The Kinetic Study on Potassium Persulfate Accelerated Fish Oil Oxidation-An Agreeing Conclusion on Chamois Tanning

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Abstract

The oxidation of fish oil is a type of chain reaction. The use of oxidizing agents enhances the rate of oxidation of the same. This study predominantly focuses on the role of potassium persulfate as an accelerating agent in fish oil oxidation, its kinetics, and application in rapid fish oil tanning. The use of potassium persulfate (1%) completes the fish oil oxidation within 4 days, confirmed by its kinetic studies. Chamois leathers made using potassium persulfate (1%) exhibited excellent water absorption capacity (454%). The physical parameters such as tensile strength, shrinkage temperature, surface morphology, and organoleptic properties of the experimental leather exhibit better results than control leathers.

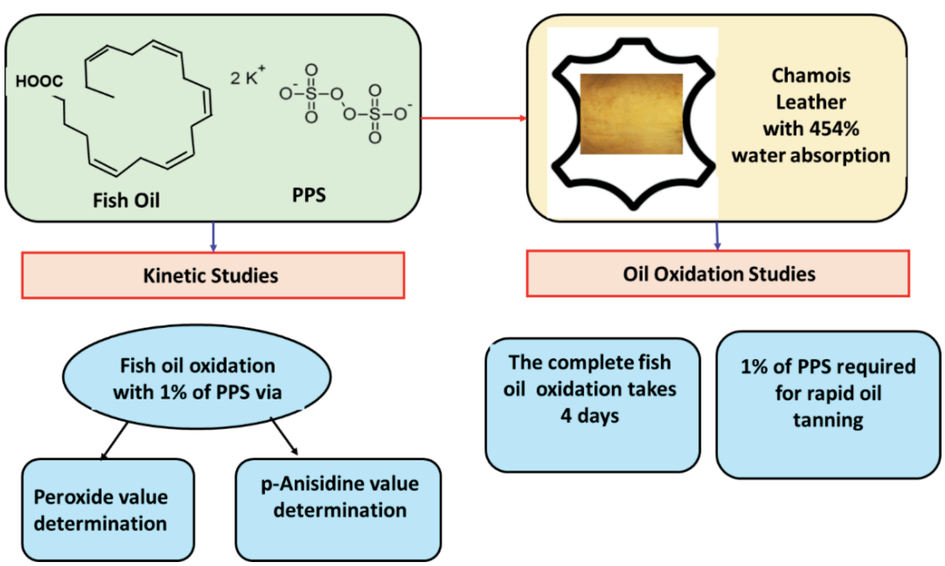
1. Introduction

The high degree of unsaturation is the foundation for the oil to be vulnerable to oxidation and other chemical reactions associated with reactions of double bonds, especially addition reactions.[1] Oil oxidation can be achieved in many ways, such as auto, thermally, photochemical, or catalytically.[2] In the case of monounsaturated fatty acids, autoxidation is performed at elevated temperatures, whereas polyunsaturated fatty acids experience instantaneous oxidation at room temperature.

The oxidation of highly unsaturated fish oil follows a free radical chain reaction where the primary oxidized products, such as allyl hydro peroxides and hydro peroxide, are prone to the formation of secondary oxidized products. These oxidized products, such as saturated and unsaturated aldehydes, short-chain ketones, alcohols, acids, esters, ethers, and hydrocarbons, can be utilized in versatile applications. The kinetic study of fish oil oxidation is determined by the Peroxide (PV) and Anisidine values (AV), which define primary and secondary oxidation products of the oil oxidation, respectively.[3-5]

Oil oxidation plays an important role in the tanning operation of leather processing, where skin protein converts into stable cross-linked

Graphical Abstract- Kinetic study of PPS accelerated fish oil tanning



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material and alters the configuration of collagen fibers. Oil tanning is one form of tanning of leather that gives highly absorbent, porous, low density, and heightened flexible leather, known as chamois leather.[6] A variety of oils have been explored for oil tanning, such as linseed oil[7], jatropha oil[8] rubber seed oil[9], oil from tannery fleshings[10], and epoxidized oil.[11,12] The most favored oil for making chamois leather is fish oil due to its high degree of unsaturation. The oil tanning takes approx. 10-12 days, depending upon ambient conditions.

Generally, antioxidants are used to prevent the oil from oxidation for various industrial uses.[13] The use of oxidizing agents to accelerate the oxidation of oil is utilized in the oil tanning process of chamois leather manufacture.

Few accelerators such as hydrogen peroxide,[14,15,16] sodium percarbonate,[17]ozone,[18] benzoyl peroxide,[6,19] benzenecarboperoxoic acid,[20] and Potassium persulfate[21] are reported with respect to the best of their activity, reaction conditions and mode of tanning.

This study investigates the influence of various percentages of Potassium persulfate (PPS) on fish oil oxidation rate and duration of the process. The current research primarily concentrates on reducing the oxidation duration from 10 days to 4 days to comprehend kinetically fish oil oxidation through peroxide and p- Anisidine values.

2. Materials and Methods

2.1 Materials

Fish oil was sourced locally in Chennai. PPS was procured from S.D. Fine Chem Ltd, Mumbai. Sheepskins were obtained from a nearby slaughterhouse. Other chemicals used for kinetic studies are obtained commercially and of analytical grade.

- p-Anisidine value measurements: p-Anisidine reagent, Acetic acid (glacial) 100%, and Iso-octane.
- Peroxide value measurements: Cyclo-hexane, 96% ethanol, 30% ammonium thiocyanate solution, 3.7% HCL, and Fe^{2+} solution.

Table I

Oil Tanning Process

Process	Chemical	Percentage (%)	Time	Remarks
Soaking	Water	300	One day	
	Preservatives	0.25		
	Wetting agents	0.50		
Unhairing and Liming	Water	20	Two days	
	Lime	10		
	Sodium sulfide (60%)	3		
Reliming	Water	300		
	Lime	10		
Fleshing				
Deliming	Water	100		
	Ammonium chloride	2	40 min	Check de-liming using phenolphthalein
	Alkaline bate	0.5	30 min	Drain
Washing	Water	200	10 min	Wash and drain
Partial pickling	Water	80		
	Salt	8	30 min	
	Formic Acid	0.5	30 min	In 1:10 dilution with water
	Sulfuric Acid	0.2		In three feeds with 1:10 dilution with water, adjust pH to 4
Depickling	Sodium bicarbonate	1		
Glutaraldehyde tanning	Glutaraldehyde	1	90 min	Drain, pile for overnight
	Soda ash dissolved	2		
Next day				
	Fish oil	25		Mix using stirrer, make paste. add to drum along with skin
	Potassium persulfate (experiment)	0.25, 0.5, 0.75,1and 1.25		
	Sodium carbonate	0.5		

*1.25% of PPS started showing patches on the skin, therefore from 0.25 to 1% of PPS only explored for the experiment

2.2 Methods

2.2.1 Method of oil tanning

After glutaraldehyde tanning, fish oil, soda ash, and Potassium persulfate are the key chemicals required for oil tanning. The mixture of a solution of 20 ml of (25% w/w ratio of sheep skin) fish oil with various percentages (0.25, 0.5, 0.75,1, and 1.25%) of Potassium persulfate and sodium carbonate (0.5%) was applied on sheep skin. The tanning process was carried out in a rotating drum approximately for 2 h. After completion of the tanning, the yellow color leathers were treated with water, soda ash, and a wetting agent to eliminate the extra oil from the experimental leathers. Further dried leathers were subjected to staking, buffing, and milling. The leather tanned only with fish oil without PPS is considered to control leather.

2.2.2 Water absorption

Chamois leather is known for its water absorption capacity. The standard method determined the extent of water absorption.[22]

2.2.3 Scanning Electron Microscope (SEM) analysis

The morphology of the leather fibers after oil tanning can be studied by SEM analysis. The analysis was carried out using Phenom Pro desktop scanning electron microscope. All leather samples were cut into 0.5X0.5 mm and mounted on sample holding stubs using a double side adhesive tape. SEM analysis was carried out at magnifications of 500x.

2.2.4 Shrinkage temperature measurement

The performance of leather towards heat is expressed by shrinkage temperature. The shrinkage temperature measurements of oil-tanned leathers were carried out by standard method.[23]

2.2.5 Physical and organoleptic properties of the chamois leather

The strength and organoleptic properties of experimental leathers were conducted as per the standard norms.[24]

2.3 Determination of kinetic study of fish oil oxidation

To determine the chemical kinetics of fish oil oxidation with and without Potassium persulfate, the following sets of experiments were carried out. The first batch of experimentations corresponds to the determination of the peroxide and p-Anisidine values of fish oil (2g) without an oxidizing agent. The next set of experiments was carried out in the presence of 1% PPS.

2.3.1 Determination of Peroxide Value

Peroxide value calculates the peroxides retained in the oil and determines this value via the iodine liberated from potassium iodide. The lipid hydroperoxides (LOOH) present in the fish oil oxidizes Fe^{+} into Fe^{3+}, which then reacts with ammonium thiocyanate to form a pink ferric thiocyanate complex. The absorbance of this formed complex is measured by using UV- spectroscopy. The absorbance of the substance is proportional to the number of lipid hydroperoxides present in the oil[25] (AOAC, 965.33).

The above procedure is repeated for the next 10 days for both the fish oil sample with and without an oxidizing agent (1% PPS), and absorbance is recorded accordingly.

2.3.2 Determination of p-Anisidine values

The p-Anisidine value (AV) is determined according to the AOCS Official Method Cd 18-90.[26]

Peroxide value (PV) and p-Anisidine value (p-AV) are used to measure the level of peroxide/hydroperoxide and secondary by-products formed during the oil oxidation. The peroxide value (PV) and p-Anisidine value (p-AV) of the oil with and without 1% of PPS are studied and compared and determine the kinetics of the fish oil oxidation.

3. Results and Discussion

The impact of Potassium persulfate on the oxidation of fish oil and its application in oil tanning is briefly discussed concerning all its physical, chemical, and organoleptic properties.

3.1 Water absorption

The intrinsic property of chamois leather is its water absorption capacity. Table II indicates the results for water absorption of experimental and control leathers. The 1% potassium persulfate shows the highest water absorption (454%) than other percentages (0.25,0.50, and 0.75). Hence, it could be inferred that 1% of PPS is sufficient for the rapid oil tanning of fish oil.

Table II

Water Absorption capacity of chamois leathers

S No	Sample	Water Absorption (%)
1	Control	375 ±20
2	Potassium persulfate(1.00%)	454 ±20
3	Potassium persulfate(0.75%)	412 ±20
4	Potassium persulfate(0.50%)	404 ±20
5	Potassium persulfate(0.25%)	378 ±20

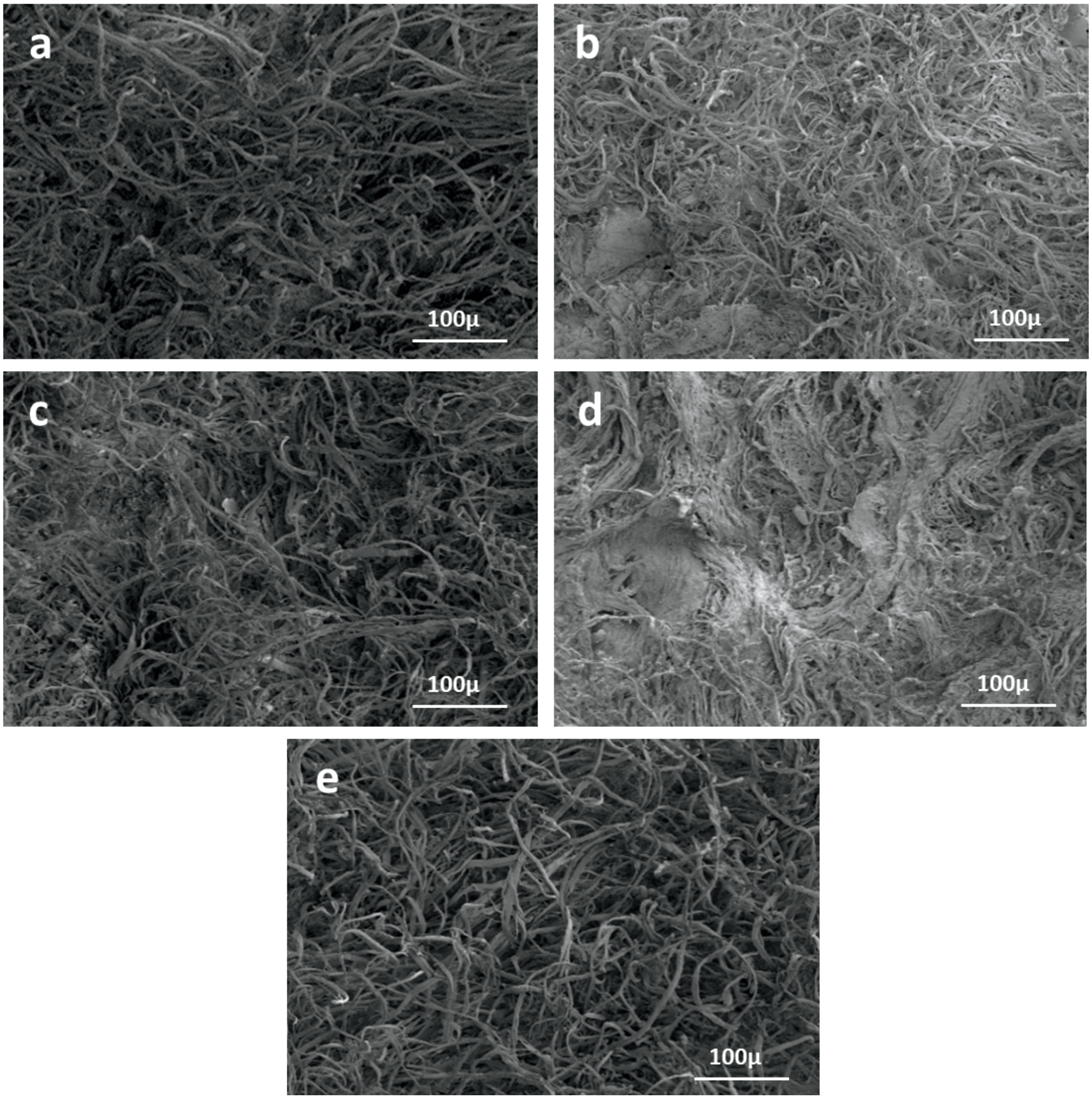

Figure 1. SEM images of chamois leather, **a)** Control, **b)** 0.25, **c)** 0.50, **d)** 0.75 and **e)** 1.0% PPS

Table III

Shrinkage Temperature measurement of chamois leather

S. No.	Sample	Shrinkage Temperature (°C)
1	Control	74±2
2	Potassium persulfate(1.00%)	78±2
3	Potassium persulfate(0.75%)	76±2
4	Potassium persulfate(0.50%)	75±2
5	Potassium persulfate(0.25%)	75±2

Table IV

Physical testing data of chamois leathers

S. No.	Sample	Tensile strength (N/mm^2)
1	Control	12.05±2
2	Potassium persulfate(1.00%)	17.69±2
3	Potassium persulfate(0.75%)	14.57±2
4	Potassium persulfate(0.50%)	13.08±2
5	Potassium persulfate(0.25%)	12.77±2

3.2 Scanning Electron Microscopy analysis of chamois leathers

The Figures 1a-e shows the morphology of the fiber structure of the oil tanned leathers. Scanning electron microscopy images of control and experimental leathers are shown in Figures 1a and 1b-e respectively. The fiber compactness in control and experimental leathers with 1% of PPS are very much aligned. Therefore, it may be inferred that the addition of 1% of Potassium persulfate will not affect the morphology of leather fiber.

3.3 Shrinkage temperature measurement

Shrinkage temperature measurement of chamois leather gives information about the resistance of the leather due to hydrothermal shrinkage. Table 3 indicates the increase in the shrinkage temperature of experimental chamois leathers obtained from 0.50% to 1% of PPS. Moreover, experimental leathers with 0.25 and 0.50% of PPS show the same and slightly higher shrinkage temperature value (75 °C) than the control values (74°C).

Table V

PV values with/without oxidizing agent

Time in days	PV value without Oxidizing Agent (meq/kg)	PV value with Oxidizing Agent (meq/kg)
1	2.807 ±0.05	5.807 ±0.05
2	5.2508 ±0.05	10.638 ±0.05
3	9.771 ±0.05	17.588 ±0.05
4	12.008 ±0.05	13.323 ±0.05
5	13.343 ±0.05	9.4248 ±0.05
6	15.7856 ±0.05	
7	17.536 ±0.05	
8	14.359 ±0.05	
9	11.221 ±0.05	
10	9.845 ±0.05	

3.4 Physical testing data of chamois leathers

Experimental leathers were tested for strength and water absorption testing. Table 4, indicates that the tensile strength of the chamois leather increased with an increase in the concentration of the potassium persulfate, which completed the oxidation of the fish oil.

3.5 Organoleptic Properties

Chamois leather organoleptic properties were evaluated for softness, color, and odor. From Figure 2, observation can be drawn that

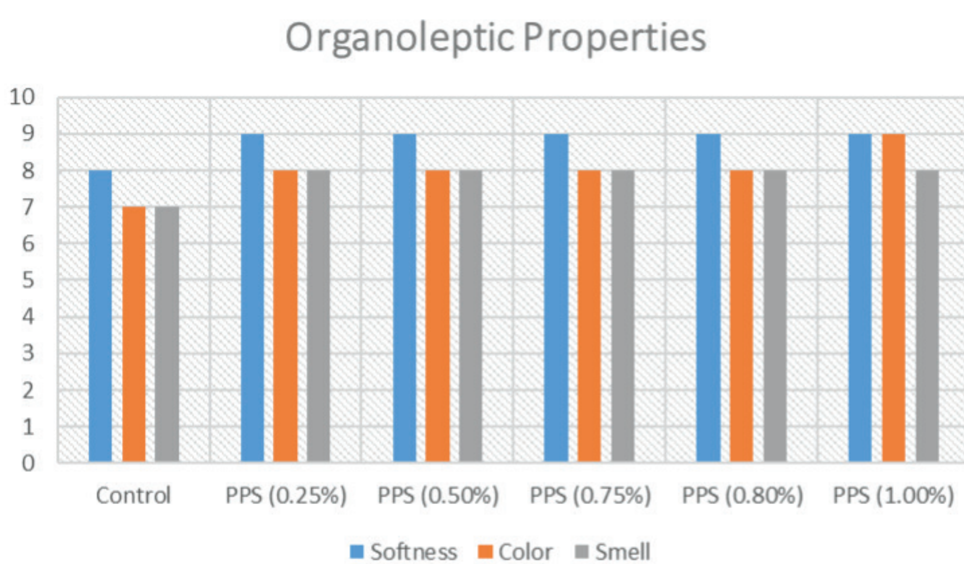

Figure 2. Organoleptic properties of chamois leathers

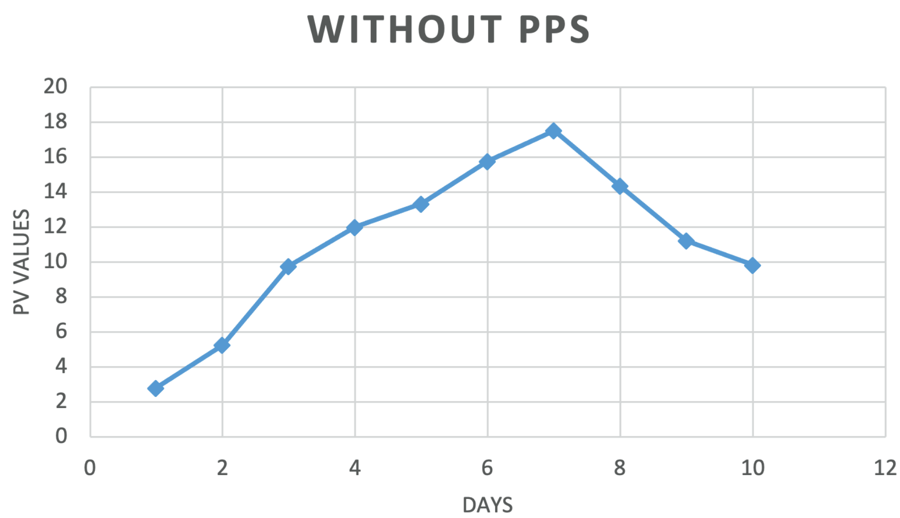

Figure 3. Peroxide values without oxidizing agent (PPS)

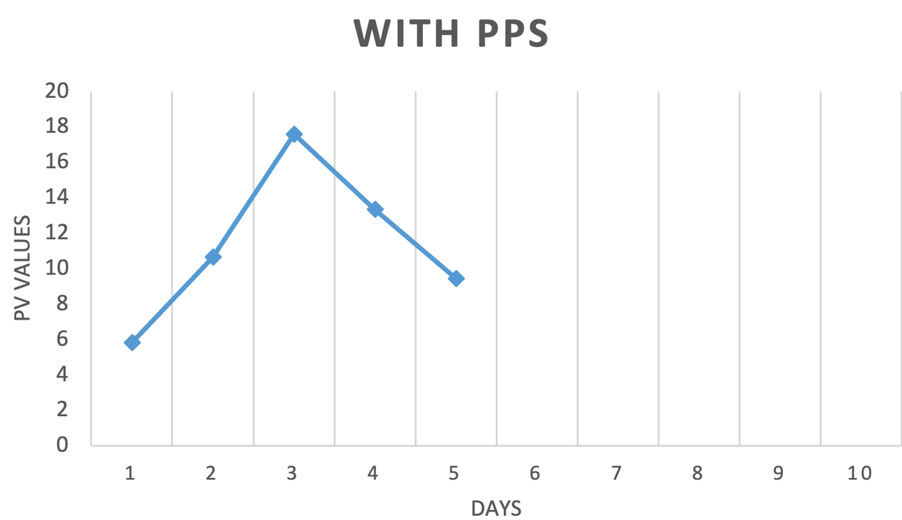

Figure 4. Peroxide values with oxidizing agent (1% PPS)

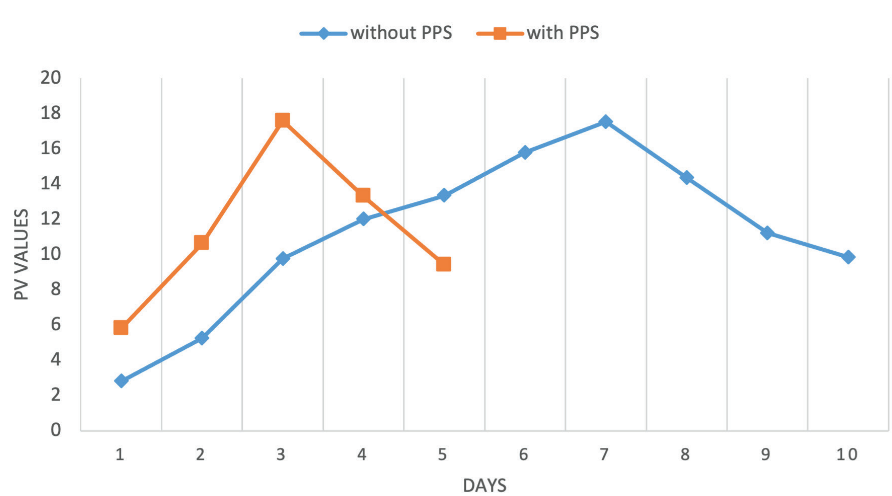

Figure 5. Comparison of peroxide values with and without PPS

the softness of chamois leathers improved with the increase in the percentage of PPS. Similarly, the color of the experimental chamois leathers with 1% potassium per persulfate showed lighter yellow than the golden yellow of the control leathers. Although chamois leathers are made using fish oil as the leading tanning agent, the odor is one of the essential qualities to assess.

4. Kinetic studies

4.1 Determination of Peroxide Values:
Figures 3 and 4 show noticeable changes in the PV value for fish oil with and without PPS. The PV values are measured with a time interval of one day for the next ten days. The fish oil without PPS exhibits an incremental growth in PV values in the initial stage, achieving maximum by the 7th day. The PV values start decreasing from the 7th day till the 10th day. This increasing and then reducing graph is due to the non-availability of a driving force for additional oil oxidation.

However, in the case of fish oil with 1% of PPS, the initial first day gives a higher value of PV till the 3rd day, where it reaches the maximum value, compared with oil without PPS. The PV starts decreasing after 3rd day, indicating a less concentration of peroxides in the system.

However, in the case of fish oil with 1% of PPS, the initial first day gives a higher value of PV till 3rd day when it reaches the maximum value, compared with oil without PPS. The PV starts decreasing after 3rd day, indicating a less concentration of peroxides in the system. The 1% of PPS is a driving force for peroxide/hydroperoxide molecules to participate in the reaction with Fe ions actively. It demonstrates that 1% of PPS improves the rate of peroxide formation, enabling the long-term stable intermediate for higher PV values. It concluded that the sample without PPS would take up to 7 days to complete the reaction. In contrast, the sample with 1% of PPS takes 3 days for the same.

4.2 Determination of p-Anisidine Values:
P-Anisidine values are necessary to analyze secondary oxidation products of fish oil oxidation with and without 1% of PPS. The secondary oxidized products of fish oil without PPS were less in concentration from day 1 to day 5 and only increased from day 6 to day 9; after that, the concentration of secondary oxidized

Table VI
p-AV values with and without 1% of PPS

DAY	PV value without Oxidizing Agent (meq/kg)	PV value with Oxidizing Agent (meq/kg)
1	0.7092 ± 0.05	0.7121 ± 0.05
2	0.9571 ± 0.05	0.9612 ± 0.05
3	0.9889 ± 0.05	7.0465 ± 0.05
4	0.9999 ± 0.05	17.7754 ± 0.05
5	10.078 ± 0.05	17.19565 ± 0.05
6	11.5012 ± 0.05	17.0783 ± 0.05
7	13.7936 ± 0.05	17.0469 ± 0.05
8	16.0871 ± 0.05	
9	17.415 ± 0.05	
10	17.2245 ± 0.05	

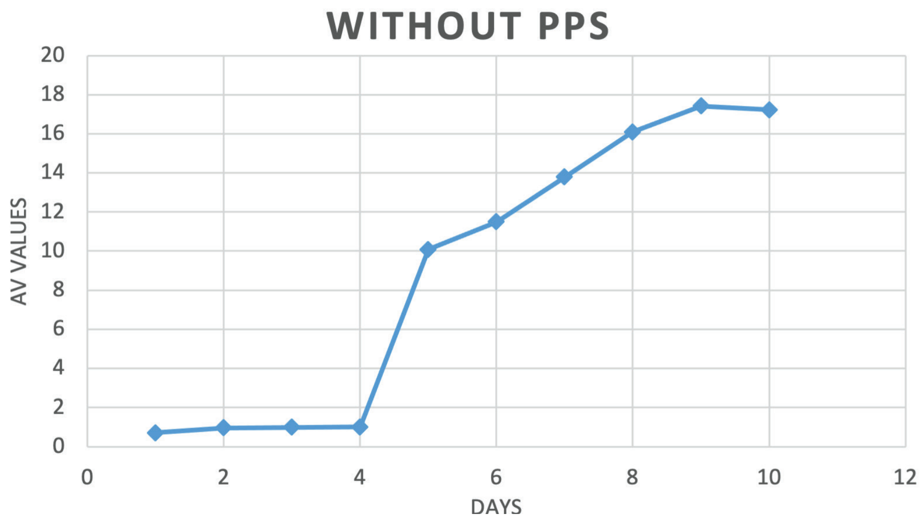

Figure 6. p-Anisidine values without oxidizing agent (PPS)

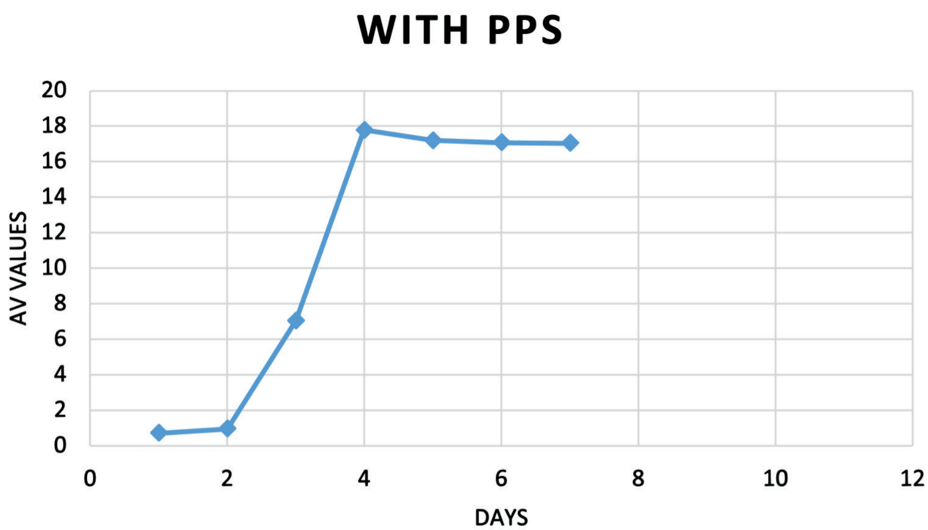

Figure 7. p-Anisidine values with oxidizing agent (1% of PPS)

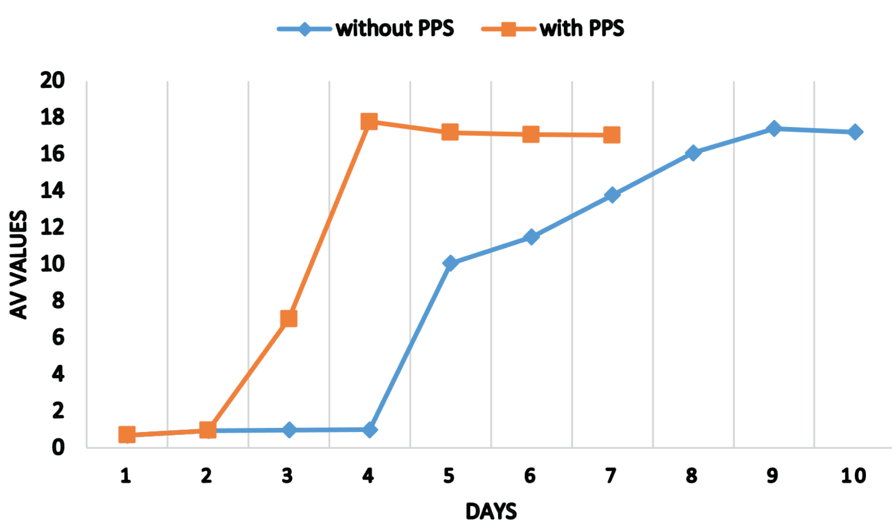

Figure 8. Comparison of p-Anisidine values with and without PPS

products started decreasing again. The graph produced is possibly due to the sluggish and steady production of secondary by-products. After attaining maxima, production begins declining.

Fish oil with 1% PPS shows high p-Anisidine values from day 2 up to day 4. It is probably due to the reaction of p- Anisidine reagent with the more secondary by-products (aldehyde, acetone, and their derivatives), which react with the amino groups of the p- Anisidine reagent.

5. Conclusions

In the present work, the kinetics of fish oil oxidation were studied, where 1% of PPS was used as an oxidizing agent. The study focused on the completion of an accelerated fish oil tanning process from 10 days to 4 days, with a remarkable increase in water absorption capacity by 454 %. The experimental leathers show better physical strength properties than control leathers. The conclusion may be drawn from the study that the use of 1% potassium per persulfate in chamois making reduces time and positively impacts the quality of final leathers.

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References

1. Nelson, D.L.; Cox, M.M., Lehninger Principles of Biochemistry, sixth ed. Freemman W. H Company, New York. 2012.
2. Rossi, I.; Muhammad, A.H.Q. A review of soybean oil lipid oxidation and its prevention techniques. *Int. J. Adv. Sci. Technol*. **29 (6)**, 5030–5037, 2020.
3. Porter, N.A. A perspective on free radical autoxidation: The physical organic chemistry of polyunsaturated fatty acid and sterol peroxidation. *J. Organic Chem*. **78**, 3511–3524, 2013. DOI:10.1021/jo4001433
4. Fereidoon, S.; Ying, Z. Lipid oxidation and improving the oxidative stability. *Chem. Soc. Rev*. **39**, 4067–4079, 2010. DOI:10.1039/b922183m
5. Huvaere, K.; Cardoso, D.R.; Homem-De-Mello, P.; Westermann, S.; Skibsted, L.H. Light-induced oxidation of unsaturated lipids as sensitized by flavins. *J. Phys. Chem B*. **114 (16)**, 5583–5593, 2010. DOI: 10.1021/jp9121744
6. Sahu, B.; Alla, J.P.; Rao, J.R.; Sreeram, K.J.; Jayakumar, G.C. Neoteric oxidizing agent for chamois process. *JALCA*, **114 (9)**, 344–349, 2019.
7. Sandhya, K.; Vedaraman, N.; Sundar, J.; Mohan, R.; Velappan, K.; Muralidharan, C. Suitability of Different Oils for Chamois Leather Manufacture. *JALCA,* **110**, 221-226, 2015.
8. Vedaraman, N.; Muralidharan, R.; Sundar, V. J.; Velappan, K.C.; Muralidharan, C. Modified jatropha oil for making chamois leather. *BTAIJ*. **9,** 203-205, 2014.
9. Suparno, O. Optimization of Chamois Leather Tanning Using Rubber Seed Oil. *JALCA*. **105, (6)**, 189-194, 2010.
10. Wainaina, N. P.; Tanui, P.; Ongarora, B. Extraction of Oil from Tannery Fleshings for Chamois Leather Tanning. *SLTC journal*. **103**, 159-162, 2019.
11. Weihua, D.; Years, B.; Rui, Z. Method for producing chamois leather using epoxidized oil. CN101550459A, 2009.
12. Weihua, D., Years, B., Rui, Z.; Method for producing chamois leather using epoxidized oil. CN101550459B, 2013.
13. Mostafa, T.; Seid, M.J. Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives, *J. Food. Sci. Technol*. **52(3)**, 1272-1282, 2015. DOI: 10.1007/s13197-013-1080-1
14. Suparno, O.; Sa'id, E.G.; Kartika, I.A.; Muslich, M. Shiva, A. Chamois leather tanning accelerated by oxidizing agent of hydrogen peroxide. *Teknik Kimia Indonesia*. **11**, 9-16, 2012. DOI: 10.5614/jtki.2012.11.1.2.
15. Suparno, O.; Sa'id, E.G.; Kartika, I.A.; Muslich, M.; Shiva, A. An Innovative New Application of Hydrogen Peroxide to Accelerate Chamois Leather Tanning. Part II: The Effect of Oxidation Times On the Quality of Chamois Leather. *JALCA*. **108**, 180-187, 2013.

16. Suparno, O.; Sa'id, E.G.; Kartika, I.A.; Muslich, M.; Mubarak, S.; An Innovative New Application of Oxidizing Agents to Accelerate Chamois Leather Tanning Part I: The Effects of Oxidizing Agents on Chamois Leather Quality. *JALCA,* **106(12)**, 360-366, 2011.
17. Hongru, W.; Yuanyue, M.; Yue, N. An oil tanning process accelerated by oxidation with sodium percarbonate. *J. Soc. Leath. Tech. Ch.* **92,** 205-209, 2000.
18. Sundar, V. J.; Vedaraman, N.; Balakrishnan, P.A.; Muralidharan, C. Chamois leathers – An approach for accelerated oxidation. *J. Soc. Leath. Tech. Ch.* **88(6)**, 256-259, 2004.
19. Sahu, B.; Alla, J.P.; Jayakumar, G.C. Studies on the Development of Benzoyl Peroxide Catalyzed Rapid Oil Tanning using Linseed Oil. *JALCA*. 116, 227-232, 2021. DOI: 10.34314/jalca.116i7.4335.
20. Sahu, B.; Alla, J.P.; Jayakumar, G.C.; Raj, A. Influence of Benzenecarboperoxoic Acid on chamois leather process. *JALCA*. **115(2)**, 49-53, 2021.DOI: 10.34314/jalca.115i2.1484.
21. Sahu, B.; Jayakumar, G.C.; Madhan, B. Impact on Potassium persulfate on Linseed Oil Tanning. *JALCA*, **117(8)**, 338-343, 2022.
22. IUP, 7. Determination of the static absorption of water. J. Soc. Leath. Tech. Ch., 84, 323, 2000.
23. IUP, 16. Determination of shrinkage temperature up to 100 °C. J. Soc. Leath. Tech. Ch., 84, 359, 2000.
24. IUP, 6. Measurement of tensile strength. J. Soc. Leath. Tech. Ch., 84, 317-321, 2000.
125. AOAC 965.33, Peroxide Values of Oils and Fats.
26. AOCS Cd 18-90, p-Anisidine value of Oils and Fats.