# Opening Remarks

*by*

President William N. Marmer

104th ANNUAL MEETING, ALCA
GRANDOVER RESORT, GREENSBORO, NC
THURSDAY, JUNE 19, 2008

## Ladies and gentlemen:

I am President Bill Marmer. Welcome to the 104th Annual Meeting of the American Leather Chemists Association. I am pleased that you were able to join me here at the Grandover. We first met here five years ago, and we knew then that we would want to return here for another meeting. I know you will enjoy all the activities here, from the technical sessions to the business meeting to the luncheons, the Fun Run, and the closing banquet.

This morning, here in this room, let me also welcome you to the technical program. This is really a seminal part of the Association. Our Bylaws state that the first two objectives are:

(1) To promote the advancement of the knowledge of science and engineering especially in regard to their application to problems facing the leather and leather products industries.

(2) To encourage and promote the full use of science and engineering in their applications to the leather and leather products industries.

The other three objectives, incidentally, are (3) to publish, (4) to develop and maintain official methods and specifications, and (5) to advance the professional welfare of its members by all legitimate means.

The task of assembling the technical sessions falls on the Association's Vice President, and so I call upon Vice President Steve Yanek, to call this session to order and to introduce the program.

(Technical Session officially opened by Stephen Yanek)

# Introduction of the John Arthur Wilson Memorial Lecture

*by*
Maryann Taylor

Mr. President, officers, councilors, distinguished guests, ladies and gentlemen:

The John Arthur Wilson Memorial Lecture was established by the American Leather Chemists Association in 1959 to honor its 16th president and one of our industry's most distinguished scientists. Since its inception, the lecture was sponsored annually through 2003 by the Salem Oil and Grease Company. Since 2004, Stahl has generously continued this sponsorship.

Following John Arthur Wilson's death in 1942, Arthur W. Thomas wrote a very moving tribute in which he stated that Mr. Wilson was a man, who before the age of 40, had become a world leader in the field of leather chemistry as well as a distinguished contributor to the progress of pure science. Owing largely to his influence, Article II of the By Laws of the American Leather Chemists Association was expanded at that time to read "To promote the advancement of chemistry and other sciences, especially in regard to their application to problems confronting the leather industry". His contributions to advancing this philosophy were numerous, and included the study of protein swelling, the fundamental mechanisms of collagen-tanning agent interactions, beamhouse and tanning processes, as well as the application of the fundamental laws of colloid and physical chemistry, in particular to the mechanism of activated sludge and dewatering of sludge, a major environmental concern. While keeping in mind these models of innovations as applied to the leather industry, our committee consisting of John Whiteman, Jerry Levy and myself, selected Professor Bi Shi from Chengdu, China, as the 49$^{th}$ lecturer in this series.

Professor Bi Shi received his bachelor's degree from the Polymer Material Department, Chengdu University of Science and Technology in 1982, and was awarded a Doctor's Degree from the Leather Engineering Department of Sichuan University in 1992. He carried out research and completed most of his PhD work at the Chemistry Department of Sheffield University, Great Britain from 1990-1992. Presently, he is the professor and director of The Key Laboratory of Leather Chemistry and Engineering of Ministry of Education in Sichuan University, widely recognized as the premier leather research institute in China. He is the Chairman of Science and Technology Committee of the China Leather Industry Association (CLIA) and a Member of the National Congress of China. He is currently the vice president of IULTCS, as well as the representative from North Asia on the IULTCS Executive committee. He was a member of the Scientific and Technical Committee, chaired by Dr. William N. Marmer, for the 2007 IULTCS meeting that was held in Washington, DC. China will be hosting the 30th IULTCS Global Congress, on October 11-14, 2009, in Beijing, and Professor Bi Shi is the Technical Chairman of this meeting. This will be only the second time that an IULTCS Congress has been held in Asia and the first time in China.

# Diversified Applications of Tanning Principles

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## Abstract

Some interesting examples of diversified applications of tanning principles in creating novel functional materials were reported. Firstly, based on the principle of vegetable tanning, a novel adsorbent which can selectively remove tannins from plant extracts was prepared by processing skin into collagen fibers with proper size. This adsorbent was more effective in removal of tannins in comparison with commonly used polyamides and macro reticular resins, indicative of a great potential of application in industries of natural beverage, plant medicine, etc. Secondly, according to the principle of vegetable tannin-aldehyde combination tanning, the tannin-immobilized adsorbent and membrane materials were prepared by immobilizing tannins onto collagen matrix. Both of them presented high adsorption capacity to heavy metal ions, such as $Hg^{2+}$, $Pd^{2+}$, $Au^{3+}$, $UO_2^{2+}$ and $Cu^{2+}$, in aqueous solutions and therefore, are expected to be used for removing toxic metal ions from wastewaters or separating precious metals from other metal ions in mixed solutions. Thirdly, in the light of the principle of metal tanning, a series of functional materials were prepared by loading metal ions, such as $Zr^{4+}$, $Fe^{3+}$ and $Pt^{4+}$, onto collagen fiber. The $Zr^{4+}$-loaded material exhibited strong adsorption to inorganic anions, such as $F^-$, $PO_4^{3-}$, $CrO_4^{2-}$ and $V_2O_7^{4-}$ in aqueous solutions, showing potential of application in environmental protection. At the same time, $Fe^{3+}$ and $Pt^{4+}$-loaded materials were proven to be the heterogeneous catalysts with high catalytic activity. Meanwhile, as a special kind of metal-loaded collagen fiber, the adsorption behaviors of chrome leather waste to organic compounds in wastewater were also investigated. It presented high adsorption capacity to anionic dyes and surfactants. Finally, in terms of the principles of versatile metal-organic combination tanning, a series of novel metal fiber and carbon fiber materials with controllable mesoporous structures were prepared by using collagen fiber as a template. They are believed to have great values in selective adsorption, chemical sensor and catalyst support.



## Resumen

Curtición es la reacción química fundamental que transforma la piel en cuero. Algunos curtidos, tal como curtición al vegetal, curtición por aldehído y curtición por metales, han sido utilizados por curtidores durante varios milenios. Los principios químicos tras estos curtidos han sido claramente elucidados en las últimas décadas y han mejorado extensamente las tecnologías del proceso del cuero. Concurrentemente las esencias científicas involucradas en estos principios iluminan nuestras inspiraciones sobre diversas aplicaciones de métodos de curtición que nos permiten crear una serie de novedosos materiales basados en el colágeno de la piel. Es por ende que ingeniosas aplicaciones son reportadas; y por lo tanto podrían inspirar ideas y conceptos más científicos en los químicos del cuero.

1. En base al principio de curtición vegetal, un novedoso agente adsorbente, el cual puede remover selectivamente los taninos en bebidas naturales y extractos medicinales de plantas, fue desarrollado. Fue preparado por medio del procesar piel en fibras de colágeno con las dimensiones idóneas. Este nuevo adsorbente se demostró ser más efectivo para este propósito, en comparación con las poliamidas y resinas macro-reticulares, comúnmente utilizadas.
2. De acuerdo con el principio de curtición combinada de vegetal-aldehído, taninos en capacidad de ligarse por coordinación con iones metálicos fueron inmovilizados sobre la matriz colagénica. Como resultado dio, un agente adsorbente inmovilizado por el tanino y materiales utilizables para membranas también fueron preparados. Ambos demostraron alta capacidad de absorción de iones de metales pesados, tales como $Hg^{2+}$, $Pd^{2+}$, $Au^{3+}$, $UO_2^{2+}$, y $Cu^{2+}$, en soluciones acuosas y como tal es de esperar sean utilizables para remover iones metálicos tóxicos de efluentes o para la recuperación de metales preciosos de soluciones mixtas.


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3. Al utilizar el principio de curtición por metal, una serie de materiales funcionales fueron preparados descargando sobre la fibra colagénica iones metálicos tales como $Zr^{4+}$, $Fe^{3+}$ y $Pt^{4+}$. Los materiales cargados con $Zr^{4+}$ y $Fe^{3+}$ exhibieron fuerte adsorción de aniones inorgánicos tales como $F^-$, $PO_4^{3-}$, $AsO_4^{3-}$, $CrO_4^{2-}$ y $V_2O_7^{4-}$, desde soluciones acuosas, demostrando su uso potencial en proteger al medioambiente. Al mismo tiempo, materiales cargados con $Fe^{3+}$ y $Pt^{4+}$ han sido experimentalmente demostrados de ser catalizadores heterogéneos de alta actividad. Paralelamente, como un producto especial formado por fibras colagénicas cargadas con metal, la adsorción por deshechos de cuero al cromo de compuestos orgánicos en efluentes también fueron investigados. Se presento alta capacidad de adsorción de colorantes, tensoactivos, y ácidos aromáticos.
4. En términos de los principios involucrados en versátiles curtidos combinados metal-orgánicos, una serie de nuevos materiales de fibras de carbono y fibras metálicas con estructuras mesopóricas controlables, fueron preparadas utilizando fibras colagénicas como patrón. Se cree que tendrían alto valor potencial en absorción selectiva, censores químicos, y apoyo para agentes catalíticos.

## Introduction

Tanning is the basic chemical reaction to transform hides or skins into leather. Some tannages, like vegetable tanning, aldehyde tanning and metal tanning, have been used by tanners for several thousand years. The main chemical principles of these tannages, revealed in recent decades, have extremely improved the technologies of leather manufacture. At the same time, the scientific essences involved in these principles are enlightening our inspirations of diversified and comprehensive applications of tanning methods to create a series of novel functional materials based on skin collagen. Herein, some interesting and ingenious applications of the tanning principles were reported, which might inspire more scientific ideas and imaginations of leather chemists.

## 1. Application of Principle of Vegetable Tanning

### Background and Idea

Vegetable Tannins are widely distributed in plant kingdom. They are found in about 80% of woody plants and 15% of herbaceous species[1] and therefore, often occur at a high level in some human consumed vegetable extracts, such as beverages and herbal medicines. It has been reported that some kinds of tannin constituents are beneficial to health and can prevent from some diseases.[2, 3] However, there are growing evidences that tannins would produce adverse effects on animals and humans.[4] For example, they lead to perturbation of mineral adsorption,[5] growth retardation,[6] inhibition of digestive enzymes and liver damage.[7] Therefore, it has received extensive attention to remove tannins from some vegetable extracts, especially from medicinal plant extracts.

In practice, it is very difficult to selectively remove tannins from a plant extract because many active/valuable constituents in the extract contain phenolic structures similar to those of tannins and have nearly the same solubility as tannins in water and organic agents. In fact, this problem has impeded the development of plant extracts related industries to some extent.

But, as for our tanners, this might not be a problem when considering the principle of vegetable tanning. As we know, vegetable tanning is mainly based on multi-hydrogen bonds interaction between tannins and collagen fibers.[8] To achieve this kind of stable association, enough molecular size and content of phenolic hydroxyls are necessary. Most of active constituents in plant extracts are not able to form multi-hydrogen bonds with collagen fibers because they have no enough phenolic hydroxyls or are lack of adjacent phenolic hydroxyls. Indeed, they are so-called “non-tannins”. This fact strongly suggested that a properly prepared collagen material could be used to selectively remove tannins from plant extracts.

### Preparation of Collagen Fiber Adsorbent

Bovine skin was cleaned, unhaired, limed, split and delimed according to the procedures of leather processing, so that non-collagen components were removed. Then the pelt was treated three times with acetic acid solution (16g/L) to remove mineral substances. The pH value was then adjusted to 4.8-5.0 using acetic acid-sodium acetate buffer solution and the pelt was subsequently dehydrated by absolute ethyl alcohol, dried in vacuum to moisture content ≤10%, ground and sieved to yield collagen fiber with particle size 1.0-2.5 mm, moisture ≤ 12% and ash content ≤ 0.3%.

15g collagen fiber and 1.5g glutaraldehyde were added into 300ml distilled water and reacted at room temperature for 4h, and then further reacted at 45°C for 4h. After being washed with distilled water and dried at 50°C in vacuum, the collagen fiber adsorbent with improved thermal and chemical stabilities was obtained.

### Application Cases

*Adsorption behavior of collagen fiber adsorbent in mixed solution of tannins and medicinal constituents*

Five typical active constituents of medicinal plants (Figure 1), baicalin (**1**), naringin (**2**), genistin (**3**), genistein (**4**) and resveratrol (**5**), containing phenolic hydroxyls, were chosen in this work to investigate the adsorption selectivity of the adsorbent. They were mixed with larch tannin, black wattle tannin and bayberry tannin, respectively, to prepare a series of aqueous solutions of active constituents-tannin, in which

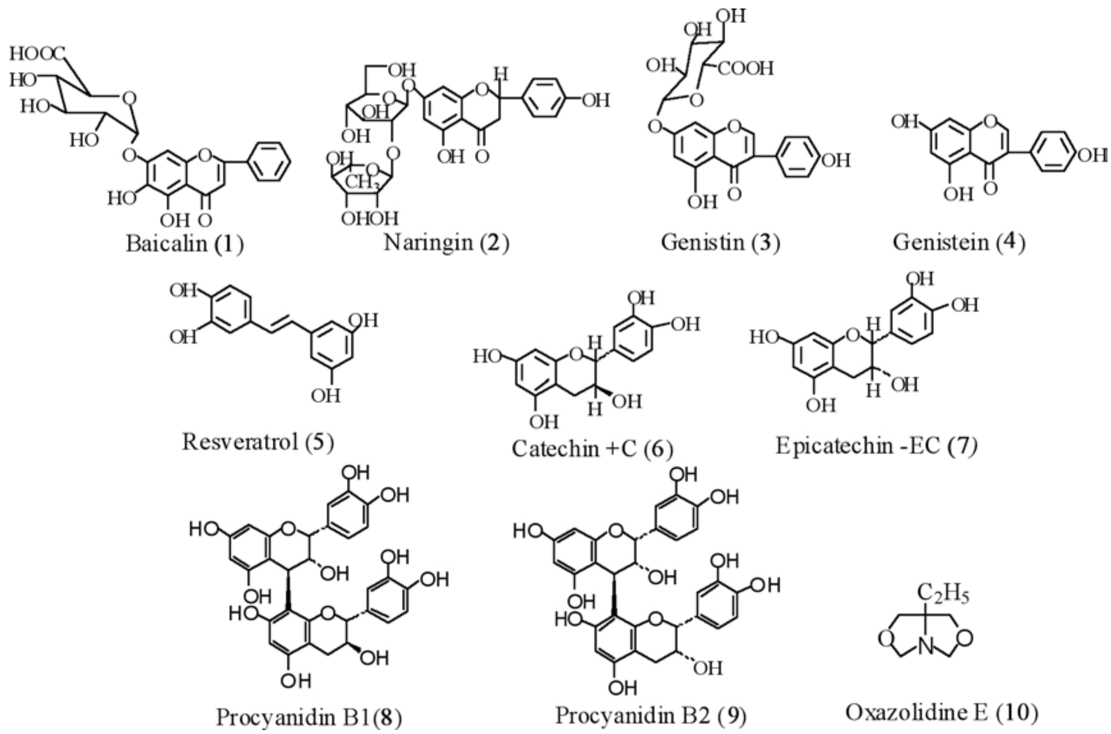



Figure 1: Structures of compounds used in experiments

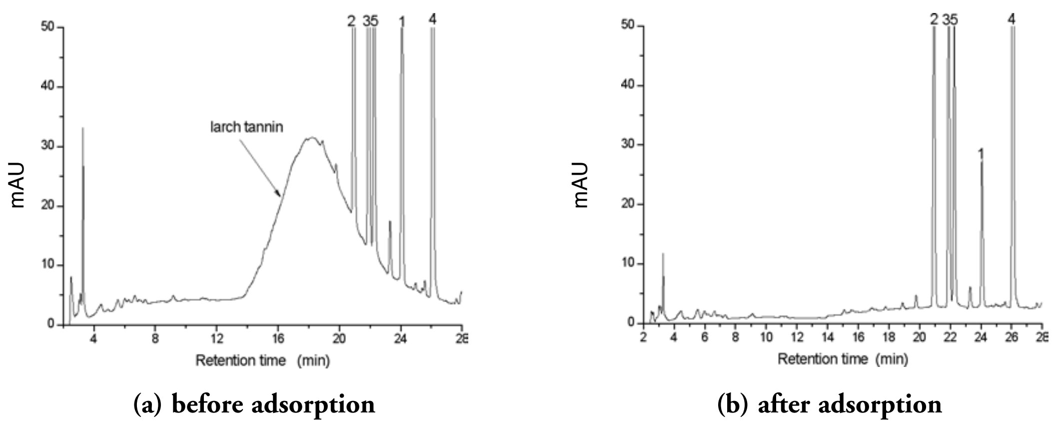


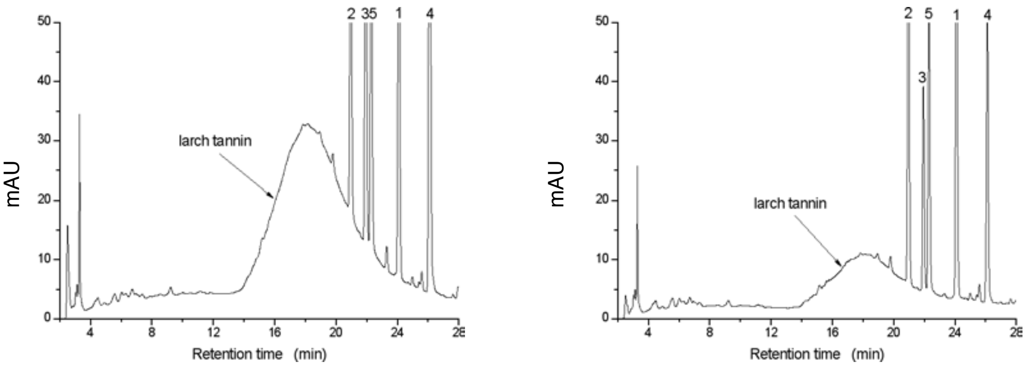

Figure 2: HPLC pattern of larch tannin-active constituents solution adsorbed by collagen fiber adsorbent. Mobile phase: A=$H_2O$(0.5%$H_3PO_4$), B= $CH_3OH$; column : Hypersil ODS $C_{18}$, 4.0×250, 5µm; flow rate: 0.8 ml/min; column temperature: 30°C; detector: DAD, 280nm; gradient: 0-10min with 18%-24%B, 10-25min with 24%-70%B, 25-35min with 70%B; injection volume: 20µL.

the content of tannin was 1000mg/L, and the content of each active constituent was 20mg/L. 0.5g collagen fiber adsorbent was suspended in 100ml of the mixture solutions and shaken at 25°C for 24h.

High Performance Liquid Chromatography (HPLC) analysis showed that the larch tannin in the mixture solution was completely adsorbed by the collagen fiber adsorbent, as presented in Figure 2.[9] For the mixed solutions containing black wattle tannin and bayberry tannin, similar HPLC patterns were obtained. In general, the removal extent of all the condensed tannins was 100% even their concentration was 50-fold that of each active constituent. Meanwhile, the average adsorption/lose extent of the active constituents was 21.5%. The selectivity of the adsorbent to tannin is remarkably higher than that of commonly used polyamide, as shown in Figure 3.[9] In the same conditions, the average adsorption extents of polyamide to tannins and active constituents were 75.4% and 33.3%, respectively.[9]

*Fractionation of proanthocyanidins*

The biological activities of oligomeric proanthocyanidins, such as antioxidation and radical scavenging, have attracted increasing interest of researchers in many fields.[10, 11] But the




**(a) before adsorption** **(b) after adsorption**

Figure 3: HPLC pattern of larch tannin-active constituent's solution adsorbed by polyamide. Chromatographic conditions were the same as those in Figure 2.

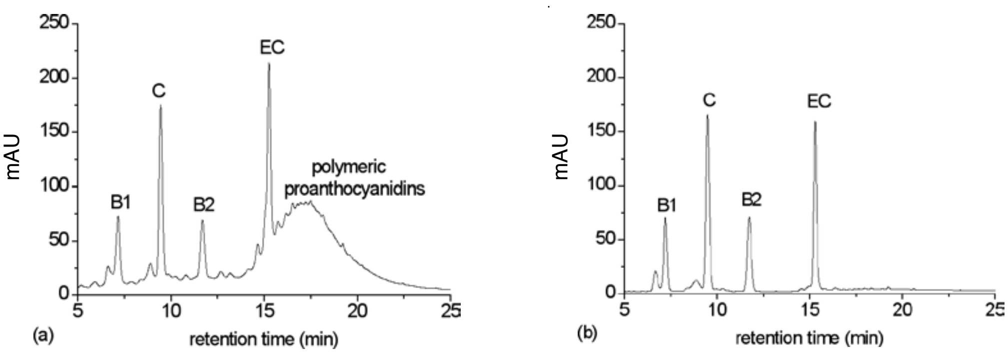



Figure 4: HPLC patterns of proanthocyanidins before and after adsorption by collagen fiber adsorbent. (a) before adsorption; (b) after adsorption. Mobile phase: A = $H_2O$ (0.5%$H_3PO_4$), B= $CH_3OH$; column: Hypersil ODS $C_{18}$, 4.0×250, 5μm; flow rate: 0.8ml/min; column temperature: 30°C; detector: DAD, 280nm; gradient: 0-10min with 18-24%B, 10-25min with 24-70%B, 25-35 min with 70%B; injection volume: 20μL.

oligomeric proanthocyanidins usually coexist with polymeric proanthocyanidins which have some negative effects in uses. So many researches have been focused on the separation of oligomeric and polymeric proanthocyanidins.

Figure 4 shows the separative duty of collagen fiber adsorbent for proanthocyanidins extracted from grape seed. The adsorption experiment was initiated by putting 0.5g adsorbent into 100mL of 1000mg/L proanthocyanidins solution (ethanol:water=30:70), and then shaken at 30°C for 24h. In fact, the polymeric proanthocyanidins are condensed tannins and therefore, they were completely removed by collagen fiber adsorbent after adsorption. As a result, the purified oligomeric proanthocyanidins (non-tannins), including catechin (C, **6**), epicatechin (EC, **7**), procyanidin B1 (**8**) and procyanidin B2 (**9**), were obtained.

## 2. Application of Principle of Vegetable Tannin- Aldehyde Combination Tanning

### Background and Idea

The removal or recovery of heavy metals from aqueous solutions is an important task in considerations of environmental protection and full utilization of resources. Vegetable tannins have multiple adjacent phenolic hydroxyls and therefore, exhibit specific affinity to metal ions. Thus they promise to be effective agents for removal or recovery of metal ions fromwastewater. However, tannins are water-soluble compounds, which restrict their practical application in this field.

Enlighten by the chemical principle of vegetable-aldehyde combination tanning, we immobilized tannins onto collagen matrices through crosslinking reaction of oxazolidine (**10**). As a result, a series of tannin-immobilized materials were prepared. As described in our previous research on the mechanism of vegetable tannin-oxazolidine reaction, condensed tannins favor this reaction and their phenolic hydroxyls are still ready for chelating with metal ions after reaction, as presented in Figure 5.[12] This implies that the tannin-immobilized materials prepared by tannin-oxazolidine combination tanning would be practically useful for removal or recovery of heavy metals from wastewater.

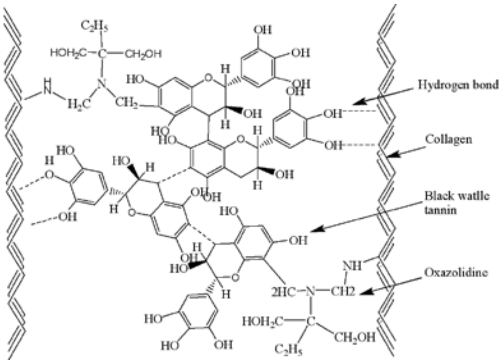



Figure 5: The mechanism of collagen-condensed tannin-oxazolidine reaction.

Figure 6: Tannin-immobilized collagen fiber (TICF).

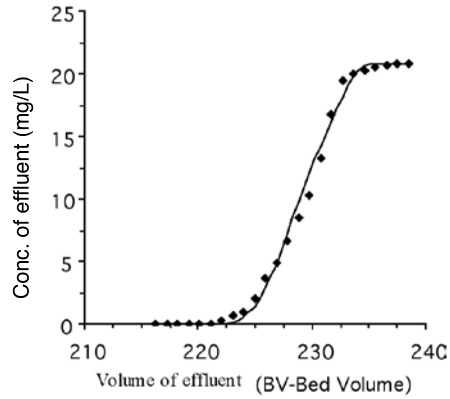



Figure 7: Breakthrough curve of $Au^{3+}$ on TICF column. Feed conc.: 239.17mg $Au^{3+}$/L; pH: 2.5; flow rate:1.93BV/h (BV=bed volume); T: 20°C.

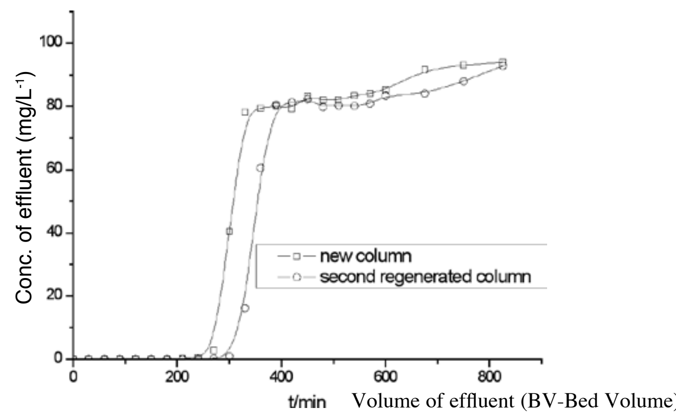



Figure 8: Breakthrough curve of $U^{6+}$ ($UO_2^{2+}$) on TICF column. Feed conc.: 595mg$U^{6+}$/L; pH: 5.0; flow rate: 1.76BV/h; T: 20°C.

## Preparation of Tannin-immobilized Materials

*Tannin-immobilized collagen fiber*

Collagen fiber was prepared according the procedures described in 2.1. 15g collagen fiber and 9g bayberry tannin extracts (tannin content 75.4%) were added in 300 ml distilled water and stirred at 25°C for 24h. After the intermediate product was collected by filtrating and washing with distilled water, 300ml of 2% oxazolidine solution with pH6.5 was added. The mixture was stirred at 25°C for 1h, and then continuously stirred at 50°C for 4h. The product was washed with distilled water and vacuum dried at 50°C for 12h, and then the tannin-immobilized collagen fiber (TICF) was obtained, as shown in Figure 6.

*Tannin-immobilized collagen membrane*

This was simply completed by employing the method of vegetable tannin-aldehyde combination tanning. In brief, the pickled goat skin was depickled to pH=5.0-5.2 and tanned by 15% bayberry tannin extracts (float 2) at 25°C for 4h. Then the vegetable tanned leather was fully washed with distilled water and retanned by 3% oxazolidine (float 2) at 55°C for 3h. After being rinsed with distilled water, dried and shaved to the thickness of 0.70mm, the tannin-immobilized collagen membrane (TICM) was obtained. In fact, they are uniform pieces of leather.

## Application Cases

*Removal or recovery of heavy metals by using TICF adsorbent*

The adsorption capacity, adsorption mechanism and optimal adsorption conditions of TICF to toxic heavy metals and precious metals in aqueous solutions were systematically investigated.[13-18] It was found that, in general, TICF has a high adsorption capacity to most of heavy metal ions, as shown in Table 1. In particular, its adsorption capacities to $Au^{3+}$, $Hg^{2+}$, $Pd^{2+}$, $Pt^{2+}$ and $UO_2^{2+}$ and are higher than those of the adsorption materials developed by other researchers.[19-22] These facts indicate that TICF can be used to remove or recover metal ions from waste water.

It was also found that TICF is suitable to be used as column adsorption material for removal or recovery of metal ions.[16, 24] When 1.5g TICF was soaked in distilled water and filled into the column of 11mm in diameter, the height of adsorption bed was around 200mm. Figure 7 and 8 are the breakthrough curves of $Au^{3+}$ and $U^{6+}$ ($UO_2^{2+}$) solutions in the column when they pass through at a constant velocity.[16, 24] It can be seen that the breakthrough points of $Au^{3+}$ and $U^{6+}$ were at 223 and 250 BV(BV=bed volume) respectively, which indicates that both $Au^{3+}$ and $U^{6+}$ can be greatly concentrated by the column of TICF. The concentration of

**TABLE 1**
**The adsorption capacities of tannin-immobilized collagen fiber (TICF) to metal ions in aqueous solution (30°C, 24 h)**

| Metal ions | Conc.(mg/L) | Volume(ml) | Optimal pH | TICF dose(mg) | $q_e$*(mg/g) | Adsorption mechanisms |
|---|---|---|---|---|---|---|
| $Pb^{2+}$ | 200 | 100 | 3.0 | 100 | 78.8 | Physical & chemical adsorptions[13] |
| $Cd^{2+}$ | 200 | 100 | 3.0 | 100 | 23.9 | Mainly by physical adsorption[13] |
| $Hg^{2+}$ | 200 | 100 | 7.0 | 100 | 198 | Mainly by chemical adsorption[13] |
| $Mo^{6+}$ | 100 | 100 | 2.0 | 100 | 82.4 | Varying with pH |
| $Cr^{6+}$ | 100 | 100 | 2.0 | 100 | 78.5 | Redox adsorption |
| $Cu^{2+}$ | 63.5 | 100 | 6.0 | 500 | 6.9 | Mainly by chemical adsorption[14] |
| $Bi^{3+}$ | 100 | 100 | 2.0 | 100 | 73.0 | Multiple adsorption mechanisms[15] |
| $Au^{3+}$ | 287 | 100 | 2.5 | 100 | 1400 | Redox and complexing adsorptions[16] |
| $Pd^{2+}$ | 100 | 50 | 5-6 | 50 | 80.4 | Chemical adsorption[17] |
| $Pt^{2+}$ | 100 | 50 | 5-6 | 50 | 72.6 | Chemical adsorption[17] |
| $UO_2^{2+}$ | 595 | 100 | 5.0 | 500 | 106.9 | Chemical adsorption[18] |
| $Th^{4+}$ | 69.6 | 100 | 3.6 | 100 | 55.0 | Chemical adsorption[19] |

*$q_e$ -adsorption capacity at equilibrium

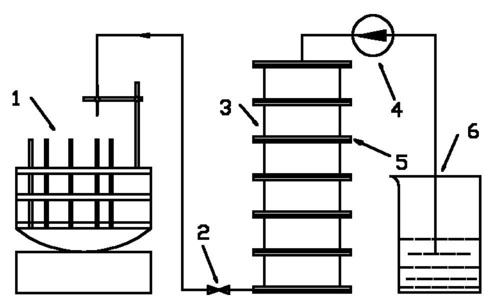


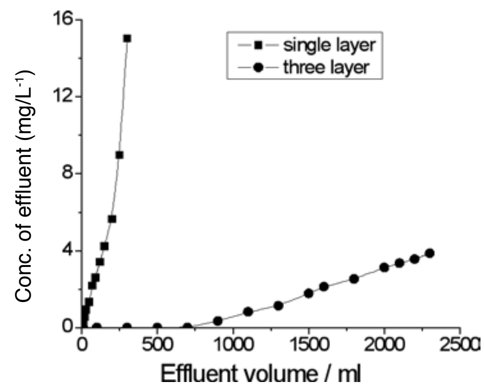

Figure 9: The scheme of continuous adsorption system.
1) automatic collector; 2) valve; 3) adsorption equipment; 4) peristaltic pump; 5) sieve plate; 6) solution.

$Au^{3+}$ and $U^{6+}$ in effluent was increased rapidly after breakthrough point, meaning that the adsorption column has high availability.

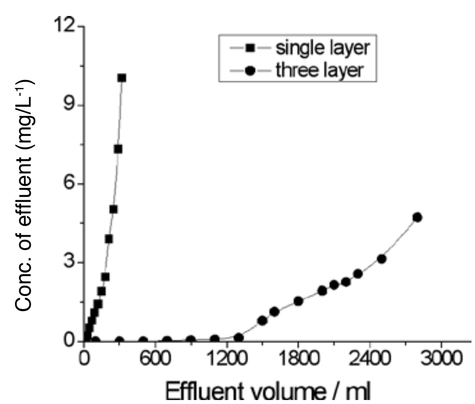
*Removal or recovery of heavy metals by using TICM*

The ability of tannin-immobilized collagen membrane (TICM) in recovery of precious metals in aqueous solutions was investigated. The continuous adsorption experiments of TICM were performed by using a continuous adsorption system, consisting of pump, adsorption equipment and automatic collector, as shown in Figure 9. The membranes were fixed on the sieve plate of adsorption equipment. The diameter of membrane was 90mm and the distance between membranes was 50mm.

Figure 10 presents the breakthrough curves of $Pt^{4+}$ and $Pd^{2+}$ on continuous adsorption system equipped with single layer and three layers of membrane.[25] For single layer membrane, the content of $Pt^{4+}$ and $Pd^{2+}$ ions in effluent increased rapidly




(a)




(b)

Figure 10: Breakthrough curves of $Pt^{4+}$ and $Pd^{2+}$ on single and three layers of membrane. (a) feed conc. of $Pt^{4+}$: 58.3mg/L(pH=3); (b) feed conc. of $Pd^{2+}$: 48.8mg/L(pH=4).

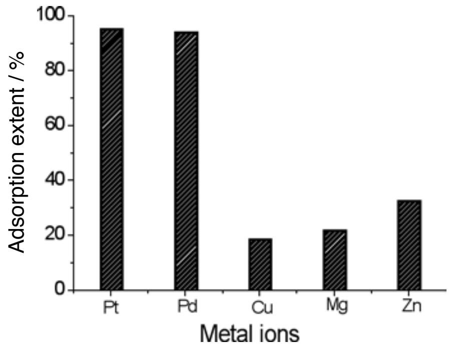



Figure 11: Adsorption extents of $Pt^{4+}$, $Pd^{2+}$, $Cu^{2+}$, $Mg^{2+}$ and $Zn^{2+}$ in continuous adsorption system equipped with single layer membrane. Effluent volume: 210ml; temperature: 20°C; pH of solution: 3.0.

at the beginning of adsorption. But for three-layer membranes, no metal ions were detected in the effluent until the effluent volume reached 700ml for $Pt^{4+}$ and 1000ml for $Pd^{2+}$. Therefore, multi-layer membranes are effective in removal or recovery of metal ions in aqueous solutions. The effectiveness of the multi-layer membranes in recovering $U^{6+}$ in aqueous solution was also observed.[26]

It was also found that TICM can be used for separation of metal ions which have different affinities to the membrane in a fixed range of pH. As an example, precious metals $Pt^{4+}$ and $Pd^{2+}$ were recovered from a mixture solution by using the membrane. The mixture solution containing $Pt^{4+}$(29.2mg/L), $Pd^{2+}$(24.4mg/L), $Mg^{2+}$(5.0mg/L), $Zn^{2+}$(5.0mg/L) and $Cu^{2+}$(5.0mg/L) was pumped into the continuous adsorption system (Figure 9) equipped with single layer membrane. As presented in Figure 11, when adsorption was saturated, $Pt^{4+}$ and $Pd^{2+}$ were mainly retained by the membrane while only a small amount of $Mg^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ was adsorbed, which shows remarkable selectivity of TICM to $Pt^{4+}$ and $Pd^{2+}$.[25]

Figure 12(a) shows that $Mg^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ adsorbed on the membrane were almost completely eluted by using 0.1M HCl, while only a little $Pt^{4+}$ and $Pd^{2+}$ was removed.[25] But after eluted by a mixture solution of 0.1M thiurea and 1.0M HCl, $Pt^{4+}$ and $Pd^{2+}$ were removed from the membrane, and a little amount of $Mg^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ was detected in the eluting solution, as shown in Figure 12(b).[25] These facts imply that $Pt^{4+}$ and $Pd^{2+}$ can be effectively separated from the mixture solution by using TICM as a separation membrane.

## 3. Application of Principles of Metal Tanning

**Background and Idea**

Some interesting ideas have been derived from the principles of metal tanning. Firstly, a series of novel adsorbents for treating inorganic anions were prepared. As we know, the removal of inorganic anions such as $F^-$, $PO_4^{3-}$, $CrO_4^{2-}$ and $V_2O_7^{4-}$ in wastewaters is essentially important for environmental protection. Chemical precipitation of these inorganic anions is subjected to costs and the problem of sludge handling, and is ineffective in the cases of low concentration of inorganic anions. Comparatively, adsorption is a more useful and economical method for removing the anions from waters. In recently years, it has been found that metal ions (like $Zr^{4+}$ and $Fe^{3+}$) loaded adsorbents have specific affinity to inorganic anions, such as fluoride, phosphate and arsenic.[27, 28] But the procedures of preparing this kind of adsorbents are usually complicated and the products are expensive. On the basis of these facts, we, as tanners, would naturally imagine that we are able to prepare the metal ion-loaded adsorbents simply by metal tanning.

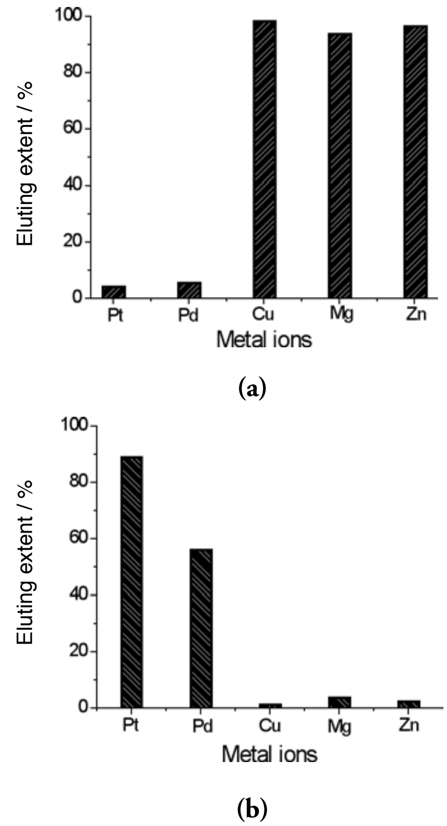



Figure 12: Eluting extent of metal ions adsorbed on the membrane by two steps: (a) firstly, eluted by 40mL 0.1M HCl; (b)secondly, eluted by 50mL mixture solution of 0.1M thiurea and 1.0M HCl. Temperature: 20°C.

Secondly, now that the adsorbents prepared by metal tanning can be used for removal of inorganic anions, why not we directly use chrome leather waste, the Cr-loaded collagen fiber, as an adsorbent to remove anionic compounds from wastewaters?

Finally, as we know, the uses of homogeneous metal catalysts always face the difficulties of separating and recovering the catalysts from reaction systems. To overcome this disadvantage, many heterogeneous metal catalysts have been developed. Recently, there is an increasing concern about using biomass as supporting materials of catalysts[29-31], and it seems that they exhibit specific activity and selectivity during catalytic processes. Therefore, the preparation of heterogeneous metal catalysts by using collagen fiber as supporting material was explored based on the principles of metal tanning.

**Preparation of Metal-loaded Collagen Fibers**

*Loading of $Zr^{4+}$ and $Fe^{3+}$ on collagen fiber*

Collagen fiber was prepared according to the procedures described in 2.1. 15.0 g collagen fiber was soaked in 400ml distilled water (pH=1.7~2.0). Then, 36g $Zr(SO_4)^2$ ($ZrO_2$ 31.5%) or 20.0g $Fe_2(SO_4)_3$ was added and reacted at 30°C with constant stirring for 6h. A proper amount of $NaHCO_3$ solution (15%, w/w) was gradually added within 2h in order to increase the pH of the solution to 4.0~4.2 and then continuously reacted at 45°C for another 4h. When the reaction was completed, the product was collected by filtrating, washing with distilled water and vacuum dried at 50°C for 12h, and finally $Zr^{4+}$ and $Fe^{3+}$-loaded collagen fibers (Zr-ICF and Fe-ICF) were obtained.

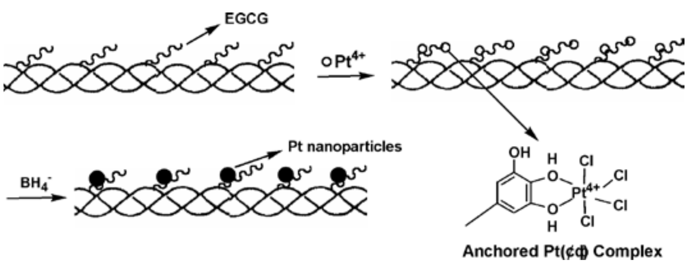



Figure 13: Anchoring $Pt^{4+}$ onto collagen fiber via EGCG and formation of Pt(0) nanoparticles.

*Adsorbent from chrome leather waste*

Chrome leather shavings were obtained from a local tannery. They were washed with distilled water, dried at 60°C for 6h and then ground into granules with particle size 0.1-0.2mm. This adsorbent contains 14.3% water and 3.21% $Cr_2O_3$ determined by Atomic Sorption Spectrophotometry.

*Pt nanoparticles supported by collagen fiber*

Eepigallocatechin-3-gallate (EGCG) was selected as the bridge molecule for better anchoring of $Pt^{4+}$. The main procedures include: 1) grafting EGCG onto collagen fiber by crosslinking of glutaraldehyde, 2) loading $Pt^{4+}$($K_2PtCl_6$) onto EGCG grafted collagen fiber, and 3) reducing $Pt^{4+}$ into $Pt^0$ by using $NaBH_4$, as shown in Figure 13.

**Application Cases**

*Removal or recovery of inorganic anions by using Zr-ICF*

The adsorption capacity, adsorption mechanism and optimal adsorption conditions of $Zr^{4+}$-loaded collagen fiber(Zr-ICF) to toxic inorganic anions in aqueous solution were systematically investigated.[32-34] Compared with other adsorbents, Zr-ICF exhibited a high adsorption capacity to inorganic anions, as shown in Table 2. The adsorption

**TABLE II**

**The adsorption capacities of Zr-ICF to inorganic anions in aqueous solution (30°C, 24 h)**

| Inorganic anions | Conc. ($mg.L^{-1}$) | Volume (ml) | Optimal pH | Zr-ICF dose (mg) | $q_e^*$ ($mg.g^{-1}$) | Adsorption mechanism/ main chemical species adsorbed |
|---|---|---|---|---|---|---|
| F- | 90 | 100 | 5-7 | 100 | 41.2 | monolayer chemical adsorption |
| PO43- | 94 | 100 | 3-8 | 100 | 86.4 | ion exchange/$H_2PO_4^-$ |
| CrO42- | 224 | 100 | 6-9 | 100 | 58.2 | ion exchange/$CrO_4^{2-}$ and $HCrO_4^-$ |
| V2O74- | 408 | 100 | 5-8 | 100 | 391.7 | ion exchange/$H_2VO_4^-$ |

*qe -adsorption capacity at equilibrium

**TABLE III**

**The adsorption capacities of chrome leather waste absorbent to organic compounds in aqueous solution (20°C, 24 h)**

| Compounds | Conc. ($mg.L^{-1}$) | Volume (ml) | Optimal pH | absorbent dose (mg) | $q_e^*$ (mg.g) | Adsorption mechanism/ main adsorption sites on absorbent |
|---|---|---|---|---|---|---|
| Acid Yellow 11 | 2000 | 100 | 3-4 | 100 | 803 | chemical adsorption/Cr, $-NH_2$ |
| Direct Red 31 | 2000 | 100 | 3-4 | 100 | 798 | chemical adsorption/Cr, $-NH_2$ |
| SDBS | 2000 | 100 | 4-8 | 200 | 375 | chemical adsorption/Cr, $-NH_2$ |
| DTB | 800 | 100 | 4-8 | 200 | 75 | electrostatic interaction |
| TX-100 | 500 | 100 | 4-8 | 200 | 25 | hydrogen and hydrophobic bonds |

*qe -adsorption capacity at equilibrium

capacity is largely influenced by pH of solution because the chemical species of inorganic anions are changed with the change of pH. In general, as a novel adsorbent, Zr-ICF promises to be a prospective material for removing inorganic anions from aqueous solutions.

*Removal of organic compounds by using chrome leather waste absorbent*

The adsorption behaviors of chrome leather waste absorbent to some organic compounds commonly existed in wastewaters were investigated.[35-36] These organic compounds include anionic dyes(Acid Yellow 11 and Direct Red 31), anionic surfactant sodium dodecylbenzenesulfonate (SDBS), cationic surfactant dodecyl trimethylammonium bromide (DTB) and non-ionic surfactant Triton X-100 (TX-100). The data shown in Table 3 indicate that anionic dyes and surfactants can be significantly adsorbed by this absorbent. This is because these anionic compounds have high affinity to amino groups and Cr(III) combined with collagen of the absorbent. But the adsorption capacity of the absorbent to cationic and non-ionic compounds is relatively lower. In summary, these results demonstrate that chrome leather waste promises to be an effective and economical adsorption material for removal of anionic compounds from wastewater.

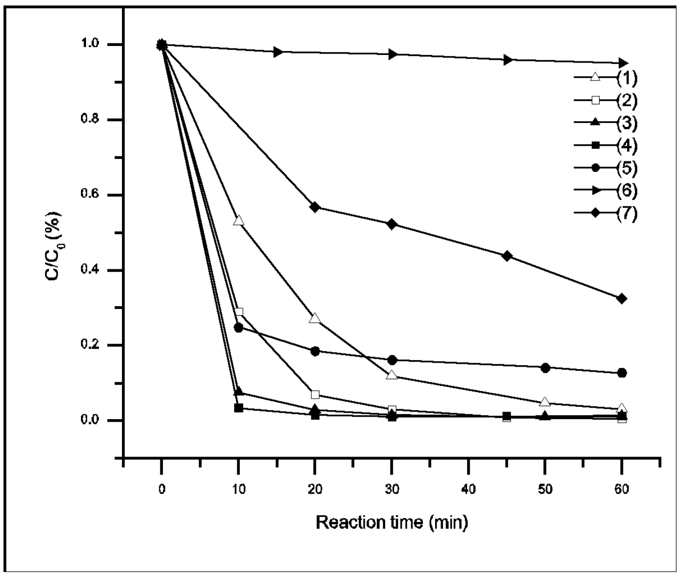



Figure 14: Degradation of Orange II (initial conc. 0.2mM, 400mL, pH=3.7) under different conditions: (1) $H_2O_2$ (5mM) + UV(4W); (2) $H_2O_2$ (5mM) + UV(8W); (3) $H_2O_2$ (5mM) + UV(4W) + catalyst(2g); (4) $H_2O_2$ (5mM) + UV(8W) + catalyst (2g); (5) $H_2O_2$ (5mM) + catalyst (2g); (6) UV(8W) only; (7) reduce of dye due to adsorption on catalyst (2g).[37]

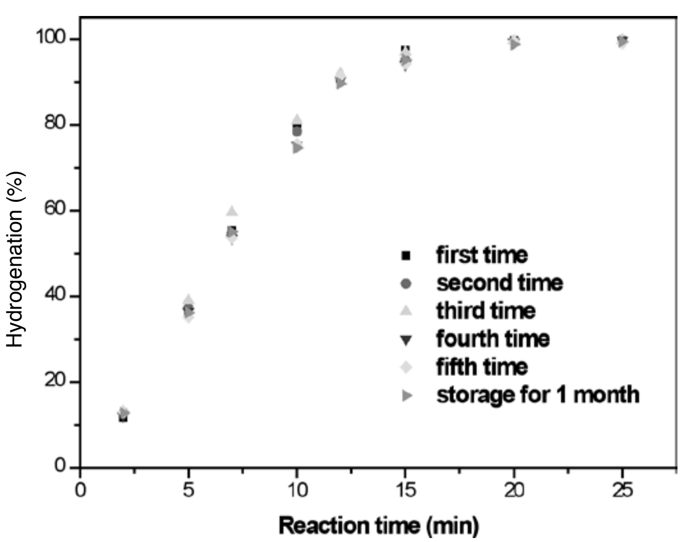



Figure 15: The effect of recycle times and storage of Pt-ICF on hydrogenation of allyl alcohol. Experimental conditions: Pt ($5.0\times10^{-3}$ mmol), allyl alcohol (5mmol), methanol (30mL), and temperature 30±2°C.

*Fe-ICF: a heterogeneous catalyst for degradation of organic compounds in wastewater*

As we know, Fenton reaction degradation are of high efficiency and low cost[1] for the treatment of wastewater containing organic pollutants. For supporting this technology, some Fe(III) immobilized heterogeneous catalysts have been developed. In this research, Orange II was used as a probe compound and its degradation behaviors in the presence of $Fe^{3+}$-loaded collagen fibers (Fe-ICF) were investigated.[37]

Figure 14 shows that no considerable degradation of Orange II took place when only irradiated by UVC (process 6), and a fast degradation rate was observed in the presence of both $H_2O_2$ and UVC (processes 1 and 2).[37] In comparison with the situations above, the fastest degradation rate was achieved in the presence of $H_2O_2$, UVC and catalyst Fe-ICF (processes 3 and 4). With the aid of the catalyst, the degradation equilibriums of Orange II were approached in only 20min, as illustrated by processes 3, 4 and 5. Comparing processes 3, 4 and 5, it can be found that the catalyst has high catalytic activity no matter whether UVC is employed, but the extent of degradation is higher with the aid of UVC.

It seems that there is no obvious difference in the final extent of degradation with or without catalyst Fe-ICF, as presented by processes 2 and 4 in Figure 14. However, our determinations indicated that the total organic compound (TOC) residuals of these two processes are around 93% and 50%, respectively, which suggests that the higher mineralization of Orange II can be attained by catalytic degradation.[37] Therefore, Fe-ICF is an efficient and economical heterogeneous catalyst for photo-assisted Fenton reaction.

*Catalytic activity of Pt-ICF for hydrogenation reaction*

Heterogeneous Pt catalysts have received a great attention due to their high catalytic activity for some reactions, such as hydrogenation, and being easy for recovery from reaction systems. In our research, the catalytic activity of Pt-loaded collagen fibers (Pt-ICF) was investigated by using the hydrogenation of allyl alcohol as a model reaction.

TEM observation (not presented) demonstrated that the Pt loaded on collagen fibers was in the state of nanoparticle. The statistical analysis indicated that the average diameter of Pt nanoparticles is 2.1nm with a narrow size distribution

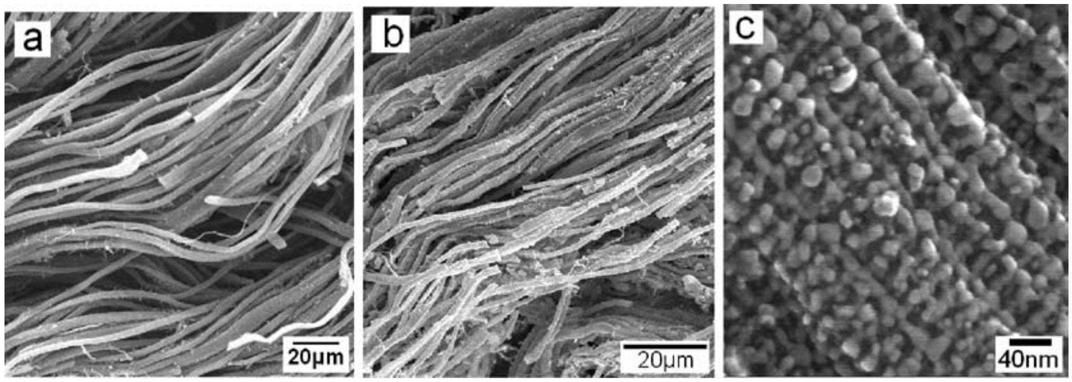



Figure 16: SEM images of AlCFC (a) and zirconia fiber(b), and FESEM image of zirconia fiber(c). (Content of carbon in zirconia fiber<0.2%, and no H, N and S were detected; FESEM image was obtained without metal coating).

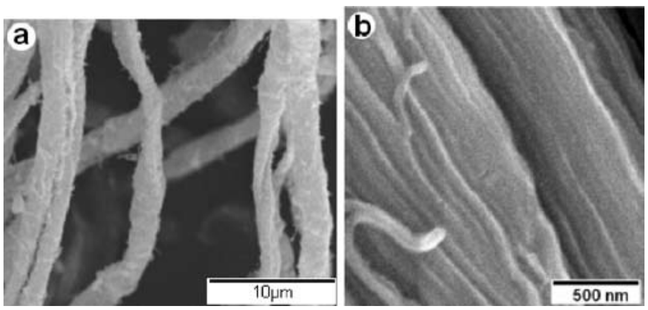



Figure 17: SEM images of alumina fiber (Content of carbon<1%, no H, N and S were detected).

($\sigma$ = 0.7 nm), implying the possibility of high catalytic activity.

Figure 15 shows that allyl alcohol was completely converted in 25min, and the selectivity of 1-propanol in the reaction was higher than 99% (determined by GC-MS, not presented). The good recyclability of the catalyst was also presented in Figure 15. The turnover frequency (TOF) value was 2988 mol/molPt·h, which is about 10-fold of that catalyzed by polystyrene-stabilized Pt colloids nanoparticles (TOF=312 mol/molPt·h)[38]. This should be attributed to the fact that Pt-ICF is in fibrous state which can significantly enhance the accessibility of substrates to active sites. Meanwhile, compared with other supported metal nanoparticle catalysts,[39] Pt-ICF exhibited better stability of storage even after being exposed in ambient condition for one month, as presented in Figure 15.

## 4. Application of Principles of Metal-Organic Combination

### Background and Idea

The structural design of inorganic materials by using organic matrices as templates has received increasing attention.[40] In particular; the organic matrices with fibrous or tubular structures are most often used to synthesize fibrous or tubular inorganic materials. Although many kinds of inorganic materials with unique structures have been synthesized by

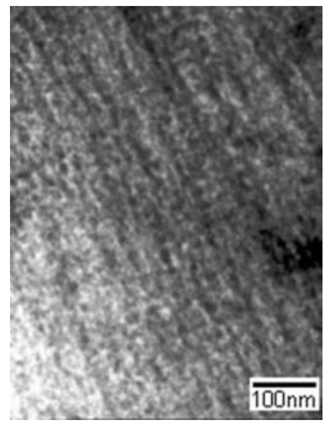



Figure 18: TEM image of alumina fiber.

these approaches, the finding of new organic matrices which can be used as structure-directing agents to synthesize new inorganic fibrous materials is still an attractive challenge.

As we know, collagen fiber is of highly ordered arrangement of collagen molecules. Therefore, it could be inferred that the fibrous inorganic materials with well-defined morphology might be prepared by using collagen fiber as a template. However, raw collagen fiber exhibits low thermal stability and weak mechanical strength, and its well-defined structure is easily destroyed during the treatments of acid, base and heating. Therefore, collagen fiber needs to be chemically modified to improve its mechanical and thermal properties, and to fix its unique structure when used as a template. For our tanners, this can be done by using different kinds of metal-organic combination tanning systems, and in fact, the versatile tannages make it possible to adjust the structural parameters of collagen fiber, as well as the fine structures of inorganic materials obtained.

### Application Cases

*Preparation of mesoporous metal fibers*

Collagen fiber was prepared according the procedures described in section 1. 15.0g collagen fiber was fully tanned by 20mL glutaraldehyde(conc.50%) at first, then reacted with 30.0g of $Zr(SO_4)_2$ ($ZrO_2$ 31.5%) to obtain Zr-collagen fiber composite (ZrCFC). The reactions were undertaken in

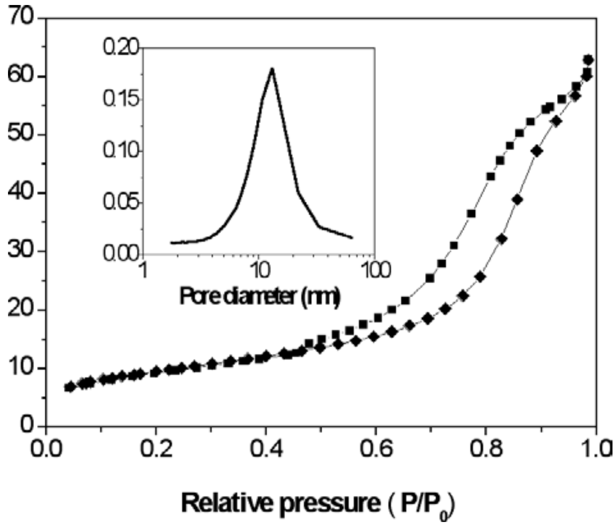



Figure 19: $N_2$ adsorption-desorption isotherms alumina and pore-size distribution plot (inserts) of (w/w)= zirconia fiber.

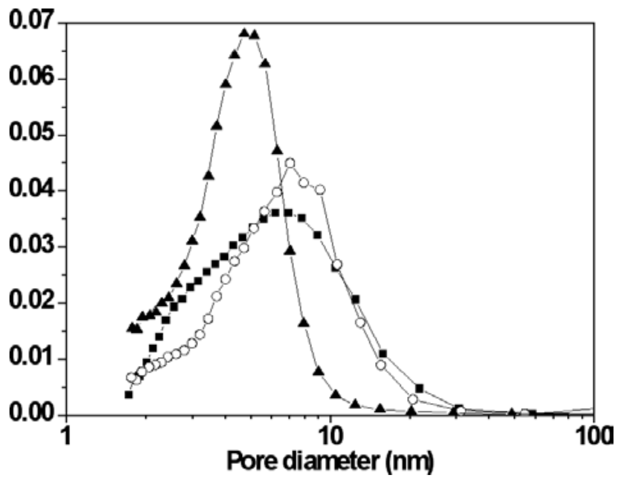



Figure 20: Pore size distribution plots of fiber. $Al_2(SO_4)_3 \cdot 18H_2O$ : collagen fiber ■ 30 : 10; ○ 20 : 10; ▲10 : 10.

the common conditions of glutaraldehyde-metal combination tanning. After filtrating, washing and vacuum-drying, the ZrCFC was heat-treated step-wisely, first at 100°C for 2h in air, then heated (4°C /min) in vacuum to 800°C and held for 2h, and then held at this temperature in air for 6h.

After removal of organic substrates by heat-treatment, the zirconia fiber with 1–4$\mu$m in outer diameter and 0.5–1mm in length was obtained, as shown in Figure 16b. Furthermore, the corn-cob-like porous structure of the zirconia fiber was presented by Field Emission Scanning Electron Microscopy (FESEM) observation (Figure 16c). These facts indicate that the synthesis of zirconia fiber by using collagen fiber as template can preserve even fine structure of collagen fiber.

Similarly, based on the technology of mimosa-Al combination tanning, Al-collagen fiber composite (AlCFC) was obtained (mass ratio of collagen fiber: mimosa: $Al_2(SO_4)_3 \cdot 18H_2O$= 10: 10: 30). After removal of organic substrates by heat-treatment as above, the alumina fiber with several levels of

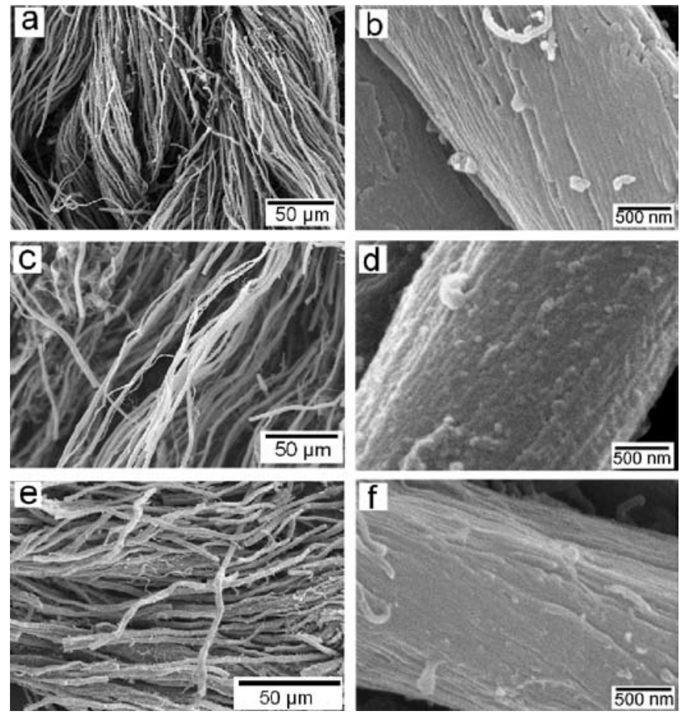



Figure 21: SEM images of the carbon fibers obtained from ZrGCFC (a,b), AlGCFC(c,d) and FeGCFC(e,f). (Carbon 85±5%, oxygen 8±2%, nitrogen 4±1%, Zr<0.4%, no Al and Fe were detected).

structural organization was also obtained, as shown in Figures 17 and 18.[41]

The determinations by $N_2$ adsorption techniques illustrated that the zirconia fiber is a kind of mesoporous material with pore size distribution of 5–30nm, as shown in Figure 19. Furthermore, it was found that the pore size of the metal fibers synthesized by this option was controllable to some extent. For example, the pore size of alumina fiber was changed with varying mass ratio of Al(III) and collagen fiber in AlCFC, as demonstrated in Figure 20.[41] Therefore, our studies indicate that collagen fiber, with hierarchical supramolecular structures, can be used as an idea template to prepare porous metal fibers which have great potential of applications in chemical sensor, selective catalysis and catalyst support.

*Preparation of controllable porous carbon fibers*

15.0g collagen fiber was fully tanned by 5g mimosa or 5mL glutaraldehyde (conc.50%) at first. Then the vegetable tanned collagen fiber reacted with 10g $Al_2(SO_4)_3$, and the glutaraldehyde tanned collagen fiber reacted with 10g $Zr(SO_4)_2$ or $Fe_2(SO_4)_3$, respectively. The reactions were conducted in the common conditions of metal-organic combination tanning. As a result, the precursors Al-tannin-collagen fiber, Zr-glutaraldehyde-collagen fiber and Fe-glutaraldehyde-collagen fiber composites (AlTCFC, ZrGCFC and FeGCFC ) were obtained. The precursors were heat-treated step-wisely, first at 100°C for 2h in air, then heated (4°C /min) in vacuum to 800°C and held at this

**TABLE IV**
**Structural parameters of carbon fibers**

| Samples | Mesopore surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Average pore size (nm) | Mesopore ratio (%) |
|---|---|---|---|---|
| Carbon fiber from ZrGCFC | 972 | 0.68 | 2.25 | 80 |
| Carbon fiber from AlGCFC | 193 | 0.36 | 2.65 | 34 |
| Carbon fiber from FeGCFC | 335 | 0.61 | 4.61 | 63 |

temperature for 6h. After heat-treatment, AlTCFC and FeGCFC were suspended in diluted nitric acid at 60°C for 6h to remove $Al_2O_3$ and $Fe_2O_3$, and ZrGCFC was suspended in $H_2SO_4$-$(NH_4)_2SO_4$ (2ml:1g) buffer solution at 60°C for 6h to remove $ZrO_2$. Finally, the porous carbon fibers were obtained via filtrating, washing and vacuum-drying, as shown in Figure 21.[42]

It was observed in our experiments that collagen fiber should first react with organic tanning agents to stabilize its fibrous structure and enhance its fixing capability for metal ions. Otherwise, carbon fibers with ordered organization can not be achieved. The data in Table 4 shows that the carbon fibers are a series of porous materials with large surface area and high mesopore ratio and therefore, promise to be applied in selective adsorption and catalyst support.[42]

## Conclusions

Hides and skins, an abundant biomass in the world, are traditionally used as raw material in leather manufacturing. The research in this paper demonstrate that this kind of renewable natural resource has great potentialities of being utilized in a wide range of functional material fields. The interesting fact is that many options of creating the novel functional materials can be derived from the scientific principles of leather making. This is not surprising and in fact, these approaches had been implicated in the theories described by John Arthur Wilson in his book "The Chemistry of Leather Manufacture", if we read the book carefully.

On the other hand, the author also believes that the explorations of making new materials from skin collagen would be beneficial to better understanding of the mechanisms of leather manufacture in a wider field of vision.

## Acknowledgments

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# Award and Acceptance of the John Arthur Wilson Memorial Lecture Plaque Awards Banquet June 21, 2008

*by*

Maryann Taylor and Bi Sh

**Maryann Taylor**
**Ladies and Gentlemen:**
Our 2008 John Arthur Wilson award and the 49th lecturer in the series, Dr. Bi Shi, is professor and director of The Key Laboratory of Leather Chemistry and Engineering of Ministry of Education in Sichuan University. He is Chairman of the Science and Technology Committee of the China Leather Industry Association (CLIA) and a Member of the National Congress of China. He is currently the vice president of IULTCS, as well as the representative from North Asia on the IULTCS Executive committee. He was a member of the Scientific and Technical Committee, chaired by Dr. William N. Marmer, for the 2007 IULTCS meeting that was held in Washington, DC. China will be hosting the 30th IULTCS Global Congress, on October 11-14, 2009, in Beijing, and Professor Bi Shi is the Technical Chairman of this meeting.

On behalf of the American Leather Chemists Association, Stahl, and members of the 2008 John Arthur Wilson Memorial lecture committee, consisting of John Whiteman, Jerry Levy and myself, we want to thank Professor Bi Shi for a very enjoyable and informative lecture. The Association very much appreciates the time that you devoted to the preparation of this Lecture and to the corresponding manuscript that will be published in the upcoming issue of JALCA. On that note I would like to present to you this plaque, which reads:

The American Leather Chemists Association, in the tradition begun by the Harold T. N. Smith Foundation and Salem Oil & Grease Company and continued by Stahl, has established, as a special feature of each Annual Meeting, The John Arthur Wilson Memorial Lecture, and hereby wishes to express its sincere appreciation for delivery of the John Arthur Wilson Memorial Lecture 2008, in a manner befitting the quality of the past lecturers in this series, to Professor Bi Shi, an outstanding researcher, educator and environmentalist who has made major contributions in the field of leather technology.
Signed: Jerome F. Levy, Representative, Stahl and William N. Marmer, President, American Leather Chemists Association

Ladies and gentleman, please join me in congratulating Professor Bi Shi.

**Bi Shi**
Good evening! Ladies and Gentlemen,
The book "The Chemistry of Leather Manufacture" written by John Arthur Wilson has been enlightening the leather science and technology of China for many years. So, as a representative of Chinese leather chemists, it is my great honor to be invited here to give the John Arthur Wilson Memorial Lecture. I greatly appreciate the America Leather Chemists Association for your confidence in me. I am very proud of being awarded this Plaque, and I believe it will remain in our library forever.

What a happy coincidence! Today is my fiftieth birthday. I am sure this plaque is the best present for my birthday!

Meanwhile, I'd like to say, during my preparation of this lecture; Ms Maryann Taylor gave me a lot of help. I thank her very much for her hard work and kind support.
Thanks to all of you!

Dr. Bi Shi accepting 2008 Wilson award from Maryann Taylor

# Presentation and Acceptance of the 2007 O'Flaherty Service Award

*by*

Harold Diephouse and Dean Didato

**Harold Diephouse:**
Esteemed colleagues, friends, and distinguished guests.
When the 2008 committee of Kadir Donmez, David Rabinovich and I discussed and reviewed the outstanding candidates for this year's O'Flaherty Service Award, we found that all the candidates have had, and still have, outstanding service to our organization.

The candidate who stood out has been a member of the ALCA since 1990, he has served on this same committee as Chairman in 2000, the Alsop Award Committee in 1992, Chairman of the nominating Committee in 2005, he served twice on the Board of Tellers, Chairman of the Research Liaison Committee 2008 to present, Vice President Elect 2001-2002, Vice President 2002-2003 and President for the 100th anniversary 2003-2004.

He also is the Laboratory Committee Chair for the Leather Industries of America since 2007 and on the Board of Directors of the LIA since 2005.

He has published a number of papers in various technical journals (including the JALCA) and made numerous presentations over the years. He holds several U.S. and International patents regarding "Potentiation of the microbicide 2 thiocyanomethylthio benzothiazole using an N-Alkyl Hetero-cylic compound" He has been quoted in both the Wall Street Journal June 21, 1999, and in Business Week October 23, 2000. In 2000 he was interviewed by author Jessica Lipnack for her book "Virtual Teams – People Working Across Boundaries with Technology". He was the keynote speaker at the Tennessee's 45th Annual Governor's Conference on Economic and Community Development in 1998.

He holds a Bachelor of Arts in Biology-Management from Marietta College in Marietta, Ohio. His working career has lead him from Industry Specialist – International Marketing to Product Development Manager – Research and Development to District Sales Representative onto Division Manager, and finally to being the youngest Vice President –Sales and Marketing for Buckman Laboratories.

Although all of the above definitely qualifies our candidate for this ALCA service award, there is one position that he quietly and without acknowledgement, assumed for the Association. Last year when our IULTCS Congress/103rd ALCA Annual Meeting was flailing, this man became a silent partner with the Association. He worked tirelessly behind the scenes to insure not only the tremendous success of the convention but the steady ongoing of the Association itself. He worked for the Association without a formal title or position and without knowledge of many of our members.

The title that we can best give now is the true ALCA supporter and the epitome of why the Fred O'Flaherty award was created. Please join me in the honor of welcoming Dean Didato as the 2008 recipient of the O'Flaherty Service Award.

**Dean Didato:**
A couple of Dicks, several coffee cups and a ferry boat

Mr. President, officers, counselors, members and guests, I am deeply humbled by your selection for this time honored award and recognition. When I learned of the 2008 nominating committee's decision, to be quite frank, I was both shocked and somewhat astonished. After all, previous recipients of this award have been the who's who of the U.S. Tanning Industry – those that I have personally reflected upon as some of the leading scientists and leather technicians of their time. Many of whom over the years I have had the privilege of receiving training from and working with.

Everyone has a story and certainly all of us in this room have one of how we came to make a career in the leather industry. Mine started with a person that many of you who have been ALCA members for several decades will recall. Ed Weiss was one of the first salesman that Dr. Stanley J. Buckman hired in 1952 to begin to sell microbicides to the leather industry. He was a graduate of the Tanner's Council Leather School located at the University of Cincinnati. For many years, Ed was the senior technical specialist for leather at Buckman Laboratories. He was an imposing figure of a man, huge really, with gigantic hands and a booming voice. He certainly gained my attention when he bellowed over the telephone that he was coming to New England to work with the new hire who was brought on to cover the Leather, Pulp & Paper, Cement, and Sugar industries.

I was hired in 1984 as Mr. Diephouse mentioned, to cover a seven state area and report to yet another Italian, Joseph Leonardi. Apparently the gentleman that I replaced, a recent graduate of the Leather Program at Nene College, was last seen speeding down the road in the company vehicle, in Peabody, Massachusetts with the windows down, wearing what was described as a toga. Shortly thereafter, I was informed that he was no longer associated with the company. I was told that tanners could be a wild lot. My employer was seeking some stability and someone who would further develop the business.

Here I was, a kid fresh out of school, given the keys to a new car and told "you have 25 tanneries, 40 paper mills and variety of other accounts to manage. Here is our product line, these are the typical applications and call us if you need help". Thank God for Ed Weiss. He came and spent weeks with me describing the tanning process, how microbiology could play havoc with the raw material and the process, and where our products could provide value to the customer. It was Ed Weiss, Gary Baldwin and Raymond Thornton (then Executive Vice President of Buckman Laboratories) that colluded to set me on a path that would lead to a career in leather.

On March 4th, 1988, I received an unexpected letter in the mail from Frank Rutland, then the Technical Director of the Department of Basic Science in Tanning Research at the Tanners Council in Cincinnati. The letter stated that I was registered for the Twenty Second Leather Technology course to be held at the Leather Industries of America laboratory that summer. It would be a four-week, grueling course taught by Rutland, Dr. Robert Lollar, Dr. Waldo Kallenberger and Randy Rowles . The cramped conference room at the lab would be our home for the month in mid-summer with daily temperature in excess of 100ºF. In the room with me were the sons of several well known U.S. tanners, Chris Sirois, Chuck Cares Jr., as well as Bruce Buehrig (Hermann Oak) and several Iraqi women. There was no air conditioning and even though windows were open, with no breeze, the students were left to listen to the towering Dr. Lollar lecture on skin & hide structure while holding what appeared to be a 2 gallon coffee mug that had been used since the beginning of time. Possibly as old as the leather industry itself we wondered?

After attending the LIA's Through the Blue and Retanning, Fatliquoring and Finishing courses that same year, I found myself packing my belongings into my VW and leaving Massachusetts for Memphis, Tennessee. Dr. Richard Ross, then Vice President of International Marketing, had offered me a position as an Industry Specialist. That first year I spent better than 26 weeks of the year traveling outside of the United States with Buckman associates, training in the field, visiting customer locations and working with distributors to make sure that they were familiar with the product offering. My job, as Dr. Ross had instructed, was to find out what other product requirements existed and how the company could expand its product offering.

I remember moving into my Memphis office upon arrival and being greeted in the hallway by Dr. Richard Lutey – one of the pre-eminent microbiologists at the firm and another of Stanley Buckman's first hires. Dick had provided me with some of my initial product & microbiological training when I was first hired. Dick asked, "Hey Didato, what are you doing here?" Well I told him that Dr. Ross had hired me to provide technical and product support for Pulp & Paper, Leather and several other industries and he glared back at me. "Your going to concentrate on leather?" he said shaking his head. "Is there enough to concentrate on?" he said as he walked away with his 2-gallon yellow stained coffee cup that looked like a drum of Busan.

So it was with this level of enthusiasm that I embarked on what has been a almost 25 year career with my employer. Not bad for a kid who in 1972 was told by his parents (both educators) that the family was packing up their things and moving from Connecticut to a "remote" island off the coast line of Massachusetts. You know there has been much published and said about Martha's Vineyard since the Clinton's found it, but believe it or not, there is a year around population of working folks out there. Largely isolated by seven miles of Atlantic Ocean, a ferry boat ride was what separated us from the mainland and at times that separation was both a hindrance and a blessing. In the dead of winter, that seven miles of water keeps one humble and thankful for what we have.

I have high school friends that went on to be an Inn Keeper, Yacht Captain, Ocean going tug boat Captain, General Contractor, a member of that local newspaper staff, a banker and Sword fishing Captain. There was only one graduate of the Martha's Vineyard Regional High School who got sucked into the allure of the leather industry. And he stands before you humbled by the recognition that you bestow upon him this evening. Yes a couple of Dicks, several coffee cups and a ferry boat all have played an important role in leading me on this journey here tonight. I thank you and respectfully accept this award with great appreciation to my family, my wife Kelly and the girls, my employer and my many friends, customers and industry associates for whom I am truly blessed.

Thank you very much.

Dean Didato, 2007 O'Flaherty Award winner

# PRESENTATION AND ACCEPTANCE OF THE 2007 ALSOP AWARD

*by*
CHENG-KUNG LIU AND WILLIAM MARMER

**Cheng-Kung Liu:**
Mr. President, members of the American Leather Association and honored guests:

The 2008 ALOP selection committee consisted of Lori Hyllengren, David Ouellette, and me. The ALSOP Award was established by ALCA council in 1939 and is given in the memory of the late W. K. Alsop. Tannin Corporation has generously donated the annual prize to be awarded for outstanding scientific or technical contributions to the leather industry.

This year's recipient is Bill Marmer of Eastern Regional Research Center (ERRC) in Wyndmoor, PA. Bill, just recently retired from the Federal Service and ARS on March 31, 2008. This award is mostly based on his significant contribution to dehairing research in recent years. For the prior 21 years, he had been the Research Leader, or manager, of what is now named the Fats, Oils and Animal Coproducts Research Unit at ERRC. There, he managed a $5M research program on chemical, enzymatic, and physical processes to add value not only to hides & leather, but also to wool, rendered protein, and fats& oils.

Bill received his B.A. degree in Chemistry from the University of Pennsylvania in 1965 and his Ph.D. degree in Organic Chemistry from Temple University in 1970. Thirty-eight years ago, in 1970, he began his career at ERRC, initially in fats & oils research as an ARS-National Research Council Research Associate. In 1972 he continued at ERRC as a Fellow of the rendering industry's Fats & Proteins Research Foundation. His status as a career scientist at ERRC began in 1975. In 1985, he left his fats & oils research to become the Lead Scientist of wool research and to initiate that program.

His managerial responsibilities as Research leader began in 1987 as RL of the Hides, Leather and Wool Research Unit. With a little irony, in 1993, his RL responsibilities doubled by the acquisition of a large program on fats & oils, including biodiesel. Since 2003, his Research Unit also has investigated non-feed utilization of rendered protein (meat & bone meal).

Bill had been supervising 13 senior career scientists and engineers and a similar number of technical support staff. He contributed personally to work on the enzymatic digestion of chrome shavings, the utilization of recovered materials from that process, and—as the Alsop Award recognizes the dehairing of hides. He is the author or coauthor of over 200 papers, including 14 patents. He and Bob Dudley shared the 2007 Robert Lollar best paper award, which was sponsored by ALCA and LIA. Bill was elected Chair of the Cellulose, Paper & Textile Division (now Cellulose and Renewable Materials Division) of the American Chemical Society for 2000, and of course is now finishing his term as President of the ALCA.

He has recently returned to ERRC in an emeritus status, where he has been assisting in the transition of leadership. He finally has time to pursue his interests in genealogy, map collecting, and tennis. He and his wife Benne—who is the Equal Employment Specialist for the North Atlantic Area of ARScontinue to reside in Fort Washington, PA, not far from their son David and a three-hour drive from their daughter Rachel and son-in-law Ben in Arlington, VA. Now, we welcome Bill to give his Alsop Award acceptance speech.

**William Marmer:**
Thank you very much C.-K. Ladies and gentlemen, this award singles out research on the oxidative unhairing of hides, but coming as it does at the end of my research career, I can't help feeling that it is being awarded to recognize 21 years of my leading the hides & leather program at ERRC. The oxidative approach to unhairing of course was promoted as an alternative to sulfide unhairing, and I was by no means alone in fostering this. Others at ERRC are deserving of major recognition in this endeavor. Dave had been the champion of rapid unhairing in the packing plant; working with Monfort, then Future Beef in this novel approach to hair removal "on the hoof," so to speak. That work led to commercial trials and the validation of the concept, but unfortunately that rapid unhairing still relied on sodium sulfide, with all its safety issues. Looking for an oxidative alternative to sulfide, Dave Bailey and Andy Gehring investigated magnesium and calcium peroxide. Following through on this, I and the person most closely involved with the day-to-day work, my research colleague, Bob Dudley, wondered whether common oxidative chemicals could replace sulfide. We settled on sodium perborate and then sodium percarbonate, both common ingredients in laundry detergents, and the rapid oxidative system indeed was proven workable. Furthermore, the relative safety, ease of handling, and low cost of sodium percarbonate made this oxidative approach a valid one for use in the tannery, too. I am happy to say that commercial trials in the beamhouse are now underway under a CRADA, a Cooperative R&D Agreement, with USDA.

There is some irony on being presented with a watch to commemorate the award. I just retired from the Federal government, at the end of March of this year, and one thing that a Federal retiree NEVER receives from Uncle Sam is the proverbial gold watch. Gold or not, I am honored to receive this watch this evening. I cannot close my remarks without recognizing the Tannin Corporation for its continuing sponsorship of the Alsop Award, and of course the selection committee for its nomination. Thank you all again.

# Closing Remarks

*by*

William Marmer and Stephen Yanek

**William Marmer:**
Ladies and Gentlemen: This has been a momentous year for me personally. As I said a few moments ago, I retired from a long career with the US Department of Agriculture, and I am ending the three-year cycle of Vice-President-Elect, Vice President, and President of your Association. Last year at this time we convened in Washington, DC, in a joint meeting with the International Union, the IULTCS. I'm proud of the accolades we received from around the world after that meeting. The Union's president at this moment is our own Elton Hurlow, who closed out our meeting's technical session today, and Professor Bi Shi, our honored Wilson Lecturer at this meeting, is the program chair for the next IULTCS Congress, its $30^{th}$, to be held in Beijing next year.

As an aside, Professor Bi Shi comes to us from the Sichuan University in Chengdu. Chengdu, as we all know, has been near the epicenter of the recent devastating earthquake. We have been informed that damage in the Chengdu metropolitan area was minimal compared to the worst of the devastation, but we cannot miss this opportunity to convey to Professor Shi our concerns and empathy for the suffering endured by the Chinese people.

I must also take note of the recent devastating floods in our Midwest. I know from private discussions here at the meeting that the leather industry and our membership were not immune to the damage caused by the high water. I therefore want to express our concerns to all those affected by the flooding.

The ALCA continues as this country's preeminent organization for hides & leather technology. We are here today at its $104^{th}$ annual meeting. I've been told that few other technical organizations in America have experienced such longevity. We of course depend heavily on the support of our employers - the hide producers and traders, the tanners, the suppliers, the research organizations - who indirectly support our participation in the Association. Without their financial support, few of us would be able to attend its functions and participate in its activities. The underlying industries, of course, are undergoing major challenges and changes. America still produces abundant and high-quality hides and is the major market for finished leather goods. Adding value to those hides is more and more an off-shore activity, but we see that there still is a vibrant, though smaller domestic tanning industry. We must not lose track of the uniqueness of the ALCA and how it differs from the trade organizations – particularly the US Hide, Skin and Leather Association and the Leather Industries of America. I say this out of great respect for those two groups but also to re-emphasize that ALCA exists and continues to serve these industries as only a scientific and technical organization can do, namelyas we observe in the ALCA bylaws—

- to encourage and promote the advancement of knowledge of leather technology and its application to the industries,
- to publish these advancements in a well-recognized scientific journal, and
- to develop and maintain official methods and specifications.

The challenge to those who inherit this establishment is to maintain its objectives. I'm reminded of what Benjamin Franklin said. Franklin, by the way, was the founder of America's first learned society, the American Philosophical Society. At the close of the Constitutional Convention in Philadelphia in 1787, Dr. Franklin was asked as he left Independence Hall, "What kind of government have you given us, Dr. Franklin?" Many of you know his reply, "A republic, if you can keep it." What kind of organization have our own founders given us? A professional learned society, a scientific and technical organization, if you can keep it.

Let me thank several among us who have worked hard this past year to keep it: I've just recognized my executive boardDave LeBlanc, Vice-President-Elect; and Steve Yanek, Vice President. I also thanked the members of our convention committee—Doug Morrison, Sarah Drayna, Susan Steele, and Lee Lehman.

At this afternoon's Business Meeting, we recognized our elected Members of Council who are retiring from their three-year termsEllie Brown (USDA) and Dave Powell (Chemtan). Let me recognize the entire Council, Ellie and Dave, and also Rob Harvey (Hermann Oak Leather), Steve Lange (Seton), Jeff Miller (GST), and Gary Rennerfeldt (Tyson). We thank the candidates who ran for election to Council this yearAlex Campbell (Rohm & Haas), Harold Diephouse (GST), C.-K. Liu (USDA), and George Stockman (Buckman), and we congratulate those who were elected—Harold Diephouse and George Stockman. We also congratulate Craig Keyser on his election as Vice-President-Elect.

- We recognize the critical and well-conducted role played by the Editor of the Journal of the American Leather Chemists Association, our Past President, Bob White, and his Editorial Board.
- At the Business Meeting, we recognized three Chairs of our standing Committees who have completed their three-year tour of duty:
    - o Education: Bob Dudley
    - o Methods & Specifications: Lori Hyllengren
    - o Collagen & Coproducts: Ellie Brown

But let me also thank all of those who lead or serve on all the standing committees as well as those who have done so on several ad hoc award committees (Wilson, Alsop, O'Flaherty).

- A very special thank-you is justified to all of you who prepared technical presentations of your research and development. Your presentations formed the heart of this Annual Meeting. Those presentations were facilitated by the excellent AV assistance by Nick Latona.
- All of us are truly indebted to the real lifeline of ALCA, its Executive Secretary Carol Adcock.
- And last but not least, I personally want to acknowledge the support and patience of my lifetime partner, my wife Benne.

It took 103 years for the ALCA to acquire a gavel. Last year, Dennis Shelly had one made of rawhide and symbolically passed the authority of the Presidency to me in Washington. I now have the honor of calling upon our Vice President, Steve Yanek, to accept the gavel from me:

Steve, a year ago, you were in a very stressful situation, looking for employment as we all held our breath. Fortunately for all of us, you have stayed in the leather industry, and we all wish you success in this next year as you take the gavel. President Yanek, the dais is yours.

**Stephen Yanek:**
Thank you, Bill. It will be an honor to lead the Association for the 2008-2009 year. As President, my focus will be on leveraging our 3 main products:

- The Annual Meeting and all that it has to offer in terms of networking, information, and dialogue,
- The Journal as a medium available to our members in both printed and electronic formats, and
- The Correspondence Course as a cost-effective means of educating those involved in the manufacture, sale, or use of leather materials

In addition to our core products, we have a very talented group of individual members in the ALCA. I hope you will agree with the fact that we are uniquely positioned to unite other domestic hide and leather industry professionals such as those in the USHSLA and the LIA. We also have a fresh opportunity to create a working relationship with the Italian leather trade groups, in particular.

As ALCA President, I will do everything within my means to help attract new members, subscribers, and students to this historic Association. My efforts will include reaching out to our customers – those who purchase and incorporate leather materials into their products for a REASON;

A REASON which is really a nothing more than a consumer's WANT that is continually and increasingly under attack from manufacturers of synthetic materials - materials that now compete directly with leather in their quality, look, feel, and need I mention, COST.

Therefore, this Meeting, the Journal, and the Correspondence Course are really the 3 tools we have to maintain the 'American leather machine' – and in doing so we will strengthen our businesses and make them more competitive in the global marketplace.

Whether your products are chemicals, hides, sides, cut parts, or finished goods, – the message is the same – membership in this Association will make your business more successful.

Thank you for the opportunity to serve as ALCA President, and please enjoy the remainder of your evening.

William Marmer passing the gavel to Stephen Yanek

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# Note from the Editor

Dear Reader,
This August Issue of the Journal starts with page number 268. This is a corrected number because page numbers were erroneously duplicated in the June and July 2008 issues. However, these issues still retain specific uniqueness for reference purposes. For example, June 2008 JALCA 103(6), 167 is different that July 2008 JALCA 103 (7), 167. We apologize for this inconvenience.

Robert F. White
Journal Editor