STUDIES ON THE QUALITY IMPROVEMENT OF FERMENTED FISH SAUCE BY TREATING WITH ADSORPTION TECHNIQUE

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Abstract

Fish sauce, salt-fermented product, is an economically important fishery product in most Southeast Asian countries. Its manufacturing processes have been conducted with various species of fish based on salt to fish ratios. In this research, the appearance and taste of fish sauce, was improved to reach the export quality product by treating with two effective methods, adsorption mechanism and high membrane technology. The characteristics of coconut coir pith activated carbon were determined and it was used as adsorbent. According to the SEM images, processed activated carbon had mesopore suitable for dye removal and micropores which were important for adsorption mechanism. The physico-chemical properties of processed fish sauce such as protein content, salt content, pH, turbidity, colour and total solids content before and after treatment by adsorption have been analyzed. Selected adsorbent, coconut coir pith activated carbon provided the colour bleaching efficiency 40.70 % and sodium chloride reducing efficiency 8.82 % in the treatment of fish sauce. After membrane filtration, turbidity and deep brown colour of fish sauce were distinctly reduced and clear fish sauce was obtained but dissolved solids that had less than (0.1 to 0.01) μm pore size cannot be removed by membrane filtration. So it was obviously seen that lignocellulosic adsorbent could effectively improve the quality of fish sauce than ultrafiltration.

Keywords: fish sauce, activated carbon, adsorption, membrane filtration

Introduction

To a large number of world's population, fish is one of the most important sources of dietary protein. Many fermented fish products are prepared in different parts of the world and the method of processing depends upon various factors, viz., availability of raw materials, consumer's preference and the climatic conditions of the region. Among other fermented fish products, fish sauce[1] can be made cheaply from various kinds of fish, which are not normally used for food. Fish sauce is a brown, liquid seasoning commonly used in Southeast Asia countries (Jones, N.R., 1962). In Myanmar, fish sauce is prepared by different ways. Fish sauce called Ngan Pya Ye is the main ingredient in Myanma dishes. Traditionally, fish sauce is produced by mixing 1:2 or 3 ratios of salt and fish and fermenting at ambient temperature (30 to 40) °C for 6 to 12 months or longer. Thus, this study analyzed the changes in the physico-chemical characteristics of processed fish sauce from snakehead mudfish with different fish to salt ratios during fermentation period. High salt content of fish sauce is leading to a health problem. And then, dark colour and strong smell of fish sauce is unattractive to the customer. So, the quality of Myanma traditional fish sauce was promoted by adsorption mechanism in this research.

Adsorption has gained importance as a purification, separation and recovery process on industrial scale. Activated carbon is perhaps one of the most widely used adsorbents in industry for environmental applications. Due to the high production cost of synthetic adsorbents, there is a

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need for an alternative material that cost less, renewable and environmentally friendly (http: //www.ijerst.com/currentissue. php).

Basically there are two different processes for the preparation of activated carbon, the so-called physical or thermal and chemical activation. Chemical activation has several advantages than physical activation (Gottipati, 2012). Fish sauce, Myanma traditional product was improved to reach the export quality product by treating with activated carbon. An attempt was made to get standardized quality fish sauce by applying high membrane technology. The focus of this research is to explore the feasibility of agricultural waste based activated carbon being utilized in improvement of processed fish sauce.

Materials and Methods

Materials

To improve the quality of fish sauce, fish sauce was produced by mixed with Nga-Pa-Naw (*Channa burmanica*) and 30 % salt. For adsorption mechanism, coconut coir pith activated carbon was applied as adsorbent and ultrafiltration process was used in membrane filtration.

Methods

Analysis of Fish Sauce

Characteristics of fish sauce (pH, total nitrogen content, protein content and sodium chloride content) were analyzed.

Analysis of Adsorbent

Physico-chemical properties (moisture, ash, volatile matter, fixed carbon content and bulk density) of coconut coir pith activated carbon were investigated. Moisture content of activated carbon was determined using ASTM D 2867-09. The volatile matter content was determined by ASTM D 5832-98.

Characteristics of activated carbon such as pH, surface area (Okibe, F.G., *et al*, 2013), iodine sorption capacity and methylene blue number (Gottipati, 2012) were studied**.** Prepared activated carbon was characterized by using SEM and XRD techniques.

Treatment of Fish Sauce by Adsorption Mechanism

Various ratios of fish sauce to activated carbon were used at room temperature (29 -31) °C for 1 hr. with stirring (200 rpm). The appropriate ratio of activated carbon to fish sauce was determined and the appropriate temperature and time for the reduction of salt content were further studied. The changes in physico-chemical properties of treated fish sauce were also analyzed. Effects of activated carbon to fish sauce ratio, agitation temperature and time on the reduction of sodium chloride content were determined.

Treatment of Fish Sauce by Membrane Technology

In this research, ultrafiltration membrane (0.01 to 0.1μm) was used in the treatment of fish sauce. Processed fish sauce by natural fermentation was treated with ultrafiltration. 30 min suction time and aeration time, 2 min were applied to complete one filtration cycle.

Figure 1 Treatment of Fish Sauce by Ultrafiltration Membrane Process Assembly Results

Results

Table 1 Physico-chemical Properties of Fish Sauce

Sr. No	Properties	Fish Sauce	Golden Boat Fish Sauce (Thailand Product)
1.	Protein content (% w/w)	20.32 ± 3.45	13.3 ± 4.66
2.	Total nitrogen content (% w/w)	2.45 ± 0.42	2.12 ± 0.03
3.	Fibre content (% w/w)	0.5	0.2
4.	Lipid content (% w/w)	0.393 ± 1.02	0.421 ± 0.1
5.	Salt content (% w/w)	28.77 ± 2.98	27.22 ± 4.55
6.	Ash content (% w/w)	12.38 ± 0.57	10.13 ± 1.01
7.	pH	6.5 ± 3.41	5.7 ± 2.61
8.	Colour (at 420 nm)	1.462 ± 1.224	0.678 ± 1.961

Table 2 Microbial Analysis of Fish Sauce

Sr. No	Examination	Fish Sauce	Golden Boat Fish Sauce (Thailand Product)
1.	Yeast and mould counts (cfu/L)	2×10^3	4×10^3
2.	Total plate count (cfu/L)	15×10^3	16×10^4
3.	*E. coli*	ND	ND
4.	Bacterial species	*Aspergillus niger, Aspergillus oryzae*	-

Table 3 Physico-chemical Properties of Activated Carbon

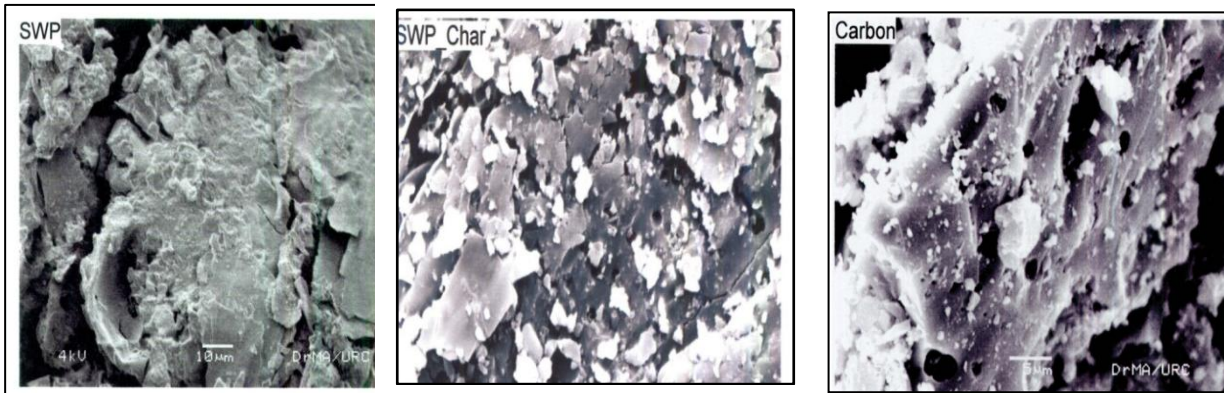
Sr. No	Physico-chemical Properties (%w/w)	Coconut Coir Pith Activated Carbon	Medicinal Charcoal (Food Grade, Germany)	Commercial AC (China Product)
1.	Moisture content	9.45	9.12	16.12
2.	Ash content	7.58	6.84	8.84
3.	Volatile matter content	5.19	4.70	7.70
4.	Fixed carbon content	77.78	79.34	67.34

Shelf-life of processed activated carbon = 3 years at (30 -33) °C

Table 4 Characteristics of Coconut Coir Pith Activated Carbon

Sr. No	Characteristics	AC-CCP	Medicinal Charcoal (Food Grade, Germany)	Commercial AC (China Product)
1.	pH	6.5	6	5.9
2.	Surface area (m^2/g)	1376	1362	1405
3.	Bulk density (g/cm^3)	0.51	0.63	0.83
4.	Iodine sorption capacity (%)	88.12	86.5	80.9
5.	Methylene blue number (mg/g)	380	395	365

AC-CCP = Coconut Coir Pith Activated Carbon



(a) **(b)** **(c)**

Figure 2 SEM Images of (a) Coconut Coir Pith Activated Carbon
(b) Commercial Activated Carbon (China Product)
(c) Medicinal Charcoal (Food grade, Germany)

Table 5 Effect of Solid to Liquid Ratio on the Abatement of Colour and Sodium Chloride Content of Fish Sauce Treated by Activated Carbon

Sr. No	Activated Carbon : Fish Sauce (% w/v)	Fish Sauce Treated by AC-CCP			
		Colour Absorbance(at 420 nm)		NaCl(% w/w)	
		After Treatment by AC-CCP	Bleaching Efficiency (%)	After Treatment by AC-CCP	Salt Reducing Efficiency (%)
1.	1:100	1.119	23.46	27.01	6.12
2.	2:100	1.012	30.78	26.52	7.82
3.	3:100*	0.959	34.40	26.28	8.65
4.	4:100	0.964	34.06	26.38	8.31
5.	5:100	0.965	33.99	26.36	8.38

* Most suitable condition

Table 6 Effect of Temperature on the Abatement of Colour and Sodium Chloride Content of Fish Sauce Treated by Activated Carbon

Sr. No	Agitation Temperature (°C)	Fish Sauce Treated by AC-CCP			
		Colour Absorbance (at 420 nm)		NaCl (% w/w)	
		After Treatment by AC-CCP	Bleaching Efficiency (%)	After Treatment by AC-CCP	Salt Reducing Efficiency (%)
1.	30*	0.959	34.40	26.28	8.65
2.	40	0.961	34.27	26.47	7.99
3.	50	0.973	33.44	27.68	3.79
4.	60	1.244	14.91	28.80	-
5.	90	1.679	-	30.93	-

* Most suitable condition

Table 7 Effect of Agitation Time on the Abatement of Colour and Sodium Chloride Content of Fish Sauce Treated by Activated Carbon

Sr. No	Agitation Time (min)	Fish Sauce Treated by AC-CCP			
		Colour Absorbance (at 420 nm)		NaCl (% w/w)	
		After Treatment by AC-CCP	Bleaching Efficiency (%)	After Treatment by AC-CCP	Salt Reducing Efficiency (%)
1.	30	1.142	21.89	27.49	4.45
2.	60	0.959	34.40	26.28	8.65
3.	90*	0.836	42.82	26.18	9.00
4.	120	0.848	42.00	26.24	8.80
5.	150	0.948	35.16	26.82	6.78

* Most suitable condition

Table 8 Physico-chemical Properties of Fish Sauce before Treatment, after Treatment and Commercial Product

Sr. No	Properties	Fish Sauce			Golden Boat Fish Sauce (Thailand product)
		Before Treatment	After Treatment by AC-CCP	After Treatment by Membrane Filtration	
1.	Ash content (% w/w)	12.38±0.57	9.43±2.1	9.76±5.12	10.13±1.01
2.	Protein content (% w/w)	20.32±3.45	19.63±4.86	15.12±2.88	13.3±4.66
3.	Total nitrogen content (% w/w)	3.25±0.42	3.14±2.88	2.42±0.32	2.12±0.03
4.	Fibre content (% w/w)	0.5	0.4	0	0
5.	Lipid content (% w/w)	0.393±1.02	0.298±1.42	0.367±0.12	0.421±0.1
6.	Salt content (% w/w)	28.77±2.98	26.18±3.89	28±3.27	27.22±4.55
7.	pH	6.5±3.41	6.7±2.56	5.8±2.81	5.7±2.61
8.	Colour (absorbance at 420 nm)	1.462±0.014	0.836±0.016	0.612±4.13	0.678±1.961

Table 9 Changes in the Physical Properties of Fish Sauce by Treating with Adsorbent and Membrane Filtration

Sr. No	Properties	Fish Sauce before Treatment	Treated Fish Sauce by Activated Carbon	Treated Fish Sauce by Membrane Filtration
1.	Turbidity (NTU)	82±2.09	31±1.34	35±2.23
2.	Total solids (mg/L)	743± 2.89	589± 2.49	628±3.89
3.	Suspended solids (mg/L)	57± 0.18	8±0.03	16±0.13
5.	Colour (at 420 nm)	1.462±0.014	0.225±0.012	0.276±0.014
6.	Colour (TCU) (Colourimeter)	43.5±1.298	21±1.561	29.5±0.871
7.	Colour (Tintometer)	Red-7, Yellow-20,	Red-5 Yellow-8	Red- 5, Yellow-12

Table (10) Microbial Analysis of Fish Sauce (before Treatment, after Treatment and Commercial Product)

Sr. No	Microorganisms	Fish Sauce			
		Before Treatment	Treated Fish Sauce by AC-CCP	Treated Fish Sauce by Membrane Filtration	Golden Boat Fish Sauce (Thailand product)
1.	Yeast and mould counts (cfu/L)	5×10^3	2×10^3	1×10^3	4×10^5
2.	Total plate count (cfu/L)	15×10^4	14×10^3	3×10^3	16×10^5
3.	*E. coli*	ND	ND	ND	ND

(a) (b) (c)

Figure3 (a) = Fish Sauce, before Treatment
(b) = Fish Sauce after Treatment by Membrane Filtration
(c) = Fish Sauce after Treatment by Adsorbent (Activated Carbon)

Discussion

Firstly, Table (1) shows that protein and total nitrogen content of processed fish sauce were higher than Thailand fish sauce. From Table (2), it could be seen that fish sauce had 2×10^3 cfu/L of yeast and mould counts and 15×10^3 cfu/L of total plate count. Table (3) shows that properties of activated carbon were similar to the medicinal charcoal (food grade).

From Table (4), it can be observed that the surface area of AC-CCP (coconut coir pith activated carbon) was 1376 m^2/g and its methylene blue number was 380 mg/g. Methylene blue numbers and iodine sorption capacity had relationship with the pore structure of adsorbents. MB number indicates the capacity of an adsorbent to adsorb large molecular size species into its macro pores, while the iodine sorption capacity is related to the degree of micro and mesopores present in the adsorbent. The methylene blue number is a measure of mesoporosity present in activated carbon and an indicator of ability of a carbon to adsorb high molecular weight substances like dye molecules. AC-CCP had higher surface area and iodine sorption capacity, indicating that it could be suitable for colour removal.

From Figure (2), it could be observed that activated carbon consisted of more canals like structure than commercial activated carbon. In AC-CCP, surfaces were pitted and fragmented.

Effect of solid to liquid ratio on the bleaching efficiency and sodium chloride content in fish sauce are shown in Table (5). When fish sauce was treated with coconut coir pith activated carbon, the colour decreased from 1.462 to 0.959 at the ratio of 3:100 activated carbon to fish sauce. Sodium chloride content of treated fish sauce (by AC-CCP) decreased at the ratio of 3:100 at 30 ºC agitation temperature. Bleaching efficiency and salt reducing efficiency increased sharply with an increase in adsorbent dose due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents. And then, beyond a certain dose, reducing efficiencies rapidly decreased with increase in adsorbent dose in all treatments.

Effect of temperature on the bleaching efficiency and sodium chloride content in fish sauces at the most suitable solid to liquid ratio (3:100) by AC-CCP at 200 rpm agitation rate for 60 min agitation time were determined and data are presented in Table (6). It was observed that bleaching efficiency and sodium chloride content decreased as the temperature was increased in fish sauces. So, 30 ºC was the most suitable agitation temperature on the bleaching efficiency and salt reducing efficiency of fish sauces.

Effect of agitation time on the bleaching efficiency and sodium chloride content of fish sauce at the most suitable solid to liquid ratio are presented in Table (7). It was found that the salt content of fish sauce decreased from 28.77 % to 26.18 % and the highest colour removal percentage, 42.82 % was observed at 90 min agitation time. In the bleaching efficiency and salt content of fish sauce treated by activated carbon, the most suitable conditions were observed at the ratio of 3:100 coconut coir pith activated carbon to fish sauce at 30 °C for 90 min agitation time.

The quality of treated fish sauces by two methods were compared to Golden Boat fish sauce (Thailand Product). The data are presented in Table (8). It can be seen that ash content of fish sauce reduced from 12.38 ± 0.57 % w/w to 9.43 ± 2.1 % w/w by the adsorption with AC-CCP. Among the fish sauces it can be seen that fish sauce treated by AC-CCP had the least amount of salt. So, it was observed that the quality of treated fish sauce had 19.63 ± 4.86 % w/w

protein content, 9.43 ± 2.1 % w/w minimum ash content, 3.14 ± 2.88 % w/w total nitrogen content and 26.18 ± 3.89 % w/w salt content, respectively.

Physical properties of treated fish sauces are presented in Table (9). After treatment, the colour of treated fish sauce changed from dark brown to golden yellow and the odour reduced significantly. Coconut coir pith activated carbon could improve the quality of fish sauce because it possessed effective micropores, mesopores and high adsorption intensity which were confirmed by SEM. Bellona (2012) stated that ultrafiltration process could not remove dissolved particles smaller than 0.1μm (pore size). Colour of processed fish sauce gradually increased due to Maillard reaction. Ultrafiltration could not reduce the dissolved sugar (0.0001 μm) in fish sauce. So, after membrane filtration, the physical properties of fish sauce were not significantly changed except turbidity. But total plate count of fish sauce was sharply reduced from 15×10^3 cfu/L to 3×10^3 cfu/L after membrane filtration. Yeast and mould counts were also decreased from 5×10^3 cfu/L to 1×10^3 cfu/L after treatment. *E. coil* was not detected in fish sauce.

Conclusion

Not only AC-CCP possessed the same characteristics of food grade activated carbon but also it occupied more micropores and mesopores and thus consequence was more advantages for abatement on colour and sodium chloride content of fish sauce. The treated fish sauce by AC-CCP had many attractive features like golden yellow colour, clear, slightly salty in flavour, and sweet aroma that was suitable for using as condiment and seasoning to complement the dish. In ultrafiltration process, colloids and microorganisms were effectively removed but it could not reduce the salt content of fish sauce. It could be concluded that the adsorption mechanism of processed activated carbon effectively improved the aroma and flavour of fish sauce to reach the standard quality.

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