MNK Publication

*International Journal of Latest Research in Science and Technology* **ISSN (Online):2278-5299**
*Volume 6, Issue 2: Page No.8-13,March-April 2017*
*http://www.mnkjournals.com/ijlrst.htm*

# PHYSICOCHEMICAL AND MECHANICAL CHARACTERISTICS OF COBIA (*Rachycentron canadum*, Linnaeus, 1766) LEATHER SUBMITTED TO DIFFERENT TANNING AGENTS IN THE RETANNING STEP.

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**Abstract-*****The objective of this study was to evaluate the physicochemical characteristics and mechanical properties of leathers from cobia skin, under different tanning agents (chrome salt; vegetable tannin; synthetic tannin; vegetable + synthetic tannin) in the retanning step. No significant difference in the thickness of cobia leathers was observed. The tanning agents used in retanning did not interfere in the tensile strength determination; however retanned leathers with synthetic tannin showed significantly less resistance to progressive tearing compared to leathers tanned with chromium salts. The withdrawal direction of test bodies has not undergone influence the action of retanning to tear and traction. But, leathers subjected to retanning with vegetable tannin showed increased elasticity in the longitudinal direction (81.89%) and lowest in the transverse (29.0%). Leathers which had better physicochemical results were those prepared with vegetable tannin. Therefore, it is more interesting to the tanning of cobia skins with vegetable tannin.***

***Keywords***- cobia, skin, leather, traction and stretching, progressive tearing, leather resistance.

## 1. INTRODUCTION

Marine fish farming is a recent activity in Brazil with a great prospect of independent growth of the species of fish to be cultivated. There is already technology available for breeding, spawning, larval rearing and fattening of numerous species of marine and estuarine fish, being one of the highlights currently cobia, *Rachycentron canadum* [1]. This species has been farmed in several parts of the world, and in Taiwan are cultivated commercially in cages (networks fish tanks). However, the high investment needed for the cultivation of cobia in cages unfeasible this activity for the small fisherman and family farming in Brazil, being restricted to large investors [2].

In need to seek alternatives that enable the production of this species and targeting the production chain, is important to use all the waste generated in the post-slaughter processing. The cobia is a big fish, thick skin, flatter than the elongated head. The remaining residues from cobia processing (which the skin is present), the skin can be used in the tanning process and leather conversion for application to garments or artifacts in general.

In general, the fish skin is considered a noble, beauty, and high-quality product, possessing strength as peculiar characteristic. In addition to this characteristic, for species of fish with scales, the lamellae protection, in the insertion of the scale [3], results, after tanning process, in a leather with typical aspect and difficult to be imitated, ensuring exclusive high patterning with visual impact [4], although currently, there are techniques in an attempt to bring the maximum of the animal's skin characteristics.

During the tanning process, the skin undergoes changes due to the use of chemicals that react with collagen fibers, giving the leather greater resistance associated with the disposition and orientation of the collagen fibers. The dermis compact collagen fibers structural arrangement as well as the thickness, it allows the skin has a high resistance to different traction forces [5]. For this reason, the skin of some fish species can be used commercially in the manufacture of various products, although it requires certain amendments in the applied techniques regarding the time or amount of certain chemicals to be used in the tanning process.

The use of the fish leather as a raw material for tanning can be applied in the manufacture of clothing, shoes, belts, handbags, wallets, watchbands, cases, folders, among others [6].Through physical and mechanical tests it is possible to confirm whether a certain fish skin is resistant, because resistance varies according to a number of factors, such as the species of fish, fish size, the composition of collagen fibers, technique tanning employed, the skin region and the leather direction (longitudinal and transversal to the fish length), type of farming, among others [6].

Nussbaum [7] reports that the most commonly used products for tanning process are chromium salts, aluminum, zirconium, and among tannins, vegetables (extracted from plants) and synthetics. Vegetable tanning is complex mixtures of many substances found in the bark, roots, leaves, and fruit; and are extracted from "barbatimão" (*Stryphnodendron barbatiman*), "angico" (*Piptadenia rigida*), "quebracho" (*Schinopsis lorentzii*), "mimosa" (*Acacia decurrens*), among others, being soluble in water [6,8]. As well as chromium, tannins can be applied in the tanning and retanning steps. Depending on the leather purpose, in the retanning step, the final and different characteristics to the leather can be given through new tanning agents action, as a tanning complementation itself, providing increased softness to the leather or a hardbound or fuller leather, with less elasticity [6].

The standard vegetable tannins have the ability to precipitate alkaloids, gelatin, and other proteins. This ability to interact with proteins was one of the factors that led for centuries its use in tanneries. The type of reaction varies with the tannin-protein ratio. Researchers have shown that the affinity of vegetable tannins for protein (collagen) is directly proportional to the size of a molecular chain of the condensed tannins. The use of tannin in tanning process has been taking the place of chromium, which is used in the tanning process, mainly the chromium (dichromates) that is highly toxic to man [9]. Thus, the fact of using the less toxic tanning agents in the retanning process promotes a reduction of its use in a tanning process. However, it is important to evaluate the quality of leather strength after the tanning process where different tanning agents were used.

Thus the objective of this study was to evaluate the physicochemical characteristics and mechanical properties of cobia leathers under different retanning techniques (chromium salts, vegetable tannin, synthetic tannin and the combination of vegetable and synthetic tannins).

## 2. MATERIAL E METHODS

### 2.1 Skin processing technique

The tanning process of cobia skins was carried out on Fish Skins Processing Laboratory, State University of Maringa, located at the Iguatemi Experimental Farm (FEI/UEM). Four kilograms of skins (previously removed from cobia) were frozen until the beginning of the experiment. The skins were submitted to the tanning process adapted from Hoinacki [8] and Souza [6] using the following steps: pre-soaking, fleshing, soaking, liming (1% lime, 8% Dermaphelplus® for 3h), deliming, purge, degreasing, pickling, tanning (8% Chromosal B) neutralizing, retanning (different treatments), dyeing, fatliquoring (10% Superderma GW®+GA®), drying, softening and finishing. To initiate the tanning processing, the skins were thawed at room temperature, stripped, and weighed. All units followed the same methodology until to the neutralization step. For retanning step, the leather samples were divided and each batch received one type of tanning agent (4% chromium salts; 4% vegetable tannin; 4% synthetic tannin; 2 % vegetable tannin + 2% synthetic tannin), and then followed the other steps until the completion of processing (Figure 1A, 1B).

### 2.2 Obtaining test bodies for physical and mechanical tests

The test bodies were removed from the leathers (Figure 1C) with the assistance of a rocker arm [10]. Thickness measurements [11] were performed for each sample to the traction and stretching for strength calculations [12] and progressive tearing [13]. Then the samples were taken to acclimatized environment (23± 2°C) and controlled relative humidity (50±5%), for 48 hours [14].For mechanical testing, the EMIC dynamometer was used, with the speed of 100±10 mm min-1 away between the loads. The load cell used in the dynamometer was 200 kgf. A calibration was performed by Emic-Dcame, calibration laboratory accredited by CGCRE/INMETRO under number 197.

### 2.3 Samples for chemical tests

Chemical analyses were carried out following the rules of ABNT [15]. Samples of leathers from different treatments were subjected to determination of chromium oxide - $Cr_2O_3$[16], determination of extractable substances with dichloromethane - $CH_2Cl_2$ [17], pH determination, and the difference value of pH in the aqueous extract [18].

### 2.4 Experimental design and statistical analysis

A completely randomized design was used in a 4x2 factorial scheme: four retanning techniques (4% chromium salts - Chromosal B®; 4% vegetable tannin - Weibull®; 4% synthetic tannin - SINTAC F®; 2% vegetable tannin - Weibull® + 2% synthetic tannin - SINTAC F®), two cutting directions (longitudinal and transversal) for test in relation to the fish leather length. The results were submitted to variance analysis using PROC GLM of SAS [19], and means were compared by Tukey test at 5% probability.


**Figure 1**. (A) Cobia skins in the liming step; (B) Swollen skin after the liming step; (C) Removal of test bodies from cobia leathers - longitudinal and transversal to the fish body length.

## 3. RESULTS AND DISCUSSION

The test bodies from cobia leathers had thicknesses ranging from 0.82mm to 0.96mm, but no significant difference was observed regarding the retanning substances used and direction of test bodies withdrawal (Table 1).The maximum force applied to the resistance test ranged from 48.63 to 76.04N for all tanning agents used, and the skins submitted to tanning with synthetic tannin showed the significantly lowest force value applied and the tanned leathers with chromium salts and vegetable tannin larger (73.2 N and 76.04 N respectively), without differences (P> 0.05).

When evaluated the cutting directions of test bodies leathers (longitudinal direction) a significantly higher maximum force value applied for progressive tearing (63.17N $mm^{-1}$) was observed compared with test bodies obtained in the transversal direction (53.49N$mm^{-1}$) (Table 1).The tanning agents and leather direction influence the force required to rupture the test bodies in the test for determining the progressive tearing, and may also be due to the influence of the collagen fibers distribution in relation to its organization or entanglement.

Figures 2A and 2B show the accomplishment of determining the progressive tearing, traction, and stretching of the cobia leathers subjected to different tanning agents and leather direction. The retanned leathers with synthetic tannin (45.44 N $mm^{-1}$) differed significantly only from the leathers retanned with chromium salts (66.57 N $mm^{-1}$) (Table 1). However, when evaluated the direction of removed bodies test, no significant difference in resistance to progressive tearing was observed (Table 1).

**Table 1**. Progressive tearing resistance tests of cobia leathers compared to the retanning procedure, and to the direction of test bodies cutting.

| Retanning | Thickness (mm) | Maximum force(N) | Tearing (N/mm) |
|---|---|---|---|
| Chromium | $0.96 \pm 0.39^{a}$ | $73.20 \pm 19.80^{a}$ | $66.57 \pm 20.60^{a}$ |
| Vegetable tannin | $0.82 \pm 0.29^{a}$ | $76.04 \pm 19.22^{a}$ | $59.52 \pm 13.91^{ab}$ |
| Synthetic tannin | $0.89 \pm 0.40^{a}$ | $48.63 \pm 11.10^{c}$ | $45.44 \pm 19.17^{b}$ |
| Veg +Synt tannin | $0.92 \pm 0.34^{a}$ | $63.31 \pm 10.78^{b}$ | $58.32 \pm 18.90^{ab}$ |
| CV (%) | 39.71 | 24.55 | 30.89 |
| *P* | 0.6722 | < 0.0001 | 0.0051 |
| **Direction** | **Thickness (mm)** | **Maximum force (N)** | **Tearing (N/mm)** |
| Longitudinal | $0.96 \pm 0.34^{a}$ | $63.17 \pm 16.38^{a}$ | $64.84 \pm 17.74^{a}$ |
| Transversal | $0.84 \pm 0.35^{a}$ | $53.49 \pm 21.01^{b}$ | $66.93 \pm 20.20^{a}$ |
| CV (%) | 39.71 | 30.89 | 24.55 |
| *P* | 0.1737 | 0.0254 | 0.7199 |

Means followed by the same lowercase letters in columns do not differ significantly by Tukey test (P> 0.05).

When the maximum force applied to the traction and stretching tests and elasticity (stretching test) was assessed, no interaction between the tanning techniques and direction analyzed was observed. However, for the traction test, there was no significant difference between treatments. When the leathers were evaluated in relation to the tanning procedure (longitudinal direction), the tanned leathers with chrome salts (164.72N) showed significantly greater force applied to the test, while tanned with synthetic tannin (120.6N) and with the tannin combination (121.80N) had the lowest values. For the transversal direction, the tanned leathers with the combination of tanning agents had significantly higher (126.89N) strength and for the retanned leathers with synthetic tannin (73.60N) the lowest value (Table 2).

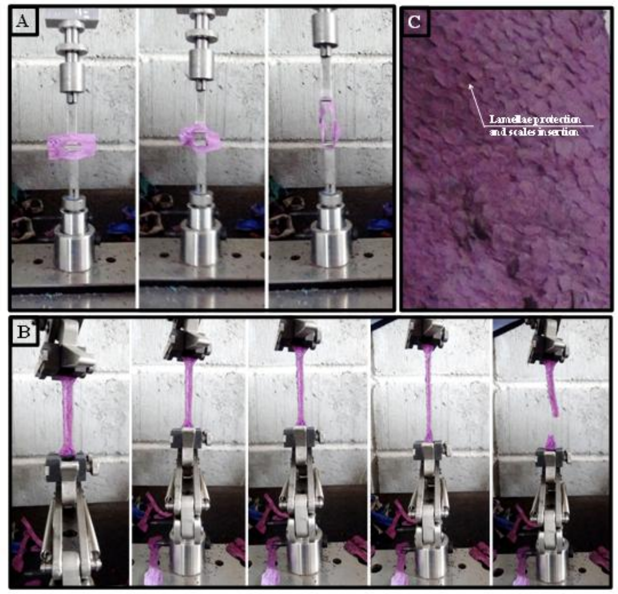


**Figure 2**. (A) Progressive tearing resistance tests for cobia leather; (B) Traction and stretching resistance tests for cobia leather; (C) Cobia leather: Lamellae protection and insertion of scales

**Table 2**. Tests to determine the traction and stretching of cobia leathers in relation to retanning and cutting direction of test bodies.

| Retanning | Maximum force (N) | | Traction(N $mm^{-2}$) | | Stretching (%) | |
|---|---|---|---|---|---|---|
| | Longitudinal | Transversal | Longitudinal | Transversal | Longitudinal | Transversal |
| Chromium | $164,72 \pm 39,4^{aA}$ | $85,50 \pm 19,5^{bB}$ | $14,95 \pm 1,9$ | $15,70 \pm 4,9$ | $71,45 \pm 25,9^{aBC}$ | $52,25 \pm 21,0^{bA}$ |
| Vegetable tannin | $150,67 \pm 43,1^{aB}$ | $73,60 \pm 22,3^{bC}$ | $13,48 \pm 7,5$ | $15,11 \pm 7,8$ | $81,89 \pm 19,4^{aA}$ | $29,00 \pm 11,5^{bB}$ |
| Synthetic tannin | $120,60 \pm 39,4^{aC}$ | $88,73 \pm 25,1^{bB}$ | $14,63 \pm 8,8$ | $13,45 \pm 5,4$ | $64,70 \pm 13,8^{aC}$ | $53,00 \pm 18,4^{bA}$ |
| Veg +Synt tannin | $121,80 \pm 39,2^{bC}$ | $126,89 \pm 38,5^{aA}$ | $15,35 \pm 6,6$ | $18,07 \pm 7,9$ | $73,40 \pm 10,5^{aB}$ | $58,90 \pm 11,2^{bA}$ |
| CV (%) | 41,74 | | 23,52 | | 14,93 | |
| *P* | 0,0258 | | 0,3577 | | > 0,001 | |

Means followed by the same lowercase/uppercase letters in columns/lines do not differ significantly by Tukey test (P> 0.05).

When evaluating the directions of test bodies within each tanning technique, it was observed that the longitudinal direction required more strength to rupture the test bodies for the leathers that used the follow tanning agents: chrome salts, synthetic tannin, and vegetable tannin. However, the transversal direction showed greater strength only for the retanned leathers with a combination or mixture of tannins (126.89 N) and the smaller strength for the leather test bodies retanned with synthetic tannin (73.6 N) (Table 2 ).Therefore, in summary, the test bodies obtained in the longitudinal direction (tanned with chromium salts) and that obtained in the transversal direction (retanned with vegetable and synthetic tannins mixture) required more strength to rupture and the lower strength was applied to the retanned test bodies with vegetable tannin in the transversal direction (Table 2).

The leathers had strength to traction ranging from 13.45 to 18.07 N $mm^{-2}$. The tanning agents and the direction of test bodies' withdrawal did not influence the traction strength (Table 2). The leathers which exhibited higher elasticity were that tanned with vegetable tannin (81.89%) and less elasticity were that tanned with the synthetic tannin (64.70%) when evaluated on longitudinal direction. The leathers, when evaluated from transversal direction, had lower elasticity values compared to the longitudinal direction, with values ranged from 29.00 to 58.90%; and from these, the leathers retanned with vegetable tannin showed lower elasticity in this direction (Table 2).Therefore, comparing the two directions of test bodies withdraw it can be seen that the cobia leathers have greater elasticity or stretching in the longitudinal direction independently of the tanning agent used in the tanning process.

Souza et al. [20] analyzed the retanning techniques (vegetable tannin; synthetic tannin; and synthetic and vegetable tannins) for Nile tilapia skins of the Nile. The tanning process was performed with 6% chromium salts and 4% tannin, and the samples were analyzed in the longitudinal direction of the body of the fish. For the tensile test and progressive tearing, the authors found no difference between the treatments, whose values were: 10.32N $mm^{-2}$ and 12.50N $mm^{-1}$; 9.27N $mm^{-2}$ and 10.27N $mm^{-1}$; 8.9N $mm^{-2}$ and 11.24N $mm^{-1}$, respectively. The results presented in Table 2 showed that the cobia leather is more resistant to progressive tearing and traction when compared to Nile tilapia leathers reported by Souza et al. [20].

In another study conducted by Souza et al. [21], analyzing Nile tilapia leathers tanned with chrome and retanned with 4% chromium salts, 6% vegetable tannin and 6% synthetic tannin, verified no significant difference in traction and progressive tearing (9.03N $mm^{-2}$ and27.91N $mm^{-1}$; 8.75N $mm^{-2}$ and 25,43N $mm^{-1}$; 8.83N $mm^{-2}$ and27.33N $mm^{-1}$, respectively). These values were also lower than those obtained in the current experiment with cobia leathers, confirming that regardless of the tanning agent percentage used in the retanning stage, the Nile tilapia leather has less resistance to these parameters compared to cobia leathers.

It is interesting that the technique used provides greater leather resistance (traction, stretching and progressive tearing), with a minimum application of chromium salts or absence of these salts. Comparing the results reported by Souza et al. [20,21] with those obtained in this experiment using cobia skin (leather), it can be inferred that in addition to the tanning agents types applied in the tanning and/or retanning, the amount applied in each step, the species is crucial to the assessment of resistance, because the architecture presents in the layout and orientation of collagen fibers determine the greater or lesser resistance to leather after processing.

Franco et al. [22] conducted an experiment of comparison the resistance of leathers from Nile tilapia (*Oreochromis niloticus*), "pacu" (*Piaractus mesopotamicus*) and "tambaqui" (*Colossoma macroporum*). The authors used 3% sodium sulfite and 3% lime (liming process), 6% chromium salts (tanning process), 2% vegetable and 2% synthetic tannin (tanning process) , and 9% oils (fatliquoring process). The authors reported that the Nile tilapia, "pacu" and "tambaqui" leathers presented, respectively 0.68mm, 0.82mm,and 0.89mm of thickness, and when measured resistance of these leathers, the "tambaqui" showed greater traction (29.494$Nmm^{-2}$) and progressive tearing (80,01$Nmm^{-1}$); and for Nile tilapia the lowest of progressive tearing (40.1$Nmm^{-1}$). However, the leather with the highest elasticity was from "pacu". Comparing these results with those obtained for cobia leather, note that the thickness of "pacu" and "tambaqui" was similar to this experiment (Table 1). Already, comparing the three species reported by Franco et al. [22] using vegetable and synthetic tannin during the retanning process (in the same percentage used for cobia leather),the greater resistance to traction (11.86 N $mm^{-2}$), stretching (52.63%) and progressive tearing (40.18 N $mm^{-1}$), was observed only for the Nile tilapia leather.

Hilbig et al. [23] evaluated the Nile tilapia leathers tanned with 10% vegetable tannin and retanned with 1% synthetic tannin and 2% vegetable tannin. The leathers showed the thickness of 0.99 mm for longitudinal direction and 0.88 mm in the transversal direction, being close to the cobia leather thickness analyzed in this experiment. These authors also reported that Nile tilapia leathers had higher resistance to traction in the transversal (height of fish) direction compared to the longitudinal (length of fish) direction (20.94 and 10.87 N $mm^{-2}$, respectively). The leather elasticity in the longitudinal direction was higher (94.46%), while the leather direction did not influence the progressive tearing (54.13 and 58.62 N $mm^{-1}$ for longitudinal and transversal, respectively). These results differ only to the cobia leather traction that in this species no difference was observed for traction, comparing to the direction of test bodies withdrawal. For the elasticity of cobia leather, it was also greater for the longitudinal direction and no significative difference for progressive tearing as to the direction of test bodies withdrawal (Tables 1 and 2). However, the values obtained for tear were superior and lower for the elasticity comparing to Nile tilapia leather.

Franco et al. [22] evaluated the salmon leather tanned with 2% sodium sulfide and 2% lime (liming process), 6% and 4% chromium salts (tanning and retanning process, respectively); and 10% oil (fatliquoring process). The salmon leathers had a thickness of 0.56 to 0.78 mm and a resistance below (10.42 N $mm^{-2}$ for traction; 18.65 N $mm^{-1}$ for progressive tearing; and 60.44% stretching, analyzing the longitudinal direction of the leather) when comparing to cobia leather (Tables 1 and 2)

The retanning process with synthetic tannin provided lower resistance for progressive tearing, however, the direction of test bodies withdrawal was not influenced by the tanning agents used in the retanning step. Regardless the tanning agent used in the retanning process of cobia leathers, the results showed greater elasticity in the longitudinal direction. However, when comparing the tanning agents, the vegetable tannin provided greater elasticity in the longitudinal direction and lower elasticity in the transversal direction, comparing to other tanning agents used in this study.

According to BASF [24], the reference values for tanned leather (for clothing use) with chromium, regardless the retanning process, should be of at most 60% for stretching at the rupture (elasticity); at least 25N $mm^{-2}$ for traction or tension; and at least 35N $mm^{-1}$ for progressive tearing resistance. Based on these values (elasticity of cobia leathers), the average values were higher than the recommended by BASF [24] for retanning leathers with chromium salts (61.85%) and the mixture of tannins (66.15%). For retanned leathers with vegetable tannin and synthetic tannin values were respectively 55.44% and 58.85%, within the indicated by BASF [24].

When comparing the average for traction strength values obtained on retanned leathers with various tanning agents, these were lower, ranging from 14.04 to 16,71N $mm^{-2}$, (independent of the direction and the leather technique) to BASF [24] reference, and for the progressive tearing, the average value obtained (independent of retanning technique, i.e., the tanning agent used in retanning and the direction of test bodies cutting) was 65.60 N $mm^{-1}$, and much higher than recommended by BASF [24].Therefore, according to the recommendations for leathers applied in clothing, the cobia leather could be used for manufactured goods in general by not showing enough resistance for traction (suitable for clothing), except if a linning together the leather, at the desired clothing manufacturing, which would help in the final resistance.

The physicochemical results for cobia leathers are presented in Table 3. The treatment which was used chromium salts, the chromium oxide content observed in cobia leather was higher (3.5%) compared to the other treatments; and should be related to the proportion of these tanning agents fixed in the collagen fibers.

**Table 3**. Physicochemical results for cobia leathers.

| Retanning | Chrome Oxide $Cr_2O_3$ (%) | pH | Differential cifra | Dichloromethane extractable substances (%) |
|---|---|---|---|---|
| Chromium | 3.5 | 3.7 | 0.4 | 16.5 |
| Vegetable tannin | 1.3 | 3.5 | 0.5 | 18.0 |
| Synthetic tannin | 1.2 | 4.0 | *** | 11.5 |
| Veg +Synt tannin | 1.2 | 3.7 | 0.4 | 17.2 |

*** Differential cifra only acts as a criterion for the presence of free strong acids or bases in the aqueous extract with pH < 4.0 or pH > 10.

According to Hoinacki [8], the minimum value of chromium oxide in the unfinished leather should be 3.0%, but, according to BASF [24], the amount of chromium oxide on the leather should be above 2.5%.The quantitative analysis of chromium oxide in cobia leathers, treated with chromium salts indicated that the leathers showed the ability to withstand high temperatures and physical and mechanical resistance. In this treatment, 8% chromium salts (in tanning step) and another 4% (in the retanning step) were added, while in the other treatments only 8% of chromium salts (in tanning step) was used, and in retanning step 4% vegetable tannins, 4% synthetic tannins, and the mixture of vegetable and synthetic tannin (4%) were used. The pH ranged from 3.5 to 4.0 among treatments (Table 3). The best pH value should be around 3.5, where the dye and oil fixing is better during the fatliquoring stage. In this experiment, the retanned leathers with vegetable tannin showed higher pH (within the recommended), but the better condition for better fixation of the retanning agent (vegetable tannins), dye and oils. Regarding the differential cifra, in the pH 4.0, there was no formation of free strong acids in the samples evaluated. For treatment with chromium salts and synthetic + vegetable tannins, the value was 0.4 and for vegetable tannin was 0.5, due to the final pH of the leathers at the time of fixing or addition of formic acid.

Due to the tanning process, the leather pH usually presents acid; however, an excessive amount of acid inside the leather can cause problems. The aqueous extract of ground leather pH is determined by the potentiometer which measuring the solution ionic concentration. Excessive acidity causes degradation of the protein chain, by acid hydrolysis, reducing the leather resistance [25], especially over time. According to Hoinacki [8], the minimum pH value in the unfinished leather should be 3.5 and the maximum 0.7 for differential cifra.

The cobia leather pH values were 3.5 to 4.0, suggesting that the formic acid was insufficient at the time of fixation, after fatliquoring of leathers submitted to retanning with chromium salts and vegetal + synthetic tannin; however the leather with synthetic tannin, the formic acid was much more insufficient, promoting the final pH of 4.0.

According to Flôres [26], the reduction in physical and mechanical resistance of leather can occur when the amount of acid is high (low pH) due to corrosive power on the collagen fibers. The same author mentions that excess acid in the leather structure, mainly sulfuric acid, affects the fibers by slowly destroying, generating weak leather. In addition, oxidation of metal components (such as rivets, buckles, and eyelets) placed in contact with the leather should occur, as well as cause allergy or irritation for the final user. The higher strength of the acids present in the leather, the greater impact on the leather; therefore, the pH value and quality (differential cifra) of these leather acids should be controlled.

For extractable substances with dichloromethane (i.e. the amount of fat fixed in cobia leathers), the variation was 11.5 to 18.0%, where the higher percentage was observed for retanned with vegetable tannin (Table 3). With this oil percentage fixed is possible the leathers to have higher elasticity and this can be proved in Table 2, which leathers in the longitudinal direction showed higher stretching value (81.89%). These oils act on the slip of the collagen fibers promoting the slide over each other as it is subjected to some kind of traction. Substances which are soluble in dichloromethane are all substances that can be removed from the sample by the solvent. This analysis indicates the content of oils and greases the leather. According to BASF [24] the extractable substances with dichloromethane should be at most from 16 to 18% for leather can be used in clothing manufacturing.

According to Gutterres [27], in the fat liquoring step, substances (natural and synthetic oils in aqueous dispersions) are introduced into the leather (in the wet state) and will coat the fibers and fibrils surfaces, providing these sliding and mobility. The main purpose of the fat liquoring process is to ensure the leather softness after drying process and provide greater tear and traction resistance. The design of the surfacing, according to Almeida [3] is characterized by lamellae protection and the scales insertion, forming inimitable mosaics in skin from fish scales. The design is specific characteristic to each species after tanning process and constituting a definition of each skin type, depending on the species. The cobia leather presents a very discreet flower design, i.e. with very small lamellae (Figure 2C).

## CONCLUSION

The cobia leathers should be tanned with chromium salts and retanned with vegetable tannin, taking into account the greener side of the tanning process and the results obtained;

both physical-mechanical tests (progressive tearing and stretching) as the physicochemical evaluated.

## ACKNOWLEDGEMENTS

The authors are grateful to the National Council for Scientific and Technological Development (CNPq) for financial support (CNPq Process No. 559527/2009-8 and No. 471905/2012-7) and to the Ministry of Fisheries and Aquaculture (MPA) for financial support (equipment acquisition) for Skins Processing Laboratory, State University of Maringa, located at the Iguatemi Experimental Farm (FEI/UEM).

## REFERENCES

1. Linnaeus C (1766). Systemanaturae per regna tria naturae, secundum classes, ordines, genera, species, cum characteribus, differentiis, synonymis, locis. Tomus I. Editioduodecima, reformata. Holmiae. (LaurentiiSalvii): 1-532.
2. Sanches EG, Von Seckendorff RW, Henriques MB, Fagundes L, Sebastiani EF (2008). Viabilidade econômica do cultivo do bijupirá (Rachycentroncanadum) em sistema offshore. Informações Econômicas, 38(12): 42-51
3. Almeida RR (1998). A pele de peixe tem resistência e flexibilidade? Revista do Couro, 127: 49-53.
4. Adeodato S (1995). Peles exóticas e ecológicas. Globo Ciência, 51: 56-60.
5. Junqueira LCU, Joazeiro PP, Montes GS (1983). É possível o aproveitamento industrial da pele dos peixes de couro? Tecnicouro, 5(5): 4-6.
6. Souza, M.L.R., 2007. Tecnología para procesamiento de pieles de pescados.Maringá: Eduem, Coleção Fundamentum 35: 61p.
7. Nussbaum DF (2002). O efeito dos sais de cromo de basicidade diferente. Revista Couro, 154: 62-71.
8. Hoinacki E (1989). Peles e Couros: Origens, Defeitos e Industrialização. 2ª Ed., Porto Alegre: Serviço Nacional de Aprendizagem Industrial Departamento Regional do Rio Grande do Sul, 319p.
9. Pott A, Pott VJ (1994). Plantas do Pantanal. Corumbá: Empresa Brasileira de Pesquisa Agropecuário, Centro Pesquisa Agro do Pantanal Corumbá. EMBRAPA, 320 p.
10. ABNT (2015). Associação Brasileira de Normas Técnicas. NBR 2418, Couro: Cortes de corpos de prova. Rio de Janeiro, RJ, Brazil, 2 p.
11. ABNT (2015). Associação Brasileira de Normas Técnicas. NBR ISSO 2418, Couro: Determinação da espessura. Rio de Janeiro, RJ, Brazil, 2 p.
12. ABNT (2014). Associação Brasileira de Normas Técnicas. NBR ISSO 3376, Couro: Ensaios físicos e mecânicos - Determinação da resistência à tração e percentual de extensão. Rio de Janeiro, RJ, Brazil, 5 p.
13. ABNT (2014). Associação Brasileira de Normas Técnicas. NBR ISSO 3376, Couro: Ensaios físicos mecânicos - Determinação da força de rasgamento progressivo. Parte 1: rasgamento de extremidade simples. Rio de Janeiro, RJ, Brazil, 4 p.
14. ABNT (2006). Associação Brasileira de Normas Técnicas. NBR 11057, Couro: Determinação do pH e da cifra diferencial. Rio de Janeiro, RJ, Brazil, 3 p.
15. ABNT (2015). Associação Brasileira de Normas Técnicas. NBR ISSO 4044, Couro: Ensaios químicos - Preparação de amostras de couro para análise química. Rio de Janeiro, RJ, Brazil, 2 p.
16. ABNT (2014). Associação Brasileira de Normas Técnicas. NBR 11054, Couro: Determinação química do teor de óxido crômico. Rio de Janeiro, RJ, Brazil, 2 p.
17. ABNT (2013). Associação Brasileira de Normas Técnicas. NBR 11030, Couro: Determinação de substâncias extraíveis em diclorometano. Rio de Janeiro, RJ, Brazil, 4 p.
18. ABNT (2014). Associação Brasileira de Normas Técnicas. NBR 10455, Climatização de materiais usados na fabricação de calçados e correlatos. Rio de Janeiro, RJ, Brazil, 2 p.
19. SAS Institute Inc. (2004). SAS/STAT User´sGuide, version 9.1 SAS Institute Inc., Cary, NC, USA.
20. Souza MLR, Ducatti T, Andrade MB, Godoy LC, Tozzi MAC, Cavallieri RFD, Franco NP, Silva LO (2004). Diferentes técnicas de recurtimento em peles de tilápia-do-Nilo (Oreochromis niloticus): qualidade de resistência. Ensaios e Ciências, 8(2): 195-204.
21. Souza MLR, Valdez MDCA, Hoch ALV, Oliveira KF, Matos IR, Camin AM (2006). Avaliação da resistência da pele de tilápia-do-Nilo (Oreochomis niloticus) nos sentidos longitudinal, transversal e diagonal, depois de submetida ao curtimento com sais de cromo e recurtimento com diferentes agentes curtentes. Acta Scientiarum. Animal Sciences, 28(3): 361-367.
22. Franco MLRS, Franco NP, Gasparino E, Dourado DM, Prado M, Vesco AP (2013). Análise comparativa das peles de tilápia do Nilo, Pacu e Tambaqui: Histologia, composição centesimal. Archivos de Zootecnia, 62: 21-32.
23. Hilbig CC, Fockink DH, Maluf MLF, Boscolo WR, Feiden A (2013). Resistência do couro de tilápia e composição centesimal da pele nas operações de ribeira e curtimento. Scientia Agraria Paranaensis, 12(4): 258-266.
24. BASF (2005). Vademécum do curtidor. Ludwighafe, 441p.
25. Jacinto MAC (1996). Características anátomo-estruturais da pele de ovinos (Ovis áries L.) lanados e deslanados, relacionadas com o aspecto físico-mecânico do couro após o curtimento. Jaboticabal: Universidade Estadual de São Paulo, Dissertação (Mestrado em Zootecnia) - Universidade Estadual de São Paulo, 90 p.
26. Flôres A (1997). Aspectos importantes na produção de couros wet-blue. Revista do Couro, 119: 66-70.
27. Gutterres M (2001). Distribuição, deposição e interação química de substâncias de engraxe no couro. In: Congresso da Federação Latino-Americana das Associações dos Químicos e Técnicos da Indústria do Couro, 15. Salvador. Anais... , p. 108-119.