a dark color and aroma of oxidized product, what generate a study of the oxidization level through the analysis of TBA. The results of the TBA, along with the data of greatest water loss and fewer solids gain served as parameter of optimum for the osmotic dehydration as pretreatment for the dry process.

To optimize the osmotic dehydration of the mapará fillets with NaCl solution, was necessary to overlay and then analyze the graphics of the boundary curves of the rate SG/WL and (TBA), as show the figures 1, 2 e 3. For, in this way, there is a better visualization of the optimum region at study.

In the figures 1, 2 e3 the graphic of SG/WL is represented through areas, while the graphic of TBA, its areas are delimited through the lines.

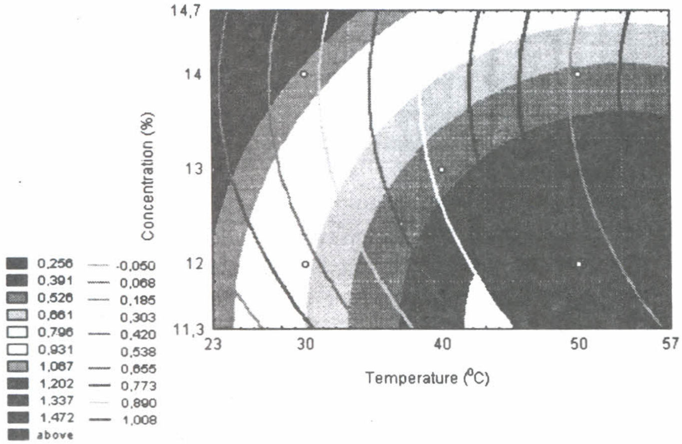

Figure 1 – overlay of the boundary curves (SG/WL) and TBA at time of 12 hours

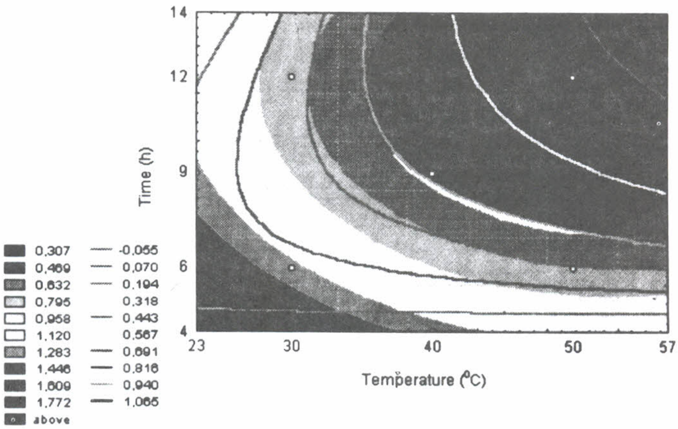

Figure 2 – overlay of the boundary curves (SG/WL) and TBA at concentration 12%

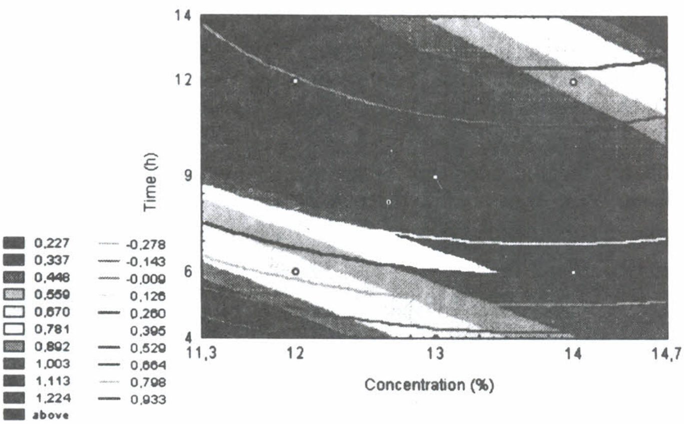

Figure 3 – overlay of the boundary curves (SG/WL) and TBA at temperature 50°C.

In the figures 1, 2, and 3 it can be observed a white region (inside the circle), considered optimum for study. At this region, the objective to obtain products with higher water loss, low solids gain and oxidization, without modifying drastically the fresh characteristics of the fish, was achieved. It was decided to work with the following optimum condition: temperature at 42°C, concentration of 11.3%, and time of 8 hours.

CONCLUSIONS

For the water loss, the correlation coefficient was 0.99 pointing that the model explained 99% of the variation of the data observed. The model computed a significant lack of fit in the same level of trust, due to the good repetition of the central points.

For the solids gain it is observed that the model presented significant regression with R^2 equal to 0.92, pointing that the model explained 92% of the experimental data variation. The regression was significant however the model can not be considered predictive.

The result of the analysis for the variance for the TBA presented a regression significant at 95% of trust. This value points a significant regression and also useful for predictive purposes.

The results showed that the variables had a significant influence on the responses at a confidence interval of 95%.

It was opted to work with the following optimum condition: temperature at 45°C, concentration of 11.3%, and time of 8 hours.

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