

ADSORPTION AND DESORPTION BEHAVIORS OF LIGNOSULFONATE DURING THE SELF-ASSEMBLY OF MULTILAYERS

Yonghong Deng,^a Yuan Wu,^a Yong Qian,^a Xinping Ouyang,^a Dongjie Yang,^a and Xueqing Qiu^{a,b,*}

Self-assembled multilayers were fabricated from lignosulfonate (LS) and poly(diallyldimethylammonium chloride) (PDAC), and the adsorption and desorption behaviors of LS on the LS/PDAC multilayers under different pH conditions were intensively investigated. Results showed that the adsorption and desorption behaviors were controlled by electrostatic attraction, hydrophobic interaction, and changes in the microstructure, which depended on solution pH. Lignosulfonates exist as colloids in solutions at low pH because of a hydrophobic interactions, and the LS colloids adsorbed on the PDAC layer because of electrostatic attraction. LS colloids started to disassociate at pH 3.5, resulting in an abrupt rise of the adsorption rate, a sharp decrease of the adsorbed amount, and a steep reduction in the surface roughness. Desorption behaviors of LS multilayers were related to the pH values of both LS dipping solution for self-assembly and the immersing solution for post-preparation treatment. Desorption of LS could be induced by a weakening of electrostatic attraction or hydrophobic interaction. A significant desorption occurred only when LS colloids dissociated in the multilayers. LS colloids were harder to dissociate in the multilayers than in the solutions because of electrostatic attraction between LS and PDAC.

Keywords: Lignosulfonate; Self-assembly; Adsorption; Desorption; Kinetics

Contact information: a: School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou, 510640, China; b: State Key Lab of Pulp&Paper Engineering, South China University of Technology, 381 Wushan Road, Guangzhou, 510640, China; *Corresponding author: cexqiu@scut.edu.cn

INTRODUCTION

Lignin is the second most abundant renewable resource, but other than as a component of wood, it is mostly present as a by-product in spent liquor from the paper and pulping industry (Dizhbite et al. 1999). Lignin can be described as a highly cross-linked polymer formed from different phenyl-propanoid units, such as guaiacyl, syringyl, and para-hydroxybenzene, but the exact structure of lignin has not been confirmed (Rencoret et al. 2009). Most research has reported that lignin is a heterogeneous network polymer, while other researchers have assumed a linear model for lignin (Freudenberg 1965; Bolker and Brenner 1970). Lignin components tend to aggregate and form associated complexes (Guerra et al. 2007; Contreras et al. 2008; Adler 1957), which results in more difficulty in determining lignin's structure.

Lignosulfonate (LS) is a byproduct in the waste liquor from acid sulfite pulp mills. It is reported that LS is formed by the random breaking of the “infinite” lignin network in wood, and the resulting LS molecule might be a randomly branched polyelectrolyte (Myrvold 2007). However, Vainio et al. (2008) believed that LS has characteristics of “soft” colloidal particles, and the average shape of the lignosulfonate particles in saline solutions is an oblate spheroid with an axial ratio of 3.5. Goring introduced a microgel model to describe the morphology of LS particles, in which LS with high molecular weight would be spherical in solution and consist of cross-linked linear chains of about 20 phenyl propane units (Goring 1962). LS exhibits favorable wettability, adsorptivity, and dispersive ability, and can be used as an anionic surfactant in various application areas, such as concrete water reducers (Ouyang et al. 2009), dispersants for water-coal-slurry (Zhou et al. 2007), corrosion and scale inhibitors (Ouyang et al. 2006), pesticide dispersants (Li et al. 2009), auxiliary substances for paper coating (Telysheva et al. 2001), dye dispersants (Burnett and Squire 1986), and oil well dispersants (Chiwetueu et al. 1994). When LS is used as a dispersant, some groups of LS act as an anchor to adsorb on the solid surfaces, and the other groups are exposed toward water. LS enhances the stability of solid suspension in water because of steric hindrance and the electrostatic repulsive force. The application of LS in the field of anionic surfactants is determined by the adsorption characteristics of LS on the solid particles. Studying the adsorption characteristics of LS on solid surface has both theoretical significance and application value.

Grigg and Bai (2004) studied adsorption and desorption of calcium lignosulfonate (CLS) on Berea sandstone and dolomite through flow-through experiments, and found that CLS adsorption isotherms follow the Freundlich isotherm law. Qiu et al. (2009) investigated the adsorption of LS on TiO₂ particles, and found the LS adsorption isotherms to be of the Langmuir type. Palmqvist and Holmberg (2008) studied the adsorption behavior of lignosulfonate on alumina surfaces by quartz crystal microbalance, and their results showed that the lignosulfonate adsorbed in low amounts and in a flat conformation, which generated thin, highly rigid layers less than 1 nm thick. Although the adsorption behaviors of lignosulfonates on solid particles have been reported, the magnitude and nature of the adsorption characteristics of LS on solid surfaces are still a matter of discussion.

The quest to understand the adsorption characteristics of an LS layer at a molecular level has become a hot topic and difficult problem, which has attracted worldwide attention. On one side, the structure of LS is complex and uncertain. The current adsorption theory about polymers or small molecules is not suitable to describe it. On the other side, existing industrial applications of LS indicate that the dispersed solid particles are of all kinds of shapes, which makes it hard to determine the microstructure of the LS layer adsorbed on the solid particles. For foundational research, the problem caused by the irregular shapes of the solid particles may be easy to overcome if regular solid plates are used as substrates for the adsorption of LS. But the monolayer of LS adsorbed on solid plates is too thin to completely cover the underlying substrate, and the adsorption characteristics are still difficult to characterize. For example, AFM images of the surface cannot reflect the pure morphology of a LS layer, but a mixed morphology of the LS layer together with the substrate. UV-Vis spectroscopy cannot be used to monitor

the adsorption process, because the absorbance at a characteristic wavelength is too weak to be detected perceptibly. Here, we put forward a novel method to measure the adsorption characteristic of lignosulfonates. That is by the use of a layer-by-layer (LBL) electrostatic self-assembly method for sensitivity improvement.

LBL self-assembly, which was first noted by Iler (1966), and then rediscovered by Decher and Hong (1991), is a simple and controllable technique of depositing multilayers by the consecutive adsorption of alternating anionic and cationic species. Although there is no clear interfacial structure for the polyelectrolyte multilayer, it is confirmed that the adsorbed amount of polyelectrolytes increases linearly with the number of deposited layers, and the newly created film surface is mostly dependent on the chosen polyelectrolytes and adsorption conditions (Decher 1997). Electrostatic interactions are initially considered as the key to the final structure of the self-assembled multilayers; however, secondary interaction such as hydrophobicity, hydrogen bonding, and dispersion forces are also reported to have an important impact on the thickness, the morphology, and the surface properties of the multilayers (Hammond 2000; Zhang 2007). The adsorption thickness and film structure can be adjusted by changing solution conditions, such as solution pH, ionic strength, temperature, concentration, and solvents. Adjusting the solution pH is generally considered as an effective method to control the self-assembly of weak polyelectrolytes, while adjusting solution ionic strength is commonly considered as an effective method to control the self-assembly of strong polyelectrolytes (Hammond 2000). Since LS is a polyelectrolyte consisting of both strong and weak ionic groups, studying the adsorption characteristic of LS self-assembled multilayers is helpful to understand the nature of LBL self-assembly with both weak and strong polyelectrolytes. Furthermore, the LBL self-assembly technique is considered as a useful method for a better understanding of the adsorption characteristics of LS on solid surfaces, as it can be well characterized by a wide variety of physical techniques.

Potential industrial applications of LS may benefit from a better understanding of the adsorption characteristics of LS with cations. The formation of LS/cation complexes will alter the surface and interface properties of LS. It can be utilized in the formation of stable crude oil emulsions containing large amounts of asphaltenes (Gundersen 2001). Recently, LS complexes with cationic polymers were considered as special additives for modification of paper strength (Fredheim and Christensen 2003). Building multilayers of cationic and anionic polymers on cellulosic fibres was reported to provide a significant increase in strength of the paper (Wagberg 2002). Until now, there are a few reports about the self-assembled multilayers of LS and cations. Paterno and Mattoso (2001) successfully fabricated the self-assembled films of poly(o-ethoxyaniline) and sulfonated lignin, and found that poly(o-ethoxyaniline) layers exhibited a granular rough aspect, while sulfonated lignin layers presented a much smoother surface. Liu et al. (2009) used LS to effectively modify the surface of a mica substrate using Cu^{2+} as binding agent via self-assembly. However, studying the adsorption characteristic of LS via self-assembly technique has not been reported up to now.

In this work, LS was used as a polyanion to fabricate LBL self-assembled multilayers with poly(diallyldimethylammonium chloride) (PDAC) as the polycation. The research effort was focused on the kinetics of adsorption and desorption of the LS layer on the already formed LS/PDAC multilayers under different pH conditions. During

investigation of the kinetics of adsorption and desorption, the adsorption characteristics of LS film, such as the driving force, the adsorbed amount, the adsorption rate, surface morphology, and microstructure, were carefully analyzed. Desorption of LS from the LS/PDAC multilayers was investigated through a post-preparation treatment process, in which the already formed LS/PDAC multilayers were immersed into water with different pH values. This work is helpful for understanding the adsorption characteristics of LS on solid surface at a molecular level, and further expanding functionalities of LS through manipulation of the adsorption capacity by changing solution pH value.

EXPERIMENTAL

Materials

Sodium lignosulfonate, obtained from Shixian Papermaking Co. Ltd (China), was purified by filtration, ultrafiltration, and gel chromatography. Through cationic exchange resin, sodium lignosulfonate became lignosulfonic acid and then was used as a polyanion. Lignosulfonic acid with a molecular weight about 20,000 and polydispersity index of 1.5 was selected to use in this work. The content of the sulfonic, carboxyl, and phenolic groups were measured to be 9.28 wt%, 3.87 wt%, and 1.59 wt%, respectively. Poly(diallyldimethylammonium chloride) (PDAC, MW 200,000 to 350,000, 20% solution, Aldrich) was used as a polycation and was diluted to a concentration of 0.1mmol/L (repeated unit). Milli-Q water (resistivity > 18 M Ω ·cm) used in the self-assembly process was obtained from a Millipore water purification system. All other solvents and reagents were purchased commercially as analytical grade products and used directly without further purification unless otherwise indicated.

Characterization

The UV absorption measurements were performed with a UV-Vis spectrophotometer (UV-2450, Shimadzu Corp., Japan). The molecular weight distribution of the LS sample was determined by using aqueous gel permeation chromatography (GPC) with Ultrahydrogel 120 and Ultrahydrogel 250 columns. The effluent was monitored at 280 nm with a Waters 2487 UV Absorbance Detector (Waters Corp., USA). The polystyrene sulfonate was used as the standard substance and the 0.10 mol/L NaNO₃ solution with pH 8 as the eluent with the velocity of 0.50 ml/min. The sulfonic, carboxyl, and phenolic groups in LS were determined by using an automatic potentiometer titration (809 Titrando, Metrohm Corp., Switzerland) as described by Dence (1992). The morphological images were observed using an AFM (Nanoscope IIIa Multimode, Veeco Co., USA) by the tapping mode. Software Version 5.30 r3sr3 (Veeco Co., USA) was used for calculating a root mean square height to determine the surface roughness of the LS coated surface

Multilayer Fabrication

LS was dissolved in water directly to obtain a 0.1 wt% polyanionic solution. Diluted sodium hydroxide and hydrogen chloride solution were used to adjust the solution pH. PDAC was used as polycation with a concentration of 0.1mmol/L. The

solutions were kept stirring for 20 min and then put aside for 72 h. The LBL multilayers were assembled on the quartz slides. The quartz substrates were sonicated in a 98% $\text{H}_2\text{SO}_4/30\%\text{H}_2\text{O}_2$ solution for 1 h, and sonicated in a $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ (5:1:1) solution for 1 h, which was then followed with a thorough rinse and drying with an air stream. A freshly treated quartz slide was first kept dipping into the polycation solution for about 10 min. The slide was thoroughly rinsed with Milli-Q water and blown dry with air. And then the slide was dipped into the polyanion solution for 10 min, rinsed with Milli-Q water and blown dry with air. This process was repeated until multilayers with the required number of layers were achieved.

RESULTS AND DISCUSSION

Fabrication of LS/PDAC Self-Assembled Multilayers

Figure 1 is the potentiometric titration curve of the lignosulfonic acid. There are three inflections in the titration curve. The first inflection, near 200 mV, is related to strong acids, such as sulfonic groups; the second inflection, near -200 mV, corresponds to carboxylic groups; and the third, near -400 mV, to phenolic hydroxyl groups. LS includes not only strong acidic groups (sulfonic groups), but also weak acidic groups (carboxylic and phenolic groups).

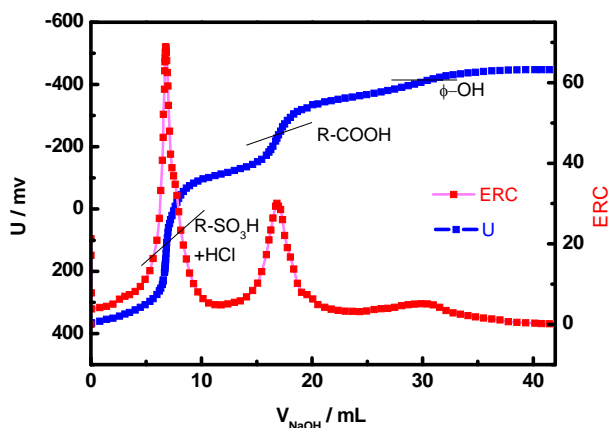


Fig. 1. Potentiometric titration curve of a lignosulfonate in the presence of an internal standard, p-hydroxybenzoic acid. 0.5wt% lignosulfonate sample was titrated with 0.05 M tetrabutylammonium hydroxide (TnBAH). ERC is abbreviation of equivalence point recognition criterion. U is potential.

Figure 2 shows pH titration curves of 0.1wt% lignosulfonate and 0.1 mM p-methylbenzene sulfonic acid. Here, p-methylbenzene sulfonic acid is a strong acid, and used as a contrast to LS. The pH titration curve for NaOH vs. p-methylbenzene sulfonic acid is a typical curve of a strong base vs. a strong acid. The pH increases slowly until very near the equivalence point. There is a really steep plunge at the equivalence point. However, LS includes both strong and weak acidic groups. The pH titration curve of NaOH vs. LS is similar to that of a weak acid and a strong base. There is no sharp change in the pH during the pH titration of LS, indicating that LS is ionized gradually with increasing pH. According to the acid-base titration curve, the pH range of LS can be

divided into three regions, recorded as pH-I (pH<3.5), pH-II (pH=3.5 to 9), and pH-III (pH>9). The carboxylic groups of LS may start to ionize at about pH 3.5, and the phenolic groups may start to ionize at about pH 9.

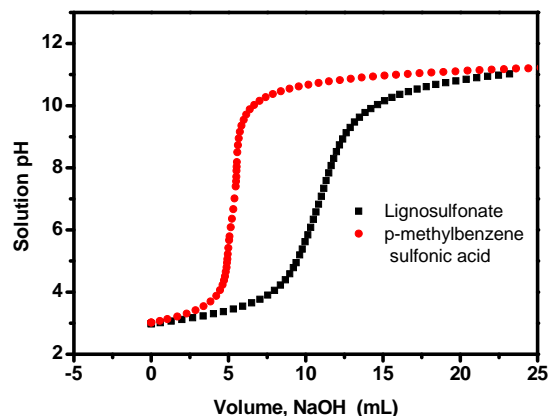


Fig. 2. pH titration curves of 0.1wt% lignosulfonate and 0.1 mM p-methylbenzene sulfonic acid. The concentration of the NaOH titration solution was 0.1mM.

LS can be completely dissolved into water and used as a polyanion to fabricate LBL self-assembled multilayers with PDAC as an oppositely charged polyelectrolyte. UV-Vis spectroscopy was used to monitor the LBL self-assembly process of LS/PDAC multilayer films. Figure 3 gives the typical UV-Vis spectra of the LS/PDAC multilayer films varying with the number of bilayers. Here, the term “bilayer” means a pair of layers including one layer of polycation and one layer of polyanion formed after each deposition cycle. The absorption band at 280 nm ($\lambda_{280\text{nm}}$) is the characteristic peak of absorption of LS. The inset of Fig. 3 shows a typical plot of the absorbance at $\lambda_{280\text{nm}}$ vs. the number of the bilayers. Except for the first three bilayers having a substrate effect, a linear increase of the absorbance with the increase of the number of bilayers indicates that the deposition process is reproducible from layer to layer and an equivalent amount of LS is deposited on the substrates in each dipping cycle.

To understand the effect of pH on the adsorption behavior of LS, a series of LS dipping solutions with different pH were used as polyanions to build LBL self-assembled multilayer films. Figure 4 shows the UV-vis absorbance of 10-bilayer LS/PDAC multilayers obtained under different pH solutions. When the LS/PDAC self-assembly film was prepared from LS dipping solution with pH 3, the absorbance at 280 nm was 0.87. If the pH of the LS dipping solution was 7, the corresponding film had absorbance of 0.49 at 280 nm. The absorbance of LS/PDAC multilayers at 280 nm was 0.44 with pH 11. Before comparing the adsorbed amount of LS during the self-assembly process under different pH conditions, we need to know how the deprotonation of phenolic groups affects the UV-vis absorbance values of LS.

It is well known that UV-vis absorbance band of phenolic groups changes with deprotonation. The content of the phenolic groups in lignosulfonates was measured to be 1.59 wt%, so UV-vis absorbance band of LS may change with deprotonation of the phenolic groups to some extent. To clearly understand the effect of solution pH on the absorbance of LS, a series of LS solutions with different pH were measured by UV-vis

spectroscopy. It was found that the peak shifted to 281 nm under alkali conditions. UV absorbance at 280 nm increases slightly with deprotonation of the phenolic groups, indicating that the molar extinction coefficient (ϵ) increases slightly.

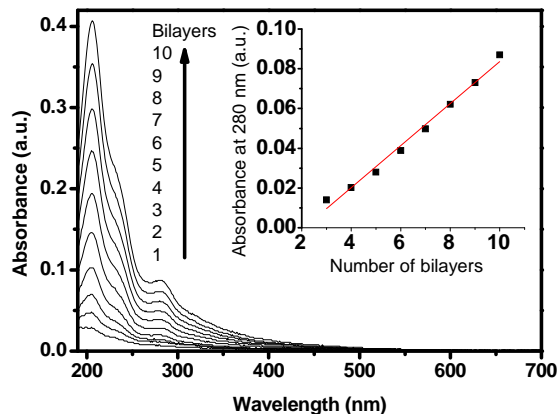


Fig. 3. UV-Vis spectra of LS/PDAC multilayers with different number of bilayers (pH=3). Insert: The absorbance of LS/PDAC multilayers at $\lambda_{280\text{nm}}$ varying with the number of bilayers.

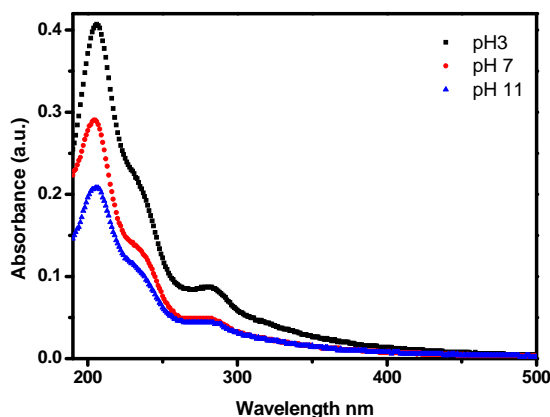


Fig. 4. UV-Vis absorbance of LS/PDAC multilayers with 10 bilayers, obtained from dipping solution with different pH.

Beer's Law states that molar extinction coefficient is constant and the absorbance is proportional to concentration for a given substance dissolved in a given solute and measured at a given wavelength. The absorbance of a sample at λ (A_λ) depends on the molar concentration (C), light path length in centimeters (L), and molar extinction coefficient (ϵ) for the dissolved substance.

$$A_\lambda = \epsilon C L \quad (1)$$

Figure 5 shows the absorbance at 280 nm of LS with different pH as a function of concentration. The standard curves of the absorbance at 280 nm (A_{280}) vs. concentration (C) can be fitted by linear equation (2), (3), and (4).

$$A_{280\text{nm}} = 14.59 * C \quad \text{where solution pH} = 11 \quad (2)$$

$$A_{280\text{nm}} = 14.01 * C \quad \text{where solution pH} = 7 \quad (3)$$

$$A_{280\text{nm}} = 13.82 * C \quad \text{where solution pH} = 3 \quad (4)$$

To undergo a transformation, equation 1 can be expressed as

$$A_{\lambda}/C = \varepsilon L \quad (5)$$

Since L was the same for UV-vis spectral measurement of the three solutions, the slope is directly proportional to ε for LS dissolved under different pH conditions. The slopes calculated by fitting the data were 14.59 for pH 11, 14.01 for pH 7, and 13.82 for pH 3. It can be inferred that ε of LS at 280 nm does not change much when solution pH is changed from 3 to 7, but it increases slightly when solution pH is changed from 7 to 11. The molar extinction coefficient of LS solution with pH 11 was 1.041 times as that for LS with pH 7.

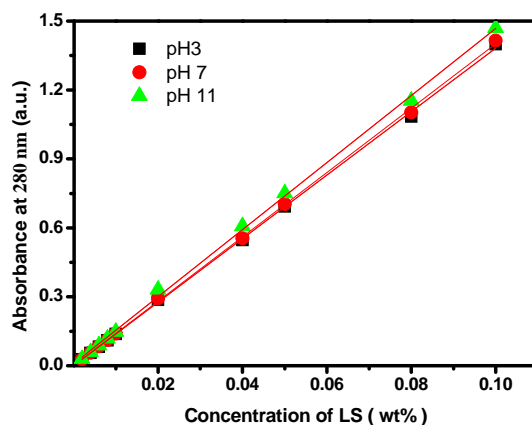


Fig. 5. Absorbance at 280 nm of LS with different pH as a function of concentration.

On the assumption that the molar extinction coefficient of LS has a similar law with pH when LS is transferred from solution to film, we can compare the adsorbed amount of LS during the self-assembly process under different pH conditions. As shown in Fig. 4, the absorbance value at 280 nm of LS/PDAC self-assembly film decreased from 0.87 to 0.49 when solution pH was changed from 3 to 7, and then decreased to 0.44 when pH reached 11. Since the molar extinction coefficient of LS increases slightly with deprotonation of the phenolic groups, we can definitely confirm that the adsorbed amount of LS/PDAC film with pH 7 was higher than that of film with pH 11, and the adsorbed amount of LS/PDAC film with pH 3 was much larger than that of film with pH 7.

Figure 6 shows the absorbance at 280 nm of the LS/PDAC multilayers with 10 bilayers as a function of the solution pH values. When the solution pH increased, the absorbance values of LS decreased, indicating that the adsorbed amount of LS decreased. There were two inflections of the adsorbed amount as a function of the solution pH

values. The first inflection was near pH 3.5, where a sharp change of the adsorbed amount occurred. The second inflection was near pH 9, where there was a slight change of the adsorbed amount. This phenomenon is caused by the specific molecular structure and the configuration characteristics. The larger adsorbed amount of multilayers under the lower pH condition can be attributed to the lower ionization degree and the less extended conformation of LS in the solutions (Yoo et al. 1998). The first inflection point of adsorbed amount at pH 3.5 was caused by ionization of carboxylic groups, while the second inflection of adsorbed amount at pH 9 was caused by ionization of phenolic groups. Besides, that sharp change of the adsorbed amount occurred at pH 3.5 are related to a large change of LS microstructure in dipping solutions.

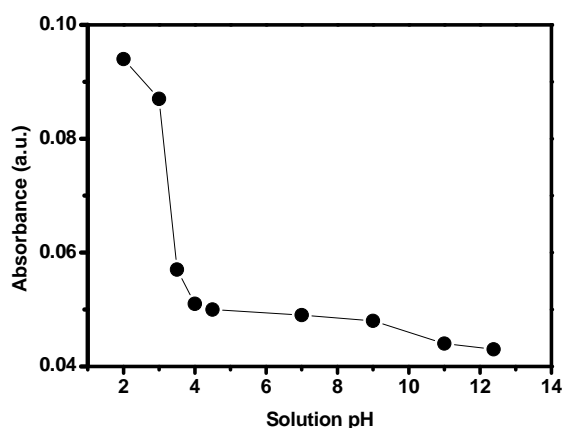


Fig.6. Absorbance at $\lambda_{280\text{nm}}$ of the LS/PDAC self-assembled multilayers with 10 bilayers as a function of the solution pH values. The multilayers were obtained from LS dipping solution with different pH.

Adsorption of a LS Layer on LS/PDAC Multilayers

To understand the adsorption process between lignosulfonates and polycationic surfaces as the pH of the solution changes, an already formed LS/PDAC multilayer with PDAC as the outermost layer was used as a substrate for the adsorption of LS, and the adsorption kinetics of a LS layer under different pH conditions was examined by UV-Vis spectroscopy. Results showed that the adsorption rate of a LS layer decreased slowly and the absorbance value increased gradually when solution pH was changed from 14 to 3.5. There was a sudden drop of the adsorption rate and an abrupt rise of the absorbance values at pH 3.5. Except for the first three bilayers having a substrate effect, the adsorption kinetics of LS/PDAC multilayers from 4 bilayers to 10 bilayers were all examined to be similar. Figure 7 shows the kinetics curves of the adsorption of LS on the 10-bilayer self-assembled multilayers under different pH conditions. The absorbance at 280 nm of a LS layer varied with the adsorption time, and it decreased when pH increases. As UV absorbance at 280nm increases slightly with deprotonation of the phenolic groups, it can be referred that adsorbed amount of a LS layer is lower with

higher pH. However, compared with the regular layer-by-layer adsorption process, the amount of adsorption of a LS layer with several drying interferences showed a significant increase (Fig.3). This phenomenon may be caused by the competitive adsorption between water and LS (Raposo et al. 1997).

The adsorption of a LS layer reaches saturation within a few minutes. The kinetics curves of absorbance (A) vs. time (t) can be fitted by second order exponential decay equation (6), and the parameters calculated by fitting the data are recorded in Table 1.

$$A=A_0+ k_1\exp(-t/\tau_1)+ k_2 \exp(-t/\tau_2) \quad (6)$$

where k_1 , and k_2 are constants, and τ_1 and τ_2 are the characteristic times. A_0 is the absorbance approaching saturation. That is to say, the absorbance grows gradually with increasing time and then level off at a saturation value. The saturation value of absorbance is A_0 , taken as proportional to the amount of adsorbed LS. The reciprocal of the characteristic times (τ) is the absorbance rate of LS during self-assembly.

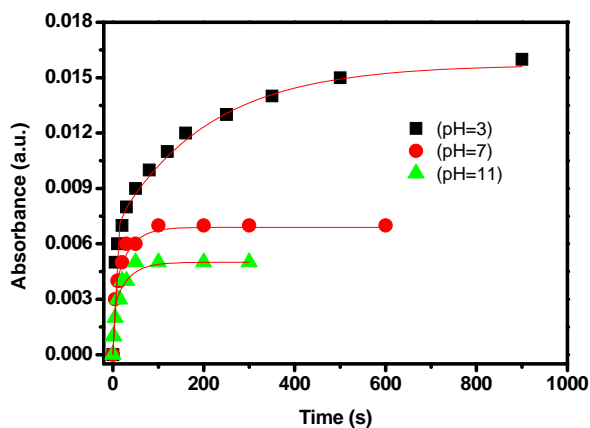


Fig.7. Absorbance at $\lambda_{280\text{nm}}$ versus immersion time for adsorption of a LS layer on an already formed LS/PDAC self-assembled multilayer with 10 bilayers. The LS layer was obtained from LS dipping solution with different pH.

Table 1. Parameters Used in Equation (6) to Fit the Experimental Data of Fig. 7

Solution pH	A_0	k_1	τ_1 (s)	k_2	τ_1 (s)	R^2
3	0.016	-0.0067	4.71	-0.0089	205	0.9947
7	0.007	-0.0032	2.45	-0.0037	35.78	0.9979
11	0.005	-0.0024	2.36	-0.0025	30.93	0.9848

Evidently, there exists a two-step process of adsorption during the self-assembly process. A fairly fast increase occurs in the initial stage of adsorption with a smaller characteristic time, followed by a very slow increase with a larger characteristic time until the saturation of absorbance is reached. The first process is related to the polymer molecules being transferred from the dipping solution to the solid surface, while the second one corresponds to the rearrangement of polymer molecules on the solid surface (Raposo et al. 1997).

The adsorption rate of an LS layer depends on the pH of the LS dipping solution. As shown in Table 1, at pH 11, τ_1 and τ_2 were 2.36 s and 30.93 s, respectively. When solution pH was changed from 11 to 7, the characteristic times (τ_1 and τ_2) increased slightly. However, the adsorption rate slowed down sharply at pH 3, where τ_1 and τ_2 were 4.71 s and 205 s, respectively.

LS is an amphiphilic random polymer. LS can be dissolved into alkali solutions to form a homogeneous solution. With decreasing solution pH, the LS configuration trends to curl up because of the protonation of lignosulphonates. When pH reaches 3.5, the solvent quality becomes progressively worse. The hydrophobic groups of LS tend to aggregate, while hydrophilic groups are still well dispersed into water. Because the hydrophobic and hydrophilic groups are connected with covalent bonds within lignosulfonates, they cannot be separated from each other. As a result, a phase separation between hydrophobic and hydrophilic groups happens. LS can form colloidal particles due to this strong hydrophobic interaction. When solution pH is below 3.5, LS exists as colloidal particles with a core consisting of hydrophobic aromatic groups and a shell including hydrophilic anionic groups. For the adsorption of LS on an already formed LS/PDAC self-assembled multilayer, diffusion of LS to the surface is controlled by LS size. Aggregated structures would move in solution much slower than single polymer chains. Therefore, the adsorption rate of LS decreases slightly when solution pH is changed from 11 to 7, but it slows down sharply at pH 3.

AFM with a tapping mode is a powerful tool to identify surface morphology and microstructure characteristics. A series of LS films were prepared from different solution pH on the already formed LS/PDAC multilayers, and the AFM images were observed. Particle-like morphology clearly appeared on the LS surface when the solution pH was lower than 3.5 (Fig. 8a), but the particle-like morphology disappeared when the pH was 3.5 or larger (Fig. 8b).

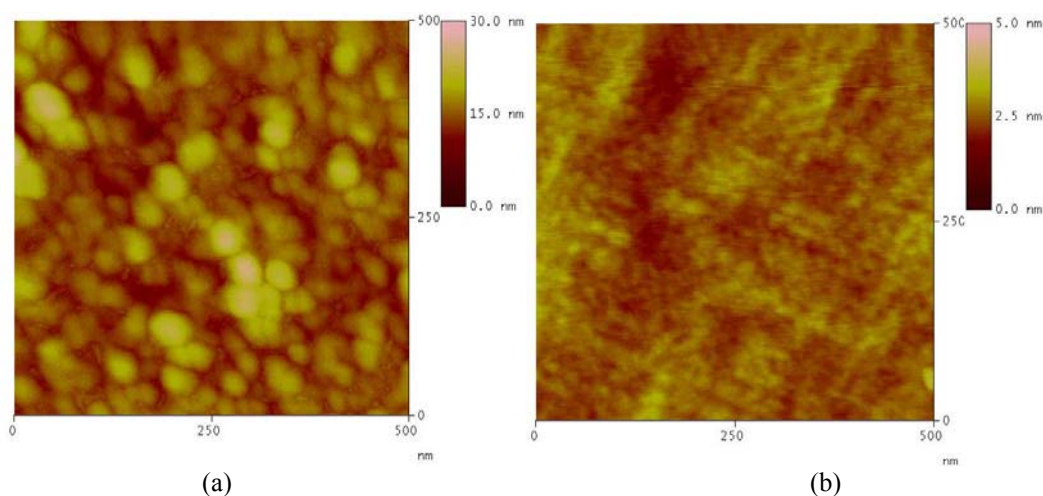


Fig.8. AFM images of a LS layer adsorbed on an already formed 10-bilayer LS/PDAC self-assembled film. Scan size: 500 nm x 500 nm. (a) pH=3 ; (b) pH=11.

The surface roughness of a LS layer can be calculated from AFM topographic images. With decreasing solution pH, the surface roughness of a LS layer rose gradually,

and then an abrupt rise occurred at pH 3.5. When the solution pH was 11, 7, and 3, the surface roughness of a LS layer was calculated to be 0.45, 0.65, and 2.15 nm, respectively. It is evident that LS exists as colloidal particles at pH below 3.5, resulting in particle-like morphology and higher roughness.

Therefore, electrostatic attraction and hydrophobic interaction play important roles during self-assembly. The larger adsorbed amount and higher surface roughness of multilayers at a lower pH can be attributed to the lower ionization degree of LS in the solutions. The abrupt change of adsorption rate at pH 3.5 was related to a sudden change of LS microstructure in the solutions. When the solution pH is lower than 3.5, lignosulfonates exist as colloidal particles with a core consisting of hydrophobic aromatic groups and a shell including hydrophilic anionic groups because of a strong hydrophobic interaction. The LS colloids with anionic groups as the outermost layers are adsorbed on the PDAC layer because of electrostatic attraction. LS colloids start to disassociate at pH 3.5, resulting in an abrupt rise of the adsorption rate, a sharp decrease of the adsorbed amount, and a steep reduce of the surface roughness. With pH further increase, the adsorbed amount and surface roughness decrease gradually owing to ionization of LS. When solution pH is above 9, a high-quality LS film with a low surface roughness can be obtained owing to ionization of carboxylic and phenolic groups.

Desorption of LS from an Already Formed Multilayer

According to Decher's self-assembly process, there are washing steps in between the adsorption of a polyanion and polycation. Therefore, when the LS/PDAC multilayers are immersed into the same media as the washing steps, this post-preparation treatment has little effect on the self-assembled films. However, when the multilayers are immersed into different media as the washing steps, this post-preparation treatment may result in desorption of LS from the self-assembled films.

To investigate desorption behavior of LS under different pH conditions, a series of LS/PDAC multilayers were immersed into water with different pH, and the absorbance change with time was monitored by UV-Vis spectroscopy. Results showed that desorption behaviors of LS multilayers were related to the pH values of both LS dipping solution for self-assembly and the immersing solution for post-preparation treatment. Except that the first three bilayers may have a substrate effect, the desorption behaviors of LS/PDAC multilayers from 4 bilayers to 10 bilayers were examined to be similar. As show in Fig. 9, two self-assembled films were fabricated at pH 11, and then separately immersed in water with a pH of either 7 or 3. Since the absorbance of LS at 280 nm increases slightly with deprotonation of the phenolic groups, the absorbance values of the LS/PDAC multilayers were expected to decrease when the films obtained from pH 11 were immersed in water with of either 7 or 3. However, the absorbance value did not decrease much when the film was immersed in water with pH 7. On one side, we can refer that there was no perceptible desorption of LS from LS/PDAC multilayers. On the other side, it suggests that once the LS/PDAC multilayers are formed, the exposed free phenolic groups of LS are not enough to affect the absorbance values. For the same reason, if there was no desorption of LS when the film was immersed into water with pH 3, the absorbance value of the LS/PDAC film was supposed to have no change. Actually, the absorbance value of LS/PDAC multilayers decreased obviously when it was

immersed into water with pH 3, indicating that desorption phenomenon of LS from multilayers occurs. The amount of desorption under pH 3 condition increased with time. The curves of absorbance (A) vs. time (t) can be fitted by first order exponential decay equation (7).

$$A = 0.041 + 0.003 \exp(-t/25) \quad (7)$$

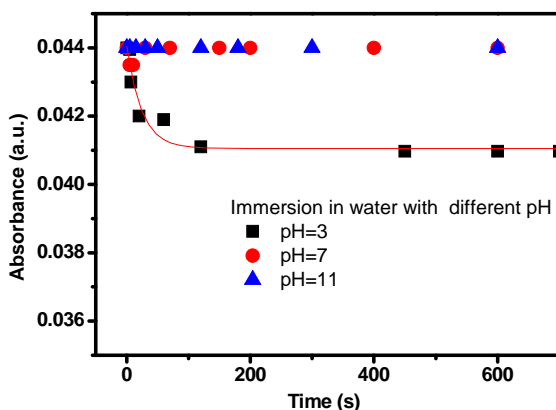


Fig. 9. The absorbance at $\lambda_{280\text{nm}}$ versus immersion time for post-preparation treatment of LS/PDAC self-assembled films with 10 bilayers. Two films were obtained from LS dipping solution with pH 11, and then immersed into water with pH 3 and 7, respectively.

Obviously, the self-assembled film was alkali-resistant, but it was sensitive to acidic conditions. As noted by Decher (1997), the use of polyelectrolytes for the LBL self-assembly rather than small molecules, is advantageous mainly because good adhesion of a layer to the underlying substrate or film requires a certain number of ionic bonds. When the LBL self-assembled film was exposed into water with pH 3, the carboxylic and phenolic groups of LS were protonated, so that some of anion-cation bonds were broken.

As shown in Fig.10, two self-assembled films were prepared at pH 7, and then separately immersed in water with pH either 3 or 11. There was a slight desorption of LS when the pH of immersion solution was 3, and the curves of absorbance (A) vs time (t) could be fitted to a first-order exponential decay equation (8).

$$A = 0.047 + 0.002 \exp(-t/127) \quad (8)$$

The absorbance value of LS at 280 nm is supposed to increase slightly with deprotonation of the phenolic groups if there is no desorption of LS from LS/PDAC film. As shown in Fig.10, the absorbance value of LS/PDAC film decreased when it was immersed into water with pH 11, indicating that desorption of LS from the self-assembled film occurred. The curves of absorbance (A) vs. time (t) could be fitted by a first-order exponential decay equation (9).

$$A = 0.044 + 0.005 \exp(-t/13) \quad (9)$$

The self-assembled film was sensitive to strongly alkaline conditions because of ionization of the phenolic groups of LS. It is reported that when strong polyanions and polycations are used for LBL self-assembly, the multilayers should have a 1:1 stoichiometry of anionic and cationic groups (Decher 1997). PDAC is a strong polycation, but LS includes both strong and weak anions, and not all of the anions are charged under this condition. Consequently, the stoichiometry of LS to PDAC in the self-assembled film can be expected to deviate from 1:1. When the film is immersed into water with a pH 11, all of the anions of LS are ionized, and then excessive lignosulfonates are removed to keep the stoichiometry at an equilibrium of anionic and cationic groups. Compared with equation 8, equation 9 shows a quicker desorption rate, indicating that desorption of LS occurred more easily in alkali solution than in acidic solution.

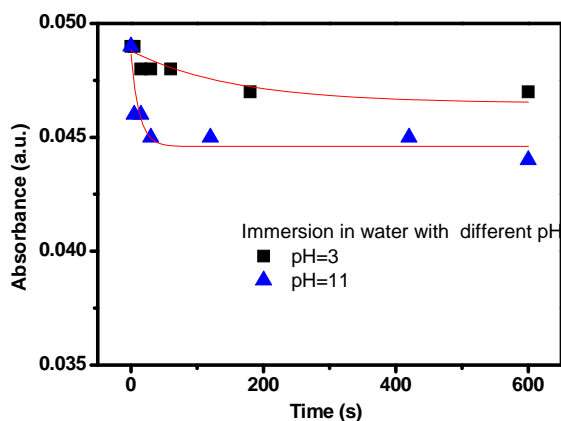


Fig. 10. The absorbance at $\lambda_{280\text{nm}}$ versus immersion time for post-preparation treatment of LS/PDAC self-assembled films with 10 bilayers. Two films were obtained from LS dipping solution with pH 7, and then immersed into water with pH 3 and 11, respectively.

As shown in Fig. 11, two self-assembled films were made at pH 3, and then separately immersed in water with a pH either 7 or 11. For the post-preparation treatment with a solution at pH 7, a desorption phenomenon was observed, and the curves of absorbance (A) vs time (t) could be fitted by a first-order exponential decay equation (10).

$$A = 0.0816 + 0.0044 \exp(-t/40) \quad (10)$$

It needs to be mentioned again that the absorbance value of LS at 280 nm is expected to increase slightly under alkali conditions. However, the absorbance value of LS had an obvious decrease when the film was immersed to water with pH 11, suggesting that the amount of desorption of LS was significant. The curve of absorbance (A) vs. time (t) could not be fitted by a first-order exponential decay equation. It could only be well fitted by a second-order exponential decay equation (11).

$$A = 0.0587 + 0.019 \exp(-t/5) + 0.0087 \exp(-t/209) \quad (11)$$

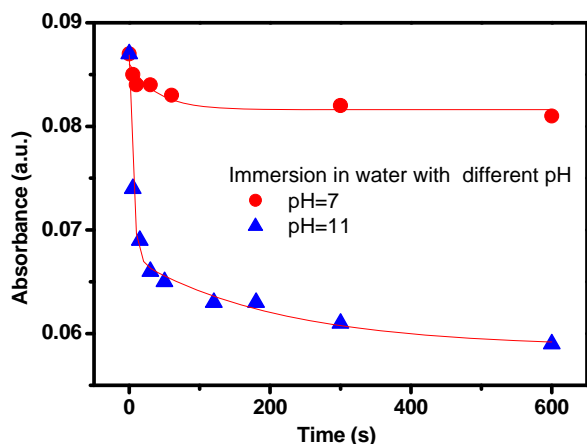


Fig. 11. The absorbance at $\lambda_{280\text{nm}}$ versus immersion time for post-preparation treatment of LS/PDAC self-assembled films with 10 bilayers. Two films were obtained from LS dipping solution with pH 3, and then immersed into water with pH 7 and 11, respectively.

It is believed that the stoichiometry of LS to PDAC in the self-assembled film deviated from 1:1 because the carboxylic and phenolic groups were not ionized at pH 3. For the post-preparation treatment with solution pH 7, the carboxylic groups of LS on the film surface were ionized, and then excess lignosulfonates were removed to keep the stoichiometry at an equilibrium of anionic and cationic groups. For the post-preparation treatment with a solution pH 11, there was a two-step process of desorption. The first process may be related to a quick dissociation of LS colloidal particles, resulting in an abrupt rise of the amount of desorption. The second process corresponds to a rearrangement of LS in the self-assembled film. The carboxylic and phenolic groups were ionized in the strong alkali solution, and excessive lignosulfonates were removed from the self-assembled film to maintain the stoichiometric equilibrium of anionic and cationic groups. In addition, more time was required to reach the desorption equilibrium due to the inter-winding of LS molecules with other LS molecules or with PDAC.

Although a desorption phenomenon of LS was observed in some cases, it was hard to detect any color change in the solutions for all the desorption experiments. Even for the samples fabricated at pH 3, the LS/PDAC multilayer film was still so thin that the film was completely transparent, and the desorbed amount of LS for the alkali adsorption experiment was not large enough to cause perceivable color change of the immersing solution. As the absorption band at 280 nm is the characteristic peak of LS, and PDAC has no absorbance at 280 nm, the observed change in absorbance of LS/PDAC multilayers for all the desorption experiments can be attributed to desorption of LS. As discussed above, the desorption behaviors of LS was affected by the pH values of both LS dipping solution and immersing solutions. When the LS multilayers were obtained from the dipping solution with pH 11, no desorption phenomenon was observed in LS multilayers after post-preparation treatment in neutral and alkali solutions, and a slight desorption of LS was detected in acidic solutions. When the LS multilayers were obtained with a pH of 7, a desorption phenomenon was observed in acidic and alkali solutions. The desorption amount was larger and the desorption rate was quicker in

alkaline solutions than in acidic solutions. When the LS multilayers were obtained at a pH of 3, desorption was observed in neutral and alkali solutions, and the desorption amount was much larger in alkali solutions than in acidic solutions.

Desorption of LS in acidic solutions was caused by the protonation of anionic groups of the LS. LS was removed from the multilayers because a few anion-cation bonds needed to be broken, owing to a weakening of electrostatic attraction. Desorption of LS in neutral and alkali solutions was caused by ionization of the anions of LS. Because of a weakening of hydrophobic interaction, the excess lignosulfonates were removed to keep a balance of anionic and cationic groups in the self-assembled films. The kinetics of desorption demonstrates that the desorption behavior of the LS self-assembled films in alkali solutions was a two-step process when the LS films were obtained from LS dipping solution at a pH 3, while the desorption behavior of LS under different conditions, as discussed above, was a one-step process. This two-step desorption process was related to a change of LS microstructure. LS exists as colloidal particles at pH 3, and the LS colloidal particles are transferred from solutions to solid films during the self-assembly process. When immersed into alkali solutions, some embedded LS colloids dissociate due to a weakening of hydrophobic interaction. The LS colloids in the dipping solutions started to dissociate at pH 3.5, however, once the LS colloids were adsorbed on the self-assembled multilayer films, the dissociation of LS colloids in the multilayers only occurred in the strong alkaline solution. It was the electrostatic interaction between PDAC and the anion groups at the outermost layer of LS colloids that prevented LS colloids from dissociation, and then, LS colloids in the multilayers were more difficult to dissociate than LS colloids in the solutions.

CONCLUSIONS

1. Lignosulfonate (LS) includes not only strong acidic groups (sulfonic groups), but also weak acidic groups (carboxylic and phenolic groups). The carboxylic groups of LS start to ionize at about pH 3.5, and the phenolic groups start to ionize at about pH 9. On the one hand, the larger adsorbed amount and higher surface roughness of LS on the self-assembled multilayers at a lower pH can be attributed to the lower ionization degree and more curled conformation of LS in the solutions. On the other hand, lignosulfonates exist as colloidal particles in the dipping solutions at low pH because of strong hydrophobic interaction, and the LS colloids with anionic groups as the outermost layer are adsorbed on the PDAC layer because of electrostatic attraction. LS colloids tend to disassociate at a pH 3.5, resulting in an abrupt rise of the adsorption rate, a sharp decrease of the adsorbed amount, and a steep reduction of the surface roughness.
2. Desorption behaviors of LS from the LS/PDAC multilayers was studied by immersing the LS/PDAC self-assembled multilayers into water with different pH values. The results indicated that desorption phenomena of LS are related to the pH values of both the LS dipping solution for self-assembly and the immersing solution for post-preparation treatment. Desorption of the LS self-assembly films in acidic solutions is caused by a weakening of electrostatic attraction, while desorption of LS

in neutral and alkali solutions is caused by a weakening of hydrophobic interaction. A significant desorption occurs only when LS colloidal film is immersed in a strongly alkaline solution, where some embedded LS colloids dissociate due to a decline of hydrophobic interaction. The electrostatic interaction between PDAC and LS colloids prevents LS colloids from dissociating, so LS colloids are harder to dissociate in the multilayers than in the solutions.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of the National Natural Science Foundation of China (20976064), the China Excellent Yong Scientist Fund (20925622), and Science and Technology Projects of Guangdong Province of China (2009B050600004).

REFERENCES CITED

- Adler, E. (1957). "Structural elements of lignin," *Ind. Eng. Chem.* 49 (9), 1377-1383.
- Bai, B. J., Wu, Y. F., and Grigg, R. B. (2009). "Adsorption and desorption kinetics and equilibrium of calcium lignosulfonate on dolomite porous med," *J. Phys. Chem. C.* 113(31), 13772-13779.
- Bolker, H. I., and Brenner, H. S. (1970). "Polymeric structure of spruce lignin," *Science* 170(3954) 173-176.
- Burnett, C. M., and Squire, R. A. (1986). "The effect of dietary administration of disperse blue-1 on the urinary system of the fischer-344 rat," *Food Chem. Toxicol.* 24(4), 269-276.
- Chiweteu, C. I., Hornof, V., Neale, G. H., and George, A. E. (1994). "Use of mixed surfactants to improve the transient interfacial tension behaviour of heavy oil/alkaline systems," *Can. J. Chem. Eng.* 72 (3), 534-540.
- Contreras, S., Gaspar, A. R., Guerra, A., Lucia, L. A., and Argyropoulos, D. S. (2008). "Propensity of lignin to associate: light scattering photometry study with native lignins," *Biomacromolecules* 9(12), 3362-3369.
- Decher, G., and Hong, J. D. (1991). "Buildup of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces," *Makromol. Chem. Macromol. Symp.* 46, 321-327
- Decher, G. (1997). "Fuzzy nanoassemblies: Toward layered polymeric multicomposites," *Science* 277(5330), 1232-1237.
- Dence, C. W. (1992). *Methods in Lignin Chemistry*, S. Y. Lin, and C. W. Dence (eds.), Springer-Verlag, Berlin. p.458-464.
- Dizhbite, T., Zakis, G., Kizim, A., Lazareva, E., Rossinskaya, G., Jurkjane, V., Telysheva, G., and Viesturs, U. (1999). "Lignin - A useful bioresource for the production of sorption-active materials," *Bioresource Technology* 67(3), 221-228.
- Fredheim, G. E., and Christensen, B. E. (2003). "Polyelectrolyte complexes: Interactions between lignosulfonate and chitosan," *Biomacromolecules* 4(2), 232-239.

- Freudenberg, K. (1965). "Lignin: Its constitution and formation from p-hydroxycinnamyl alcohols: Lignin is duplicated by dehydrogenation of these alcohols; intermediates explain formation and structure," *Science* 148(3670) 595-600.
- Goring, D. A. I. (1962). "The physical chemistry of lignin," *Pure Appl. Chem.* 5(1-2), 233-254.
- Grigg, R. B., and Bai, B. J. (2004). "Calcium lignosulfonate adsorption and desorption on Berea sandstone," *Journal of Colloid and Interface Science.* 279(1), 36-45.
- Guerra, A., Gaspar, A. R., Contreras, S., Lucia, L. A., Crestini, C., and Argyropoulos, D. S. (2007). "On the propensity of lignin to associate: A size exclusion chromatography study with lignin derivatives isolated from different plant species," *Phytochemistry.* 68(20), 2570-2583.
- Gundersen, S. A., Ese, M. H., and Sjoblom, J. (2001). "Langmuir surface and interface films of lignosulfonates and Kraft lignins in the presence of electrolyte and asphaltenes: Correlation to emulsion stability," *Colloids and Surfaces A - Physicochemical and Engineering Aspects* 182(1-3), 199-218
- Hammond, P. T. (1999). "Recent explorations in electrostatic multilayer thin film assembly," *Current Opinion in Colloid & Interface Science* 4(6), 430-442.
- Iler, R. K. (1966). "Multilayers of colloidal particles," *J. Colloid Interface Sci.* 21(6), 569-594.
- Li, Z. L., Pang, Y. X., Lou, H. M., and Qiu, X. Q. (2009). "Influence of lignosulfonates on the properties of dimethomorph water-dispersible granules," *BioResources* 4(2), 589-601.
- Liu, H., Fu, S. Y., Li, H., and Zhan, H. Y. (2009). "Layer-by-layer assembly of lignosulfonates for hydrophilic surface modification," *Industrial Crops and Products* 30(2), 287-291.
- Myrvold, B.O. (2007). "The polyelectrolyte behavior of randomly branched lignosulfonates," *Tappi Journal* 6(11), 10-14.
- Ouyang, X. P., Ke, L. X., Qiu, X. Q., Guo, Y. X., and Pang, Y. X. (2009) "Sulfonation of alkali lignin and its potential use in dispersant for cement," *Journal of Dispersion Science and Technology* 30(1), 1-6.
- Ouyang, X. P., Qiu, X. Q., Lou, H. M., and Yang, D. J. (2006). "Corrosion and scale inhibition properties of sodium lignosulfonate and its potential application in recirculating cooling water system," *Industrial & Engineering Chemistry Research* 45(16), 5716 -5721.
- Palmqvist, L., and Holmberg, K. (2008). "Dispersant adsorption and viscoelasticity of alumina suspensions measured by quartz crystal microbalance with dissipation monitoring and in situ dynamic rheology," *Langmuir* 24(18), 9989-9996.
- Paterno, L. G., and Mattoso, L. H. C. (2001). "Effect of pH on the preparation of self-assembled films of poly(o-ethoxyaniline) and sulfonated lignin," *Polymer* 42(12), 5239-5245.
- Qiu, X. Q., Yan, M. F., Yang, D. J., Pang, Y. X., and Deng, Y. H. (2009). "Effect of straight-chain alcohols on the physicochemical properties of calcium lignosulfonate," *Journal of Colloid and Interface Science.* 338(1), 151-155.

- Raposo, M., Pontes, R. S., Mattoso, L. H. C. and Oliveira, O. N. (1997). "Kinetics of adsorption of poly(o-methoxyaniline) self-assembled films," *Macromolecules* 30(20), 6095-6101
- Rencoret, J., Marques, G., Gurierez, A., Nieto, L., Jimenez-Barbero, J., Martinez, A.T., and del Rio, J. C. (2009). "Isolation and structural characterization of the milled-wood lignin from Paulownia fortunei wood," *Industrial Crops and Products* 30(1), 137-143.
- Telysheva, G., Dizhbite, T., Paegle, E., Shapatin, A., and Demidov, I. (2001). "Surface-active properties of hydrophobized derivatives of lignosulfonates: Effect of structure of organosilicon modifier," *J. Appl. Polym.Sci.* 82(4), 1013-1020.
- Vainio, U., Lauten, R. A., and Serimaa, R. (2008). "Small-angle X-ray scattering and rheological characterization of aqueous lignosulfonate solutions," *Langmuir* 24(15), 7735-7743.
- Wagberg, L., Forsberg, S., Johansson, A., and Juntti, P. (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: Modification of paper strength," *Journal of Pulp and Paper Science*. 28(7) 222-228.
- Yoo, D., Shiratori, S. S., and Rubner, M. F. (1998). "Controlling bilayer composition and surface wettability of sequentially adsorbed multilayers of weak polyelectrolytes," *Macromolecules* 31(13) 4309-4318.
- Zhang, X., Chen, H., and Zhang, H. Y. (2007). "Layer-by-layer assembly: From conventional to unconventional methods," *Chem. Commun.* 1395-1405.
- Zhou, M. S., Qiu, X. Q. Yang, D. J., Lou, H. M., and Ouyang, X. P. (2007). "High-performance dispersant of coal-water slurry synthesized from wheat straw alkali lignin," *Fuel Processing Technology* 88(4), 375-382.

Article submitted: January 23, 2010; Peer review completed: March 28, 2010; Revised version received: April 10, 2010; Further revisions and acceptance: April 16, 2010; Published: April 18, 2010.