Modification of fish skin collagen film and absorption property of tannic acid

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Abstract Fish collagen is a biomacromolecule material and is usually used as a clarifying agent. However, fish collagen is not recyclable, and sedimentation usually occurs in the clarification process using fish collagen so that the filtration process is inevitable. This work aimed to provide a recyclable modified fish skin collagen film (MFCF) for adsorption of tannic acids. The collagen from channel catfish skin was extracted and used for preparation of the fish skin collagen film (FCF) and MFCF. The result indicated that the mechanical properties of MFCF were improved by addition of 2 ml/L glycerol, 6 ml/L polyvinyl alcohol (PVA) and 2 ml/L glutaraldehyde in 15 g/L collagen solution. As the most important property of adsorption material, the hydroscopicity of MFCF was only 54%, significantly lower than that of FCF (295%). Therefore, MFCF would not collapse in water. The infrared and thermal properties of MFCF were also investigated in this work. Results indicated that, in comparison to FCF, the physical and chemical properties of MFCF had been improved significantly. MFCF had higher shrink temperature (79.3 °C) and it did not collapse in distilled water at normal temperature. Furthermore, absorption and desorption properties of tannic acid were studied. MFCF showed good capability of absorption and desorption of tannic acid, which led to the suggestion that MFCF could have potential applications in adsorption material.

Keywords Adsorption · Collagen film · Fish · Modification · Tannic acid

Introduction

Tannin is a diverse group of polyphenols that are formed as secondary metabolites in plants (Hvattum 2002). It has been applied in the field of pharmaceutical, food processing and tanning industries (Madhan et al. 2005) for its potential antiviral, antibacterial and antiparasitic effects and antioxidant property. However, some extracts of plants contain excess tannins which usually debase the quality of those products. What makes things even worse is that most of traditional Chinese medicines are derived from tannins-contained plants, which would be toxic for human when given by intravenous injection. Meanwhile, tannins in the surface and ground water is toxic to aquatic organism (An and Dultz 2007). Therefore, it is important to remove the tannins from traditional Chinese medicine and some kinds of foods.

Although some materials have been used to remove tannin in waste streams in chemical process industries or in natural waters (Chang and Juang 2005; An and Dultz 2007), collagen is still an appropriate material to clarify the tannin in foods and some traditional Chinese medicine for safety.

Collagen is the major and the richest protein (higher than 30%) contained in animal origin and has been extracted from skins of some vertebrate species, especially pig and calf. It is generally known that the bovine and pig skins are the main sources of industrial collagens, which have been used in functional foods, biomedical materials and cosmetics. In recent years, some pilot studies on fish skin collagens were performed (Kimura

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and Ohno 1987; Nagai et al. 2002; Muyonga et al. 2004a; Liu et al. 2007; Fernandes et al. 2008; Nagarajan et al. 2011). Compared to mammal collagens, fish collagens have some unique characteristics because of their different structures and contents of amino acid (Liu et al. 2007). Fish collagen which is extracted from the skins of various fish is an appropriate material for tannine clearance. However, one of the most important problems is the precipitation occurring when collagen binds tannic acid in solution. The non-recycled using of fish collagen restricts the application of fish collagen or gelatin as clarifying agent.

Collagen is one of biocompatible polymer materials, which can be used to prepare adsorption film (Lee et al. 2001). For mechanical stability, the adsorption film must be prepared using a suitable material. Although the mechanical properties of collagen film in solution are poor, appropriate modification by chemical and physical treatments can greatly improve mechanical functionality of the collagen film, and prevent it collapsing in solution. As a kind of collagen, fish collagen can be also prepared and similarly used as a potential adsorption material of tannine.

With the increasing needs of the aquiculture products in food industry in China, more and more farmers and fishermen began to learn cultivating fish. The yield of aquatic products of China has been the maximum in the world in recent years (Wang et al. 2006). Although there is an attempt to utilize the waste from the processing, a great amount of fish skins has been dumped every year. We extracted the collagen and gelatin from channel catfish and studied their characteristics for further usage (Liu et al. 2007, 2008a, b, 2009).

A major goal of this paper was to prepare MFCF and study the related absorption and desorption properties of tannine. In order to prevent it collapsing in tannin solution, MFCF was prepared by addition of modifying agent in collagen solution therefore to improve physicochemical properties and water resistance. Additionally, there are two main categories of tannins, hydrolyzable tannins and condensed tannins (Reed 1995; Vellingiri and Hans 2011). Hydrolysable tannins are much more toxic by intramuscular or subcutaneous injection than condensed tannins. Then tannic acid which is one of hydrolyzable tannins was used in the experiment to determine the adsorptivity of MFCF.

Materials and methods

Extraction of collagen

Freezing skin of Channel catfish (*Ictalurus Punctatus*) was provided by Jiangtai Food Co. Ltd. (Jiangsu province, China), and stored at -20°C . Before use, the skins were cut into 2–5 mm pieces. The pieces were allowed to thaw below

10°C , washed with chilled water for 20 min, mixed with 5 volumes (v/w) of the 50 g/L NaCl at 4°C to remove noncollagenous proteins and other residues. Fat in the skin was extracted for 2 days successively with ether and hexane (4°C), respectively, then washed with distilled water (4°C) and lyophilized (Liu et al. 2007).

The residues were extracted with acetic acid (1.0 g of skin per 100 ml of 0.5 mol/L acetic acid) and pepsin (1,100U/mL) at 4°C for 54 h. Then the sample was filtered with a double layer of gauze. The viscous solution was centrifuged at $4000\times g$ for 15 min. The supernatants were salted out by adding NaCl to a final concentration of 0.7 mol/L. The precipitated collagen was separated by centrifugation at $4000\times g$ for 15 min, re-dissolved in 0.5 mol/L acetic acid, dialyzed against distilled water and finally lyophilized.

Preparation of collagen film and modified collagen film

The collagen solutions (5, 10, 15, 20, 25, 30, 35 and 40 g/L) were obtained by dissolving channel catfish skin collagen in 0.1 mol/L acetic acid (10°C , 12 h). FCF was formatted in synthetic glass molds and dried for 24 h at 30°C and 50% humidity. The reagents glycerol, 25% (v/v) glutaraldehyde and 25% (v/v) PVA were mixed in the collagen solution (15 g/L) to a final concentration of 2 to 8 g/L, 1 to 2 g/L and 2 to 6 g/L respectively. The mixture was well stirred, deaerated under ultrasonic for 10 min. The MFCF was finally formed by the same method to FCF. MFCF adsorbed with tannic acid and desorbed by 50% (v/v) ethanol were dried at the same condition as FCF.

Film hydroscopicity

Film hydroscopicity of each sample was carried out with small pieces of FCF and MFCF which were immersed in 100 ml beakers containing 50 ml of distilled water for 24 h at room temperature (Elizondo et al. 2009). Film hydroscopicity was calculated using the following equation:

$$\text{Film hydroscopicity} = \frac{(W_s - W_d)}{W_d} \times 100 \quad (1)$$

Where W_s is swollen weight and W_d is the dried weight of samples.

Film thickness

Five to 8 thickness measurements were taken on each film by a micrometer with sensitivity of 0.001 mm, and took the average as the results.

Mechanical properties

Mechanical properties of the films were determined from tension test by a TA-XT2i Texture Analyzer (Stable Microsystems Ltd., UK). Films were cut into strips (20 mm × 80 mm) with a surgical scissors. The samples were clamped between grips (A/GT) and the initial grip separation was 40 mm. Forces and deformations were recorded during extension at 1.0 mm s⁻¹ of crosshead speed (Priscila et al. 2011).

Fourier transform infrared spectroscopy

Collagen and modified collagen films were analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The spectra were obtained using a Nicolet Nexus FT-IR spectrometer (Thermo Electron Corporation) by absorption mode at 4 cm⁻¹ intervals and 16-times scanning, in the wavenumber region 500–4000 cm⁻¹ (Guerrero et al. 2011).

Thermal properties

The thermal stability of FCF and MFCF were determined by the differential scanning calorimetry (DSC), using a Perkin-Elmer Pyris 1 DSC instrument (Perkinelmer, Inc., USA). Samples were hermetically encapsulated in aluminium pans and heated from 30 to 200 °C at a heating rate of 5 °C min⁻¹. The denaturation temperatures were determined as the onset value of the occurring endothermic peak.

Scanning electron microscopy

FCF and MFCF were gold-coated using a sputter coater (BAL-TEC, SCD 005, Witten, Germany) prior to observation. Scanning electron micrographs (SEM) of each specimen were obtained using a scanning electron microscope (SEM, QUANTA-200, FEI, Czech).

Adsorptivity of tannic acid

Tannic acid determination

The content of tannic acid was determined by the Folin-Denis method. The tannic acid concentration for this study was obtained between 1–7 mg/L in preliminary studies, so that it fitted within the linear portion of the Folin–Denis assay standard curve (Isenburg et al. 2004). Adsorbance was calculated by following equation:

$$Q = \frac{(C_0 - C_1) \times V}{1000W} \quad (2)$$

Where Q is adsorptivity of tannic acid (mg/g), C₀ is the tannic acid concentration of initial solution (mg/L), C₁ is the tannic acid concentration of reacted solution (mg/L), V is the volume of the reaction solution, W is the weight of modified collagen film added in the solution (g).

Adsorption isotherm

Tannic acid was prepared as 100 ml solutions at the concentrations of 25, 50, 100, 150, 200, 300, 400 and 500 mg/L respectively. After the pH of the solution was adjusted to neutral using 0.05 mol/L HCl or 0.05 mol/L NaOH, 4.0 g modified collagen film was immersed into the solution. Then the flask was shaken continuously at 150 rpm for 2 h (based on adequately performed test). The adsorption was repeated at 35, 45 and 55 °C respectively. The tannic acid concentration was subsequently determined by the Folin-Denis method.

Kinetics of tannic acid adsorption

Tannic acid was prepared as 100 ml solutions at the concentrations of 50, 100, 200 mg/L, were prepared respectively. After the pH of the solution was adjusted to neutral, 4.0 g modified collagen film was immersed into the solution. Then the flask was shaken continuously at 150 rpm for 2 h at 35 °C. The tannic acid concentration was determined every 15 min.

Desorption of tannic acid

Desorption of tannic acid were performed firstly by adsorbing the tannic acid onto MFCF and then mixed with 100 ml 50% ethanol. After that the sample was shaken with 150 rpm at 35 °C for 35 min. Finally, the tannic acid concentration of reacted solution was tested. The elution rate of tannic acid was calculated by following equation:

$$R = \frac{Q_1}{Q_0} \times 100 \quad (3)$$

Where R is elution rate of tannic acid (%), Q₁ is total content of tannic acid in desorption solution (mg), Q₀ is total content of tannic acid adsorbed by modified collagen film (mg).

Statistical analysis

The film hydroscopicities were obtained by five measurements for each treatment. Tensile strength (MPa) and deformation at break (%) of the samples were determined from eight replicates testing. All chemical experiments were performed in triplicate. Data in this experiment were analyzed by Microsoft excel 2007. The results obtained were subjected to analysis of variance (ANOVA) and Duncan's test.

Results and discussion

Effects on mechanical properties of different additives

The surface morphologies of FCF were recorded by a Canon G12 camera. As shown in Fig. 1, the surface morphology was affected by concentrations of collagen solution. FCF prepared by 15 g/L fish collagen solution was more smoother. In contrast, FCF became rougher with the increase of collagen concentration. Then, fish collagen solution at a concentration of 15 g/L was more appropriate for FCF preparation. The thickness of FCF was 11 ± 2 μm .

Glycerol was used as plasticizer of FCF. As shown in Fig. 2a, tensile strength of the film increased when glycerol concentration was under 2 g/L, then decreased while the glycerol was kept adding. Unlike tensile strength, the elongation-at-break of the film increased steadily as glycerol concentration increases. As shown in Fig. 2b, mechanical properties of the film were both improved greatly when PVA concentration was 6 g/L. Because a mass of hydroxyl groups present in the PVA molecule, plenty of hydrogen groups formed between PVA and collagen to reinforce the film structure. Nevertheless, tensile strength and elongation at break reduced at a higher concentration of PVA. Unlike gelatin film (Bigi et al. 2008), mechanical properties of fish collagen film were not improved by glutaraldehyde. Tensile strength and elongation at break of fish collagen film reduced substantially as soon as only a small quantity of glutaraldehyde was mixed (Fig. 2c).

Film hydroscopicity

Effects on film hydroscopicity of different additives were also studied. As shown in Fig. 3, glycerol and PVA enhanced the hydroscopicity of film, because PVA and glycerol had plenty of hydroxyl bounded water while they cross-linked with collagen. On the contrary, glutaraldehyde reduced hydroscopicity greatly. This was mainly due to the improved covalent crosslink between peptides of collagen and decreased amount of hydrogen bonds between collagen and

water. Therefore, glutaraldehyde was chosen to increase the water resistance to avoid the collapse in water. Then 2 ml/L glycerol, 6 ml/L PVA and 2 ml/L glutaraldehyde at final concentrations were chosen as the optimal conditions for preparation of MFCF. As shown in Fig. 3, hydroscopicity of the modified film was 54%, lower than that of FCF significantly.

Fourier-transformed infrared spectroscopy

Mechanical properties and film hydroscopicity can be determined by macro means, such as texture and weight method. Also, crosslinking density can be determined by microcosmic measures, such as FTIR. The infrared spectra of FCF and MFCF were depicted in Fig. 4. The amide A band position was found in FCF at 3318.55 cm^{-1} , which was due to hydrogen-bonded hydroxyl groups (O–H). A shift of amide A band to lower frequencies (3311.3 cm^{-1}) was observed in MFCF, which could mean an increase in hydrogen bonding between collagen molecules. The spectrum of FCF dispersions also demonstrated the characteristic pattern reflecting the amide I band at 1652.36 cm^{-1} , the amide II band at 1557.83 cm^{-1} , and the amide III band at 1239.93 cm^{-1} , respectively. The amide I band which is associated with secondary structure of protein and the amide III band demonstrated the existence of helical structure (Surewicz and Mantsch 1988; Muyonga et al. 2004b; Rai et al. 2011). The amide I band in MFCF shifted to a higher frequencies (1654.58 cm^{-1}), which suggested that crosslink by covalent bonds was strengthened between collagen molecules.

Thermal properties

The thermal stability of FCF and MFCF were determined by the differential scanning calorimetry (DSC). As shown in Fig. 5, values of glass transition temperature (T_g) between FCF and MFCF were identical. Shrink temperatures (T_s) of MFCF ($79.3\text{ }^\circ\text{C}$) was obviously higher than that of FCF ($56.5\text{ }^\circ\text{C}$). T_s of collagen would increase by addition of crosslinker and plasticizer. It was no wonder that T_s of

Fig. 1 Surface morphology of FCFs made by different concentration of fish collagen solutions. **a**:the concentration of 15 g/l; **b**:the concentration of 20 g/l; **c**:the concentration of 30 g/l

Fig. 2 Changes of tensile strength and elongation at break of the film due to increasing of additive concentrations in collagen solution. **a:** Glycerol; **b:** PVA; **c:** Glutaraldehyde. Estimations were determined from eight replicates testing. Values are means ($n=8$) $\pm$ standard deviation

Fig. 3 Effects of different additives on film hydroscopicity. **a:** 2 ml/L glutaraldehyde; **b:** 2 ml/L glycerol; **c:** 6 ml/L PVA. Estimations were determined from five replicates testing. Values are means ($n=5$) $\pm$ standard deviation. Values in columns followed by same letter are not significantly different at $\alpha=0.01$

Fig. 4 Infrared spectra of FCF and MFCF. FCF: Fish collagen film. MFCF: Modified fish collagen film

MFCF was improved compared to FCF, because the cross-linking between collagen molecules in MFCF was strengthened due to large numbers of covalent bonds and hydrogen bonds provided by glutaraldehyde and PVA. Therefore, MFCF did not collapse when it was immersed in a solution with a higher temperature. Additionally, T_s of MFCF (79.3 °C) was also higher than that of collagen film modified by catechin (70 °C) (Madhan et al. 2005), collagen film modified by curcumin (78 °C) (Gopinath et al. 2004).

Adsorptivity on tannic acid

Adsorption isotherm

The mechanism for tannic acid adsorption is still not very clear. It may be hypothesized that tannin acid cross-linked gelatin by the functions of hydrophobic bonds, hydrogen bonds or esterification (Cao et al. 2007). Although the Langmuir equation is more suitable for the gas systems, its theoretical background is quite useful and convincible for comparison in liquid-phase adsorption (Chang and Juang 2004).

The analysis of the isotherm data is important to develop an equation which accurately represents the results (Ho and McKay 1998). The Langmuir adsorption isotherm (Langmuir 1918) was applied to analyze the sorption processes of tannic acid at low temperatures of 35 °C, 45 °C and 55 °C, because

Fig. 5 DSC thermograms of FCF and MFCF. FCF: Fish collagen film; MFCF: Modified fish collagen film

tannic acids usually exists in thermosensitive materials. A linear form of the Langmuir equation is given below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (4)$$

Where C_e (mg/L) is the equilibrium concentration of tannic acid on MFCF in the tannic acid solution, Q_e (mg/g) is the amount of tannic acid adsorbed per unit mass of MFCF at equilibrium, Q_m (mg/g) is the adsorption maximum, and K_L is an adsorption coefficient related to the bonding energy. Results were shown in Fig. 6.

Figure 6a illustrated the equilibrium adsorption of tannic acid. It was found that the adsorption capacities of MFCF were almost the same when the working temperatures were around 35 °C and 45 °C, but increased greatly as the temperature raising to 55 °C. Additionally, adsorption capacity did not increase while the concentration of tannic acid is higher than 100 mg/L.

According to Fig. 6b, it was found that the Langmuir equation was suitable for the description of adsorption isotherms of tannic acid at 35 °C and 45 °C. The regression coefficient of 35 °C ($R^2=0.9757$) was higher than that of

Table 1 Parameters of Langmuir equation

Temperature (°C)	Parameters		
	Q_m (mg/g)	K_L	R^2
35 °C	29.07	0.0509	0.9757
45 °C	34.01	0.0485	0.9837
55 °C	243.90	0.0025	0.1169

Q_m (mg/g) is the adsorption maximum of tannic acid

K_L is an adsorption coefficient related to the bonding energy

R^2 is the regression coefficient linear regression equation

45 °C ($R^2=0.9837$). This showed a chemical reaction or bond being involved in the sorption process with the increase in temperature (Ho and McKay 1998).

However, as shown in Table 1, the adsorption of tannic acid on MFCF at 55 °C did not fix the Langmuir equation ($R^2=0.1169$). A possible explanation was that the surface of MFCF was damaged at a higher temperature. Therefore, Q_e was greatly improved due to the increased area of the contact surface.

Fig. 6 Isotherms of adsorption and the Langmuir model fit for isotherms of adsorption of tannic acid onto MFCF at 35 °C, 45 °C and 55 °C. **a**: Isotherms of adsorption (Values are means of triplicate determinations ($n=3$) $\pm$ standard deviation); **b**: The Langmuir model fit for isotherms of adsorption

Fig. 7 Time profiles of amounts of tannic acid and pseudo-second order model for adsorption of tannic acid onto MFCF. **a**: Time profiles of amounts of tannic acid (Values are means of triplicate determinations ($n=3$) $\pm$ standard deviation); **b**: The pseudo-second order model for adsorption of tannic acid

Table 2 Parameters of adsorption pseudo-second order equation

Initial concentration of tannic (mg/l)	Parameters		
	Q _e (mg/g)	K (g/mg·min ⁻¹)	R ²
50	10.28	0.0201	0.9982
100	27.93	0.0519	0.9997
200	32.47	0.0039	0.9983

Q_e (mg/g) is the amount of tannic acid adsorbed per unit mass of MFCF at equilibrium

K (g/mg·min⁻¹) is the equilibrium rate constant of pseudo-second order chemical sorption the value of rate constant

R² is the regression coefficient linear regression equation

Kinetics of tannic acid adsorption

Figure 7a illustrated the time profiles of the amount of adsorption at different initial concentration of tannic acid solution at 35 °C. The kinetics sorption of tannic acid can be represented by a pseudo-second order chemical sorption process (Ho and McKay 1998):

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2 \quad (5)$$

Where Q_e (mg/g) is the amount of tannic acid adsorbed per unit mass of MFCF at equilibrium, Q_t (mg/g) is the amount of tannic acid adsorbed at time t.

The Eq. 5 can be rearranged to obtain a linear form of

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t \quad (6)$$

Where k(g/mg·min⁻¹) is the equilibrium rate constant of pseudo-second order sorption.

The results were shown in Fig. 7b. It was found that adsorption on MFCF followed the pseudo-second order model for tannic acid. The Table 2 indicated Q_e, k and the regression coefficients (R²) for the pseudo-second order equation. The results showed that the correlation coefficients were all significantly (≥0.990). Namely, the data showed a good compliance with the pseudo-second order equation. It suggested that a chemical reaction or bond was becoming more predominant in the sorption process (Ho and McKay 1998).

Surface morphology

The Fig. 8 presented SEM micrographs of the surface morphology of FCF and MFCF, respectively. It indicated that FCF and MFCF both had a dense top layer. But the surface of MFCF looked smoother than FCF and had fewer pores. It was mainly due to the enhanced crosslinking between collagen molecules in MFCF by glutaraldehyde and PVA.

Fig. 8 SEM micrographs of the surface morphology of FCF, MFCF, MFCFA and MFCFD. **a**:FCF: Fish collagen film; **b**:MFCF: Modified fish collagen film; **c**: MFCFA: Modified fish collagen film

adsorbed with tannic acid; **d**:MFCFD: Modified fish collagen film desorbed by 50% ethanol

The Fig. 8 pointed out the significant changes of surface morphology of MFCFA (MFCF adsorbed with tannic acid) and MFCFD (MFCF desorbed by 50% (v/v) ethanol). A large number of flaky crystals, which might be the sediment of tannic acid, were observed on the surface of MFCFA. However, a little flaky crystals were found on the surface of MFCFD. Elution rate of tannic acid on MFCFA was calculated to be 84%. Meanwhile, the color of MFCFD became light obviously. All above findings were in agreement with the aforementioned results of adsorption experiments.

Conclusion

In order to reuse the fish collagen in the process of tannin binding, MFCF were prepared by addition of modifying agent in collagen solution. Compared to FCF, physicochemical properties, especially water resistance of MFCF were successfully improved. In addition, MFCF had higher shrink temperature, then it would not collapse or dissolve when it was immersed in a tannin solution with a higher temperature. More importantly, MFCF showed good capability of absorption and desorption of tannic acid solution. MFCF overcame the drawback of collagen or FCF, and could be reused in the process of tannin binding.

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References

- An JH, Dultz S (2007) Adsorption of tannic acid on chitosan-montmorillonite as a function of pH and surface charge properties. *Appl Clay Sci* 36:256–264
- Bigi A, Cojazzi G, Panzavolta S, Rubini K, Roveri N (2008) Mechanical and thermal properties of gelatin films at different degrees of glutaraldehyde crosslinking. *Biomaterials* 22:763–768
- Cao N, Fu YH, He JH (2007) Mechanical properties of gelatin films cross-linked, respectively, by ferulic acid and tannin acid. *Food Hydrocolloid* 21:575–584
- Chang MY, Juang RS (2004) Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay. *J Colloid Interface Sci* 278(1):18–25
- Chang MY, Juang RS (2005) Equilibrium and kinetic studies on the adsorption of surfactant, organic acids and dyes from water onto natural biopolymers. *Colloid Surf A* 269:35–46
- Elizondo NJ, Sobral PJA, Menegalli FC (2009) Development of films based on blends of *Amaranthus cruentus* flour and poly(vinyl alcohol). *Carbohydr Polym* 75:592–598
- Fernandes RMT, Couto NRG, Paschoal CWA, Rohling JH, Bezerra CWB (2008) Collagen films from swim bladders: preparation method and properties. *Colloid Surf B* 62:17–21
- Gopinath D, Rafiuddin Ahmed M, Gomathi K, Chitra K, Sehgal PK, Jayakumar R (2004) Dermal wound healing processes with curcumin incorporated collagen films. *Biomaterials* 25:1911–1917
- Guerrero P, Stefani PM, Ruseckaite RA, Caba K (2011) Functional properties of films based on soy protein isolate and gelatin processed by compression molding. *Food Eng* 105:65–72
- Ho YS, McKay G (1998) Kinetic models for the sorption of dye from aqueous solution by wood. *Process Saf Environ* 76(2):183–191
- Hvattum E (2002) Determination of phenolic compounds in rose hip (*Rosa canina*) using liquid chromatography coupled to electrospray ionisation tandem mass spectrometry and diode-array detection. *Rapid Comm Mass Spectrom* 16:655–662
- Isenburg JC, Simionescu DT, Vyavahare NR (2004) Elastin stabilization in cardiovascular implants: improved resistance to enzymatic degradation by treatment with tannic acid. *Biomaterials* 25:3293–3302
- Kimura S, Ohno Y (1987) Fish type I collagen: tissue specific existence of two molecular forms, (α1)2α2 and α1α2α3 in Alaska pollack. *Physiol B Biochem Mol Biol* 88B(2):409–413
- Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc* 40:1361
- Lee CH, Singla A, Lee Y (2001) Biomedical applications of collagen. *Int J Pharm* 221:1–22
- Liu HY, Li D, Guo SD (2007) Studies on collagen from the skin of channel catfish (*Ictalurus punctatus*). *Food Chem* 101:621–625
- Liu HY, Li D, Guo SD (2008a) Extraction and properties of gelatin from channel catfish (*Ictalurus punctatus*) skin. *LWT-Food Sci Technol* 41(3):414–419
- Liu HY, Li D, Guo SD (2008b) Rheological properties of channel catfish (*Ictalurus punctatus*) gelatine from fish skins preserved by different methods. *LWT-Food Sci Technol* 41(8):1425–1430
- Liu HY, Han J, Guo SD (2009) Characteristics of the gelatin extracted from Channel Catfish (*Ictalurus Punctatus*) head bones. *LWT-Food Sci Technol* 2(42):540–544
- Madhan B, Subramanian V, Rao JR, Nair BU, Ramasami T (2005) Stabilization of collagen using plant polyphenol: Role of catechin. *Int J Biol Macromol* 37:47–53
- Muyonga JH, Cole CGB, Duodu KG (2004a) Characterisation of acid soluble collagen from skins of young and adult Nile perch (*Lates niloticus*). *Food Chem* 85:81–89
- Muyonga JH, Cole CGB, Duodu KG (2004b) Fourier transform infrared (FTIR) spectroscopic study of acid soluble collagen and gelatin from skins and bones of young and adult Nile perch (*Lates niloticus*). *Food Chem* 86:325–332
- Nagai T, Araki Y, Suzuki N (2002) Collagen of the skin of ocellate puffer fish (*Takifugu rubripes*). *Food Chem* 78:137–177
- Nagarajan M, Robinson JS, Durairaj S, Jeyasekaran G (2011) Skin, bone and muscle collagen extraction from the trash fish, leather jacket (*Odonus niger*) and their characterization. *J Food Sci Tech*. doi:10.1007/s13197-011-0440-y
- Priscila MAA, Rosemary AC, Izabel CFM, Carla GL, Ana MQBB, Paulo JAS (2011) Development of films based on blends of gelatin and poly(vinyl alcohol) cross linked with glutaraldehyde. *Food Hydrocolloid* 25:1751–1757
- Rai MA, Faqir MA, Muhammad IK, Moazzam RK, Imran P, Muhammad N (2011) Application of Fourier transform infrared (FTIR) spectroscopy for the identification of wheat varieties. *J Food Sci Tech*. doi:10.1007/s13197-011-0424-y
- Reed JD (1995) Nutritional toxicology of tannins and related polyphenols in forage legumes. *J Anim Sci* 73:1516–1528
- Surewicz WK, Mantsch HH (1988) New insight into protein secondary structure from resolution enhanced infrared spectra. *Biochim Biophys Acta* 952:115–130
- Vellingiri V, Hans KB (2011) Effect of certain indigenous processing methods on the bioactive compounds of ten different wild type legume grains. *J Food Sci Tech*. doi:10.1007/s13197-010-0223-x
- Wang JX, Min WQ, Guan M, Gong LJ, Ren J, Huang Z, Zheng HP, Zhang JP, Liu HJ, Han YZ (2006) Tench farming in China: present status and future prospects. *Aquacult Int* 14:205–208