Adsorption of FFA in Crude Catfish Oil onto Chitosan, Activated Carbon, and Activated Earth: A Kinetics Study

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ABSTRACT: The feasibility of using chitosan, activated carbon, and activated earth to remove FFA from crude catfish visceral oil, and the adsorption kinetics of the procedure were evaluated. The effect of adsorbents on water activity and the 18:3 and 22:6 content of crude catfish visceral oil was also studied. The initial adsorption kinetic coefficients of FFA (mL g^{-1} min^{-1}) were 0.1, 0.07, and 0.03 for chitosan, activated carbon, and activated earth, respectively. The external film mass-transfer coefficient (0.001 mL s^{-1}) was similar for the three adsorbents. The adsorption capacity of FFA at saturation (mg g^{-1}) was 71.2 for chitosan, 65.5 for activated carbon, and 57.0 for activated earth. The intraparticular diffusion coefficients (mg mL^{-1} $min^{-0.5}$) were 0.14, 0.12, and 0.09 for chitosan, activated carbon, and activated earth, respectively. Water activity of the crude oil decreased with increased contact time of the adsorbents. Results indicated that chitosan was a better adsorbent than activated carbon and activated earth for FFA removal from crude catfish visceral oil.

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KEY WORDS: Adsorption kinetics, catfish oil, free fatty acid.

There is a sizable and growing world market demand for high-quality fish oils, and commercial fish oil production can be quite profitable if suitable raw materials are available. Channel catfish (*Ictalurus punctatus*) is now the fourth most popular fish product consumed in the United States (1). The by-products of catfish processing consist of heads, frames, skin, and viscera, which often end up in landfills or rendering plants. The average weight of viscera is about 265 g, which is about 10% by weight of a live whole catfish. The fat content of catfish viscera is 33.6% (wet basis) (2), and the viscera can be used for recovering oil that could be converted into edible products.

Unrefined catfish oil contains non-TG, such as FFA and oxidized components, that reduce the oil quality. The removal of impurities and non-TG components from crude catfish oil is necessary to produce refined oil with a desirable and acceptable shelf life. The longer these components remain in the oil, the greater their negative effect on the quality of the refined oil. Finding more lucrative markets for catfish oil requires well-designed purification steps.

The conventional fish oil-refining steps include degumming, neutralizing, bleaching, and deodorizing. FFA are precipitated as soaps and removed during the neutralization process (3). Bleaching clays adsorb pigments from the oil, and oxidized components can be removed by deodorization. Although adsorbents are used to remove pigments during oil refining, they potentially adsorb FFA (4).

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Many studies have shown that an adsorption process used for edible oil purification removes non-TG (5). Adsorption is a process that involves the mass transfer of adsorbate from the fluid phase to the adsorbent surface until the thermodynamic equilibrium of the adsorbate concentration is reached. Therefore, adsorption kinetics is a function of adsorbate–adsorbent interaction. Several theoretical and empirical models have been proposed to explain the adsorption process (6). Catfish oil is a new product and has not yet been produced on a pilot scale. Selecting the most appropriate adsorbent to remove FFA along with other impurities and predicting the performance of an adsorption system for catfish oil are worth investigation. Therefore, the objectives of this study were to evaluate the feasibility of using adsorbents (activated carbon, activated earth, or chitosan) to remove FFA from crude catfish visceral oil and to understand the adsorption kinetics for FFA removal. The effect of adsorbents on water activity and the content of 18:3 and 22:6 of the crude catfish visceral oil was also studied.

EXPERIMENTAL PROCEDURES

Catfish oil extraction. Catfish viscera were obtained in three separate batches from a local seafood store in Baton Rouge, Louisiana. Oil was extracted from the catfish viscera according to the method of Sathivel *et al*. (7). The viscera were frozen at –20°C for 2 d. A thawed 1-kg portion of viscera was finely ground in a Hobart chopper bowl (Model 84181D; Hobart Corporation, Troy, OH) at 3,450 rpm for 10 min. Water was added (water/ground viscera, 5:1 vol/wt), and the mixture was heated at 70°C for 15 min. The solid particles were separated from the liquid phase by filtering through cheesecloth, and the particles were pressed to remove most of the liquid. The crude oil was separated from the water phase and viscera particles by centrifuging at 5,000 rpm (2,560 × *g*) for 30 min. Three separate experimental crude oil extractions were conducted. The resulting crude oil was collected and stored at –20°C for 2 d prior to the adsorption studies.

Esterification of FA. FAME were prepared according to AOAC procedure 969.33 (8). The crude oil was placed into a 50-mL flat-bottomed boiling flask containing approximately 4 mL of methanolic sodium hydroxide (2 g of NaOH dissolved in 100 mL of methanol), and 10 boiling chips were then added to the flask. The condenser and reflux units were attached to the flask, and refluxing took place for 12 min immediately after the addition of 7 mL of boron trifluoride through the condenser. The esterified FA were extracted from the mixture by adding 5 mL of heptane and refluxing for 1 min. The esterified solution was allowed to cool to room temperature. A saturated solution of sodium chloride

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was added, and the flask was gently rotated. Saturated sodium chloride solution was added until the heptane solution containing FAME reached the neck of the flask. The heptane solution containing FAME was recovered, dehydrated with 1.5 g anhydrous sodium sulfate, and stored under nitrogen in Teflon-capped vials at –20°C until analyzed.

FA analysis. FA analysis was done according to the method of Sathivel *et al.* (2). The FAME were quantified with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 7673A autosampler (Agilent Technologies, Palo Alto, CA) and interfaced to a 5970 mass selective detector (Agilent Technologies). The gas chromatograph was equipped with an EZ-Flash fast-temperature programmable column (Thermedics Detection, Inc., Chelmsford, MA). The column phase was RTX-2330 (90% biscyanopropyl/10% phenylcyanopropyl polysiloxane) with the following dimensions: 5 m long, 0.25 mm i.d., with a 0.2-µm phase thickness. One microliter of FAME was injected in the split mode. The head pressure was set at 2 psi, and the split vent flow was 7 mL/min. The injector temperature was 260°C. The column flow rate at 2 psi was 0.68 mL/min, and the split ratio was 10.4:1. The column temperature was held at 50°C for 6 s, ramped from 50 to 260°C at 1°C/s, and held at 260°C for 84 s; run time was 5 min. The transfer line temperature was 280°C, and the mass selection detector was operated in the selected ion-monitoring mode. FA were identified by retention times obtained from commercial FAME standards (Sigma Company, St. Louis, MO). Concentrations of FA were calculated from the standard curves. The internal standard (IS) solution used for quantification of the FA contained 1 mg nonadecanoic acid (19:0)/mL heptane. For the recovery studies, 1 mg nonadecanoic acid methyl ester/mL heptane was used as the IS. The calculated concentration of 18:3 and 22:6 through the standard curves was reported as w/w% (of the total FA content), taking into account the recovery of IS and sample weight. Three experimental replications (batches) were conducted, each with three extractions and three gas chromatograph injections per extraction.

FFA analysis. The FFA content of the oils was determined in duplicate by the titration method according to AOAC Official Method 940.28 (8). FFA content was expressed as milligrams oleic acid per gram of oil.

Water activity. The water activities of the oils were measured in triplicate using a water activity meter (AW Sprint, Novasina, Switzerland) at 25°C.

Batch mode adsorption study. Activated earth (American Oil Chemists' Society, Champaign, IL), crab chitosan with a degree of deacetylation of 80% (Vanson Inc., Redmond, WA), and CO_2-activated carbon from pecan shells (USDA-ARS-SRRC, New Orleans, Louisiana), were used in this study. The batch adsorption study was conducted in a 50-mL vial sealed with a Teflon cap. Twenty-five milliliters of crude oil was placed into each vial, and 0.8 g of an adsorbent (activated earth, chitosan, or activated carbon) was added separately for each time point. The adsorption reaction was carried out with constant agitation using a magnetic stirrer at 25 ± 1°C. Samples were analyzed at 1-, 2-, 3-, 4-, and 5-h intervals for FFA and water activity. Experiments were repeated three times.

Adsorption kinetics of FFA onto adsorbents. The initial adsorption kinetic coefficient was calculated by using Equation 1 as described by Kadirvelu *et al.* (9):

$$c = \left(\frac{dC}{dt}\right)_{t \to 0} \frac{V}{mC_o} \quad [1]$$

where c is the initial adsorption kinetic coefficient (mL g^{-1} min^{-1}), t is time (min), C is the concentration of FFA (mg of oleic acid/g of catfish oil) at time t, C_o is the initial concentration of FFA (mg of oleic acid/g of catfish oil), m is the adsorbent weight (0.8 g), and V is the volume of catfish oil (25 mL). The external film mass-transfer coefficient, K_sA, (mL s^{-1}) was calculated from Equation 2 according to Kadirvelu *et al.* (9):

$$-\ln\left(\frac{C}{C_o}\right) = K_sA\frac{t}{V} \quad [2]$$

The intraparticular diffusion coefficient, K_w (mg mL^{-1} $min^{-0.5}$), was calculated from Equation 3 according to Kadirvelu *et al.* (9):

$$\frac{m}{V}q = K_w t^{0.5} \quad [3]$$

where q (mg g^{-1}) is the adsorption capacity at time t. The adsorption capacity was calculated as $q = (C_o - C_t)V/W$, where C_o is an initial FFA concentration (mg of oleic acid/mL of catfish oil), C_t is the concentration of FFA (mg of oleic acid/mL of catfish oil) at time t, V is the volume of catfish oil (25 mL), and $W = m$ is the weight of the adsorbent (0.8 g). The catfish oil density of 0.9112 g/mL was used to convert the FFA unit from mg oleic acid/g of oil to mg oleic acid/mL of catfish oil. The adsorption capacity at saturation was calculated as $q_s = (C_o - C_s)V/W$, where C_o is an initial FFA concentration (mg of oleic acid/mL of catfish oil), C_s is the concentration of FFA (mg of oleic acid/mL of catfish oil) at saturation, V is the volume of catfish oil (25 mL), and W is the weight of the adsorbent (0.8 g).

Statistical analysis. ANOVA was performed to determine differences in the FA content attributable to the adsorption time. Tukey's Studentized range test was performed for *post hoc* multiple comparisons at $\alpha = 0.05$.

RESULTS AND DISCUSSION

The 18:3 and 22:6 FA content. Changes in the 18:3 and 22:6 content of crude catfish oil were monitored during a 5-h adsorption process (Table 1). The initial 18:3 and 22:6 contents were 4.5 and 1.2 w/w, respectively. Although no significant reduction of 22:6 was observed during adsorption up to 5 h, the 18:3 was reduced significantly when activated earth was used as an adsorbent.

Water activity. Table 2 shows the relationship between water activity and adsorption (contact) time. Regardless of the adsorbent used, water activity of the crude oil decreased with an increase in the contact time of the adsorbents. The initial water

TABLE 1
18:3 and 22:6 Content of Crude Catfish Visceral Oil (w/w %) During Adsorption[a]

		Adsorption time (min)					
Adsorbent	FA	0	60	120	180	240	300
Chitosan	18:3	4.5	4.1	4.1	4.0	3.9	3.9
		(0.7)	(0.4)	(0.6)	(0.3)	(0.8)	(0.5)
	22:6	1.2	1.2	1.2	1.2	1.2	1.2
		(0.2)	(0.1)	(0.1)	(0.1)	(0.3)	(0.1)
Activated carbon	18:3	4.5	4.0	3.9	3.9	3.9	3.9
		(0.7)	(1.0)	(0.7)	(0.6)	(0.6)	(0.7)
	22:6	1.2	1.2	1.2	1.2	1.2	1.2
		(0.2)	(0.1)	(0.2)	(0.1)	(0.2)	(0.2)
Activated earth	18:3	4.5[a]	3.7[a]	3.5[b]	3.5[b]	3.4[b]	3.2[b]
		(0.7)	(0.2)	(0.5)	(0.6)	(0.4)	(0.3)
	22:6	1.2	1.2	1.2	1.2	1.2	1.2
		(0.2)	(0.1)	(0.1)	(0.1)	(0.2)	(0.3)

[a] Numbers in parentheses are the SD. In each row, only mean values with different superscript letters are significantly different ($P < 0.05$).

activity of crude oil was 0.86, and it gradually fell to 0.68, 0.71, and 0.79 for chitosan, activated carbon, and activated earth, respectively, after 5 h of adsorption.

Adsorption kinetics and mass transfer of FFA. Table 3 shows the effect of the contact (adsorption) time and the type of adsorbent on FFA. The initial FFA concentration of catfish oil was 4.5 mg/g of oil. The amount of FFA adsorbed onto the adsorbent increased with increasing contact time. After 4 h of adsorption, chitosan, activated carbon, and activated earth were possibly saturated with FFA, and FFA content was reduced to 2.0, 2.2, and 2.5 mg/g of oil, respectively. Among the three adsorbents, chitosan was slightly more effective in adsorbing FFA. Increasing the adsorption time to 5 h did not further reduce the FFA in the oils.

A comparison of the kinetic parameters of chitosan, activated carbon, and activated earth is given in Table 4. Chitosan had the highest adsorption capacity at saturation (q_s). The milligrams of FFA bound per gram of adsorbent was expressed as a function of time (Fig. 1). The adsorption efficiency of the three adsorbents sharply increased up to an adsorption period of 4 h. Chitosan adsorbed more FFA from crude catfish oil than did activated carbon or activated earth (Fig. 1). The maximum in milligrams of FFA adsorbed per gram of an adsorbent was 71.2, 65.5, and 57, respectively, for chitosan, activated carbon, and activated earth (Table 4). The K_sA values depend on the gradient concentration of the adsorbate between the fluid phase and the adsorbent surface. The values of K_sA observed for chitosan, activated carbon, and activated earth were similar (Table 4). Some of the factors that might affect the magnitude of the driving force for FFA include interaction of the adsorbent surface with other lipids, as well as interaction of FFA with other oil components in the liquid phase and on the adsorbent surface (10).

The c and K_w values were higher for chitosan than for activated carbon and activated earth. The higher values of c and K_w for chitosan may be due to faster intraparticular diffusion of FFA through the chitosan porosity network (11). Chitosan is a biopolymer, and its solid state exhibits a complex network. The network and the brittle nature of chitosan make it disperse readily in liquid (12). Therefore, dispersion of chitosan in crude catfish oil may have provided more surface area to adsorb a greater amount of FFA than the other two adsorbents. The chitosan's nitrogen atoms were an excellent functional group for adsorbing impurities.

The c, qs, K_sA, and K_w values give us important information about FFA adsorption. These kinetic parameters are affected by other components in the crude catfish oil such as phospholipids and complex metals (notably iron, calcium, and magnesium minerals) that are highly interactive with the oil. However, their effects were not evaluated in this study. The results (Table 4) indicate that chitosan has a greater ability to adsorb FFA in crude catfish oil than activated carbon or activated earth. Therefore, it is possible to use chitosan as an adsorbent for the removal of FFA from crude catfish visceral oil.

TABLE 2
Water Activity of Catfish Oils at Different Adsorption Time Intervals

Time (min)	Chitosan	Activated carbon	Activated earth
0	0.86 ± 0	0.86 ± 0	0.86 ± 0
60	0.77 ± 0.002	0.83 ± 0	0.85 ± 0.001
120	0.71 ± 0.003	0.75 ± 0.001	0.84 ± 0.004
180	0.68 ± 0.001	0.74 ± 0.001	0.83 ± 0
240	0.68 ± 0.001	0.71 ± 0	0.79 ± 0.001
300	0.68 ± 0.002	0.71 ± 0.002	0.79 ± 0.003

TABLE 3
FFA[a] in Catfish Oils at Different Adsorption Time Intervals

Time (min)	Chitosan	Activated carbon	Activated earth
0	4.5 ± 0.01	4.5 ± 0	4.5 ± 0
60	3.6 ± 0.07	3.9 ± 0.06	4.3 ± 0.02
120	2.7 ± 0.05	3.3 ± 0.03	3.9 ± 0.02
180	2.4 ± 0.04	2.7 ± 0.02	3.1 ± 0.01
240	2.0 ± 0.06	2.2 ± 0.11	2.5 ± 0.03
300	2.0 ± 0.1	2.2 ± 0.03	2.5 ± 0.01

[a]Expressed as milligrams oleic acid per gram of oil.

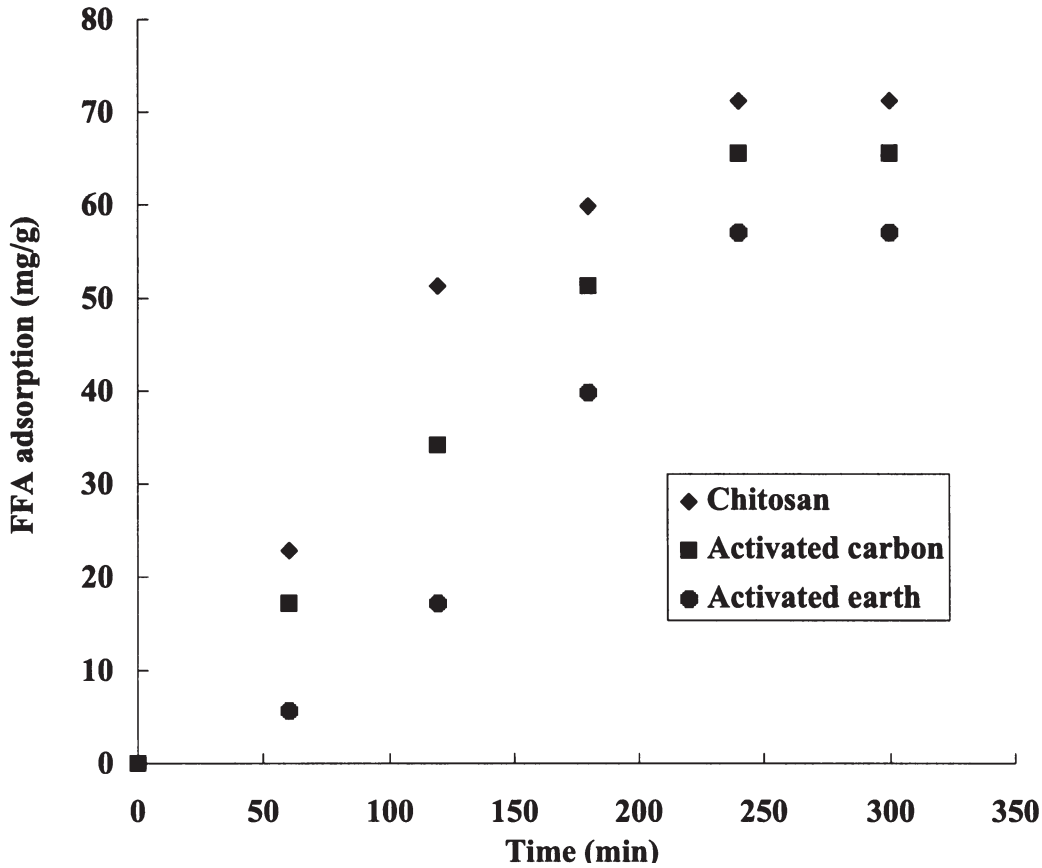

FIG. 1. FFA adsorbed per gram of adsorbent at different adsorption time intervals.

TABLE 4
FFA Adsorption Kinetic Parameters[a] as Affected by the Type of Adsorbent

	K_sA (mL s^{-1})	K_w (mg $mL^{-1}min^{-0.5}$)	q_s (mg g^{-1})	c (mL g^{-1} min^{-1})
Chitosan	0.001	0.14	71.2	0.10
Activated carbon	0.001	0.12	65.5	0.07
Activated earth	0.001	0.09	57.0	0.03

[a]K_sA, external film mass-transfer coefficient; K_w, intraparticular diffusion coefficient; q_s, adsorption capacity at saturation; c, initial adsorption kinetic coefficient.

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