

Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: the origin of sorption capacity improvement

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Abstract

Juniper (*Juniperus monosperma*), a small-diameter underutilized material, has been studied as a lignocellulosic biosorbent for removing heavy metals from water. In this study, juniper wood was modified by sulfonation to enhance sorption capacity for cadmium in water. The origin of the enhancement was investigated by observing the sorption behaviors and the change in surface functional group concentrations. Cadmium sorption by all juniper wood biosorbents studied was fast and the sorption capacity decreased with decreasing pH, similar to results found for other biosorbents. Sulfonated juniper was found to have at least twice the sorption capacity for cadmium removal from water compared to that of untreated juniper, though the sorption capacity increased with increasing pH. A slight increase in carboxylate content after sulfonation was likely responsible for a small portion of the enhancement. Elemental analysis showed an increase in sulfur content after sulfonation. Diffuse reflectance infrared Fourier transform (DRIFT) spectra showed a decrease in the band at 1660 cm^{-1} in the range of carbonyl groups as a result of sulfonation. This indicates that coniferaldehyde groups in the lignin of juniper wood corresponding to this band were substituted into sulfonic acid groups after sulfonation. This interpretation was supported by both the color forming reaction with phloroglucinol–hydrochloric acid and the reaction mechanisms from the acid sulfite pulping process. Consequently, the enhancement of cadmium sorption capacity of juniper wood by sulfonation mainly originated from the production of sulfonic acid groups, which are binding sites for heavy metals.

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1. Introduction

Water contaminated by heavy metals remains a serious environmental and public problem. Cadmium is a toxic heavy metal that not only causes choking, abdominal pain, anemia, renal dysfunction, and diarrhea, but

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also has been listed as a carcinogen by the Environmental Protection Agency (Gaballah and Kibertus, 1998). Diverse technologies have been used to reduce the contents of heavy metals in water, including chemical precipitation, ion exchange, activated carbon adsorption, separation by membrane, electrolytic process, and biological treatment (Gaballah and Kibertus, 1998). Recently, adsorption methods using biosorbents have been widely noticed because of their low cost. Bark, a by-product of the timber industry, has been introduced as a low-cost and effective biosorbent (Gaballah and Kibertus, 1998). Research has suggested that the active species that chelate heavy metals in water are the chemical structures of polysaccharide and polyphenolic compounds in bark (Vazquez et al., 1994; Gaballah and Kibertus, 1998; Bailey et al., 1999). Seaweed and algae were also applied to heavy metal biosorption (Fourest and Volesky, 1996; Romero-Gonzalez et al., 2001; Yun et al., 2001; Davis, Llanes, et al., 2003). In those biosorbents, uronic acids of alginate present in the outer cell wall of the brown algae are the main binding sites for heavy metals (Davis, Mucci, Volesky, 2003). In addition, peat moss (Crist et al., 1992, 1996; Ho and McKay, 2000), alfalfa (Tiemann et al., 1999), husk (Saeed and Iqbal, 2003), and sugar beet pulp (Reddad et al., 2002) have been identified as potential biosorbents for heavy metal removal.

Juniper (*Juniperus monosperma*) and modified juniper have been used as biosorbents for removal of heavy metals in lab-scale tests (Han, 1999; Min et al., 2004). Juniper is a small-diameter and underutilized forest material. More than 19 million hectares of land in the southwestern United States is covered with pinyon juniper woodland. Over the years, these trees have overgrown and dominated large areas of rangeland (Buckman and Wolters, 1986). In addition, abundance of these trees has led to a buildup of biomass that contributes to wildfire fuel loading (LeVan-Green and Livingston, 2001). Accordingly, it is desirable to produce value-added products such as biosorbents from juniper to find uses for this underutilized raw material resource and to reduce fuel loading.

Raw biosorbents have generally been modified with chemical treatments to increase their sorption capacity. Metal ion binding to lignocellulosic biosorbents is thought to occur through chemical functional groups, such as carboxyl, amino, or phenolic groups (Tiemann et al., 1999). Sodium hydroxide treatment has long been used in saponification to produce carboxylate sites that serve as the binding sites for heavy metals (Gardea-Torresdey et al., 1990; Tiemann et al., 1999; Min et al., 2004). Morita et al. (1987) used carbon disulfide and amidoximes to modify wood surfaces. Fourest and Volesky (1996) found that sulfonate groups in various types of biomass contribute to heavy metal binding. Even in polymer membranes used for removing heavy metals,

sulfonation has been employed to produce active sites for heavy metals (Choi et al., 2003). According to Sjöström (1993), sulfonation in acidic sulfite pulping can generate hydrophilic sulfonic groups as well as free phenolic groups. Therefore, when juniper wood is treated under a mild acidic sulfite pulping condition, its sorption capacity is expected to be improved as a result of the production of sulfonic sites that serve as new binding sites for cadmium ions.

In this study, we demonstrated, through sorption tests, that sulfonation enhances the cadmium ion sorption capacity of a lignocellulosic biosorbent. The origin of the enhancement of sorption capacity can be explained by the change in surface functional groups on the biosorbent caused by sulfonation.

2. Materials and methods

2.1. Materials

Juniper trees were randomly collected from New Mexico and shredded into small chips. Chips were separated from the bark and then ground to pass through a 3-mm screen using a Wiley mill. This untreated material is denoted UJW.

Sulfonation of juniper wood was carried out under an acidic condition as follows. 25.2 g of Na_2SO_3 (Aldrich Chemical Co., Milwaukee, WI) was dissolved in 300 ml of deionized (DI) water; 20 g of juniper wood was added to the solution and the pH was adjusted to 3.0 by adding 1.0 M HNO_3 . The solution was then stirred at 70 °C for 1 d. After reaction, sulfonated juniper wood was filtered, washed thoroughly with DI water, and dried overnight at 60 °C in an oven. The sulfonated juniper wood is denoted SJW. Other juniper wood was treated at pH 3.0 for 1 d at 70 °C with no sulfite addition (AJW). This material was prepared to evaluate the effect of the acidic condition in the sulfonation on sorption capacity and surface functional groups.

2.2. Elemental analysis and DRIFT spectroscopy

Elemental analysis of sulfur and cadmium was conducted with an inductively coupled plasma atomic emission spectrometer (ICP-AES, ULTIMA, Jobin Yvon Inc., Edison, NJ) in order to quantify the sorption capacity of sorbents and amount of sulfur loaded onto sorbents.

Diffuse reflectance Fourier transform infrared (DRIFT) spectra were collected with a Mattson Galaxy 5020 (Mattson Instruments, Madison, WI) fitted with a Harrick Scientific diffuse reflectance accessory (Harrick Scientific Co., Ossining, NY). Each spectrum was acquired through 4000 scans. The resolution of infrared spectra was 4 cm^{-1} . Prior to analysis, samples were

finely ground using a Wiley mill and sieved with a 0.18-mm screen. For comparison, each spectrum was baseline corrected at 400, 840, 2000, and 4000 cm^{-1} and normalized against the 1320 cm^{-1} band associated with the C–H bending mode (Yang et al., 1996).

2.3. Color forming reaction test

UJW (control), AJW, and SJW were reacted with a color-forming reagent to detect coniferaldehyde functional groups via a color-forming reaction (Lin-Vien et al., 1991). The reagent was prepared by mixing 50 ml of 0.5 g phlorocinol dihydride (Aldrich Chemical Co., Milwaukee, WI) in 95% ethanol and 25 ml of concentrated hydrochloric acid. The first images of each wood sample were taken before the reaction with the reagent. When the reagent was added dropwise to the wood samples, a reddish violet color appeared instantaneously. After 30 min, the second images of the wood samples were taken to compare the change in the color of the wood.

2.4. Sorption isotherms

Cadmium sorption isotherms were acquired through batch experiments. Wood samples weighing between 0.02 and 1.0 g were placed in 125-ml plastic bottles with 50 ml of 0.178 mmol l^{-1} -cadmium ion solution (C_0). The initial cadmium solution was prepared by serial dilution of standard 1000 mg l^{-1} reference solution (Fisher Scientific, Pittsburgh, PA). The initial pH of the solution was adjusted to 5.0 ± 0.1 . However, the pH of solution was not controlled during isotherm experiments, so that final pH of solution ranged in 4.6–5.0 for UJW and 4.4–4.8 for SJW, respectively. The sealed bottles were shaken at 150 rpm for 1 d at 25 °C. The supernatants of the solutions were filtered by 0.45- μm (pore size) membrane filters, and then measured for dissolved cadmium concentration by ICP–AES. The final concentration (C_f), measured in millimoles per liter, differed according to varying wood amount in the solutions. The uptake capacity (q_{max}), the amount of cadmium ions adsorbed at equilibrium (mmol g^{-1}), was calculated by mass balance between C_0 and C_f .

2.5. Sorption kinetics

Sorption kinetic experiments were performed in 1000-ml solutions with 2.0 g of wood samples at three different pH conditions (pH = 4, 5, and 6). The initial cadmium concentration of the solution was 0.178 mmol l^{-1} , and the pH of the solution was constantly maintained within ± 0.1 during the experiment using 0.1 M HNO_3 and 0.1 M NaOH . The suspension was stirred by a magnetic bar, and supernatants were taken at various times during the 2-h experiment. Cadmium

concentrations of the filtered solutions were measured with ICP–AES.

According to the correlation coefficients obtained on fitting of the experimental data, the pseudo-second-order model gave the best fit in comparison to the other tested kinetic models: pseudo-first-order, Elovich, and parabolic diffusion models. Therefore, the cadmium uptake (q_e) and rate constant (k) of sorption were determined from the pseudo-second-order rate equation (Ho and McKay, 2000). This model assumes that sorption follows the Langmuir equation.

The kinetic rate equations can be written as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1)$$

where q_t , and q_e are the amount of cadmium sorbed at time t and equilibrium (mmol g^{-1}), respectively, and k is the equilibrium rate constant of the second-order sorption (g (mmol min)^{-1}).

3. Results and discussion

3.1. Sorption kinetics and isotherms

Sorption kinetics conducted at pH 5 for cadmium removal are shown in Fig. 1. On the whole, sorption of cadmium ions onto the biosorbents was very fast, as the equilibrium state was reached within 60 min. These fast sorption kinetics are similar to the results obtained with other biosorbents (Ho and McKay, 2000; Reddad et al., 2002). However, cadmium ion sorption capacity (cadmium uptake) of sulfonated juniper wood (SJW) was much higher than that of untreated juniper wood (UJW), implying that sulfonation improved the sorption capacity of the wood. To quantitatively analyze sorption

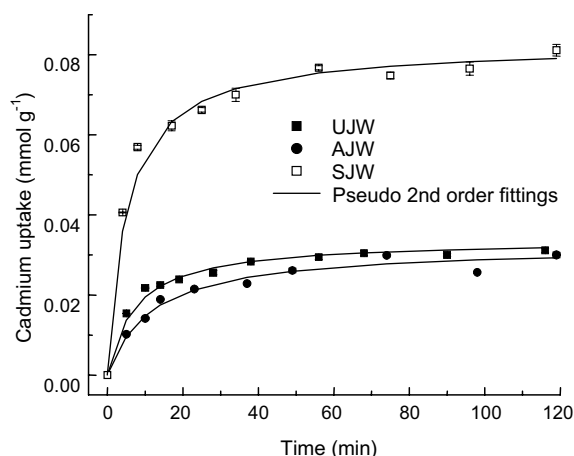


Fig. 1. Sorption kinetics of cadmium ion removal for sorbents and blank runs. Initial cadmium ion concentration = 0.178 mmol l^{-1} . Solution pH maintained at 5.0 ± 0.1 .

Table 1
Parameters from fits to the pseudo-second-order model

Sample	Parameter		
	R^2	q_e (mmol g ⁻¹)	k (g (mmol min) ⁻¹)
UJW	0.999	0.0325	5.04
AJW	0.979	0.0322	2.63
SJW	0.998	0.0825	2.34

capacity, the kinetic data were fitted to the pseudo-second-order model that has been widely used in the analysis of heavy metal removal by biosorbents (Ho and McKay, 2000; Reddad et al., 2002). Parameters acquired from the fits are presented in Table 1. The model was well represented by kinetic data with correlation coefficients of over 0.97. The model showed 0.0325, 0.0322, and 0.0825 mmol g⁻¹ of q_e (amount of cadmium sorbed onto sorbents at equilibrium) for UJW, AJW, and SJW, respectively. Since the q_e of AJW was almost the same as that of UJW, acid treatment had little effect on the sorption capacity of juniper wood. Likewise, the acidic conditions of sulfonation probably had little effect on the sorption capacity of SJW. From Table 1, the ratio of q_e (SJW) to q_e (UJW) was 2.54, which implies that sulfonation enhanced the sorption capacity of the biosorbent by 2.54 times.

Fig. 2 shows the q_e acquired from the fits to kinetic tests conducted at different pH conditions. By and large, sorption capacity of both samples for cadmium ions were decreased with lower solution pH, which is consistent with results found by others (Romero-Gonzalez et al., 2001; Yun et al., 2001). However, it is interesting that the sorption capacity of SJW at pH 4 was still high (0.0649 mmol g⁻¹), whereas that of UJW at pH 4 fell to 0.00978 mmol g⁻¹. In other words, the sorption performance of SJW was still excellent even at low pH.

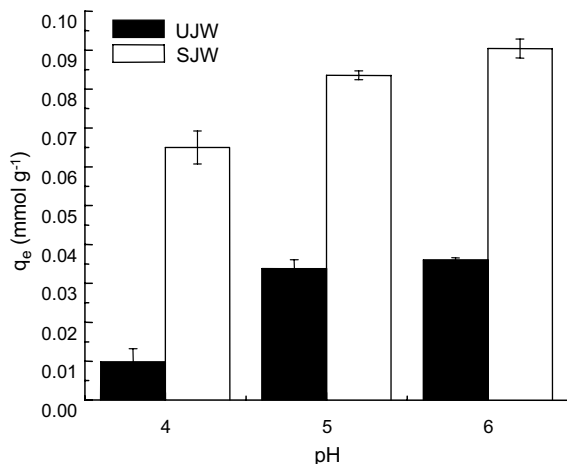


Fig. 2. q_e values of UJW and SJW acquired from fits to kinetic tests conducted at different pH conditions.

Removal of heavy metals using seaweed biomass showed that (1) two types of binding sites in the biomass—carboxyl and sulfonate groups contribute to heavy metal removal and (2) contribution of a strong acidic sulfonate group to heavy metal binding is increased at low pH, while a weak acidic group such as carboxyl groups is dominant at neutral pH in the heavy metal uptake (Schiewer and Volesky, 1995; Fourest and Volesky, 1996). Therefore, the reason why the sorption capacity of SJW was outstanding even at low pH may be the continued activation of the sulfonic acid group at pH 4 and the weak contribution of carboxyl group to metal binding.

Sorption isotherms are shown in Fig. 3. As Fig. 3 clearly shows, sorption capacity of SJW was much higher than that of UJW, as is the case of the sorption kinetics shown in Fig. 1. The fitting of the isotherms to the Langmuir equation and the Freundlich equation resulted in low correlation coefficients, which may be due to different final solution pH in isotherm data. Because of this, quantitative comparison of the sorption capacity of both samples was conducted based on the cadmium uptake at 0.08 mmol g⁻¹ of final concentration. Cadmium uptake at 0.080 mmol l⁻¹ was about 0.025 mmol g⁻¹ and 0.15 mmol g⁻¹ for UJW and SJW, respectively. The sorption capacity of SJW was more than six times higher than that of UJW.

In the sorption kinetics and isotherms, the results show that the chemical treatment (sulfonation) improved the sorption capacity of juniper wood, a lignocellulosic biosorbent, by more than a factor of two. Sulfonation should change properties of juniper wood such as surface functional groups and chemical composition. The change in surface properties of the sorbents

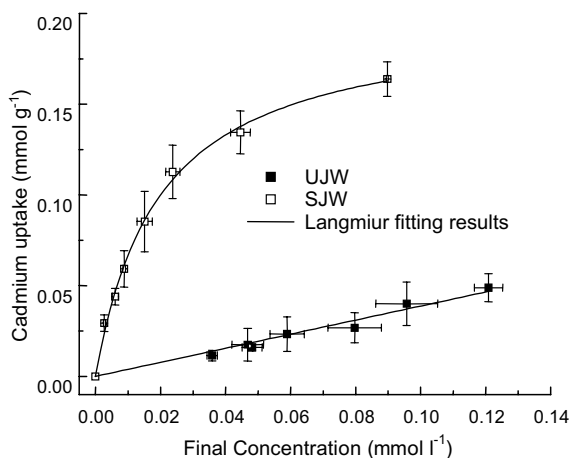


Fig. 3. Sorption isotherms of cadmium ion removal for UJW and SJW. Initial cadmium ion concentration = 0.178 mmol l⁻¹. Initial solution pH = 5.0 ± 0.1. The final solution pH ranged in 4.6–5.0 for UJW and 4.4–4.8 for SJW respectively.

by sulfonation accounts for the improvement in cadmium uptake.

3.2. Elemental analysis and chemical composition

Sulfur contents of each solid sample were analyzed by means of ICP–AES. Samples taken before sulfonation (UJW and AJW) contained 0.0047 and 0.0034 mmol g⁻¹ of sulfur, respectively. In contrast, the sulfur content of the sulfonated solid sample (SJW) increased to 0.240 mmol g⁻¹, which implies that the sulfur component was well impregnated into the juniper wood.

The chemical composition of UJW, AJW, and SJW was analyzed according to standard methods (Davis, 1998). As a result, UJW contained 38% lignin and 33% cellulose with a yield of 89%. The composition of acid-treated juniper wood (AJW) remained similar to that of UJW. However, after sulfonation, the percentage of total carbohydrate increased slightly because lignin content decreased as a result of the mild sulfite pulping condition.

3.3. DRIFT spectra

DRIFT spectra of the solid samples are shown in Fig. 4. The characteristic IR bands for wood materials can be divided into four regions: the broad hydroxyl bands (3200–3600 cm⁻¹), the stretching bands of CH₂ and CH₃ (2800–3000 cm⁻¹), the stretching bands of carbonyl groups (1550–1750 cm⁻¹), and the fingerprint region (below 1550 cm⁻¹) in which the assignment of IR peaks is not clear because of the complex interaction of their vibration systems. In this study, the characteristic IR bands of the sulfonic group occurred in the fingerprint region and the IR pattern of carbonyl group was greatly

changed by sulfonation (arrows in Fig. 4). The characteristic bands of sulfonic group usually appear around 1150–1190 cm⁻¹ and 1300–1390 cm⁻¹ for symmetric stretching and asymmetric stretching modes, respectively (Lin-Vien et al., 1991; Choi et al., 2003). Unfortunately, because those regions were superimposed on the fingerprint region, it was difficult to find meaningful change in this region. In contrast, IR bands in the region of carbonyl groups changed dramatically after sulfonation. Fig. 5 shows the detailed IR spectra between 1450 and 1850 cm⁻¹ where several IR bands of carbonyl groups appeared. Assignments of each of the IR bands in 1550–1850 cm⁻¹ are listed in Table 2. The IR bands around 1600 cm⁻¹ were composed of the aromatic ring stretching (1592 cm⁻¹) and the antisymmetric stretching frequency of the carboxylate functional groups (–COO–, 1605 cm⁻¹) (Chatjigakis et al., 1998; Francioso et al., 1998; Pappas et al., 1999; Zhang and Kamdem, 2000; Brown et al., 2001; Chapman et al., 2001). The bands were barely changed by acid treatment except for a small increase in the band of the antisymmetric stretching of carboxylate after sulfonation. The IR bands around 1740 cm⁻¹ originated from the carbonyl groups of esters (Chatjigakis et al., 1998; Pappas et al., 1999; Brown et al., 2001; Min et al., 2004). The bands were little changed by acid treatment, but sulfonation lowered the intensity of the carbonyl group of esters. These two IR bands are well identified in saponification or esterification (Chatjigakis et al., 1998; Min et al., 2004). Base treatment changes the carbonyl groups of esters into carboxylate groups. Accordingly, part of the carbonyl group of esters was converted to carboxylate during sulfonation. The most interesting observation in Fig. 5 appears around 1660 cm⁻¹. Whereas acid treatment did not affect the functional groups in this range,

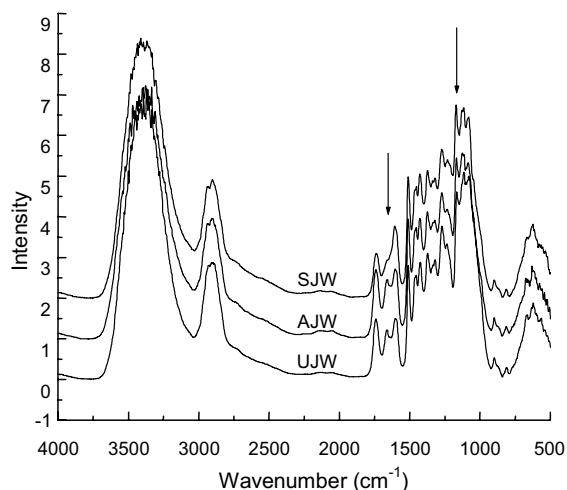


Fig. 4. DRIFT spectra for UJW, AJW, and SJW.

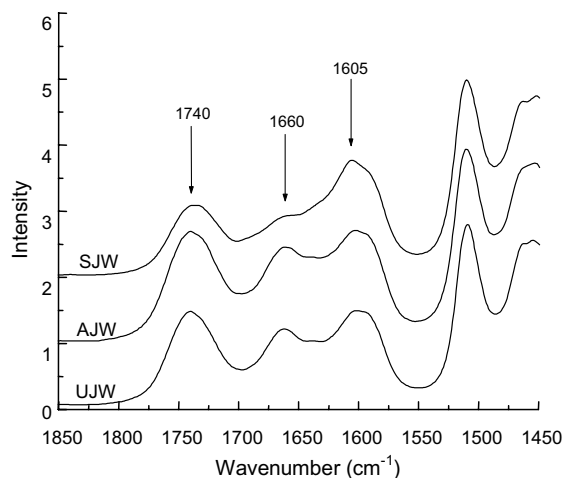


Fig. 5. DRIFT spectra between 1450 and 1850 cm⁻¹ for UJW, AJW, and SJW.

Table 2
Assignments of IR bands in range of 1550 and 1800 cm^{-1}

Frequency (cm^{-1})	Assignment
1592	Aromatic ring stretching
1605	Antisymmetric stretching of carboxylates ($-\text{COO}^-$)
1630	Water bending
1660	$\text{C}=\text{O}$ stretching of coniferyl aldehyde groups or aryl ketones
1734	$\text{C}=\text{O}$ stretching of aromatic esters
1744	$\text{C}=\text{O}$ stretching of alkyl esters

sulfonation decreased the intensity of the band dramatically. The IR band decrease is associated with carbonyl stretching of either coniferaldehydes or aryl ketones (Sarkanen and Ludwig, 1971; Pappas et al., 1999; Zhang and Kamdem, 2000). It is difficult to determine whether the IR bands originate from aryl ketones or coniferaldehydes. Therefore, it is hard to determine, from IR results alone, which surface functional groups are responsible for the remarkable decrease of the IR band after sulfonation.

3.4. Color forming reaction

With DRIFT spectra, sulfonation reduced the intensity of the band at 1660 cm^{-1} that can be assigned to either aryl ketones or coniferaldehydes. To determine which of those groups was the origin of the band reduced by sulfonation, we used a colorimetric method to distinguish coniferaldehydes from aryl ketones. Coniferaldehydes produce a strong coloration with phloroglucinol-hydrochloric acid reagent through the reaction shown in Fig. 6 (Lin and Dence, 1992), whereas aryl ketones do not. The color of samples turns purple by the reaction. The change of the color is proportional to the amount of coniferaldehyde groups.

Before the reaction, all of these samples were the same yellowish color. After the reaction, UJW and AJW turned dark purple. In contrast, SJW became bright purple. The color of SJW was less intense than that of the other samples, indicating the smaller amount

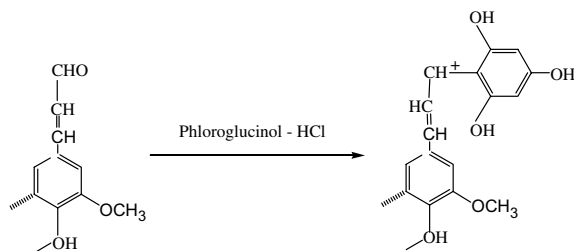


Fig. 6. Color forming reaction between coniferaldehyde and phloroglucinol hydrochloric acid (Lin and Dence, 1992).

of coniferaldehyde in SJW after sulfonation. Therefore, the reduction of the IR band at 1660 cm^{-1} for SJW is ascribed to the disappearance of the coniferaldehyde group through sulfonation. Peng and Westermarck (1997) used the same technique to determine the morphological distribution of coniferaldehyde group in the cell wall of spruce wood fiber. They found that preferential sulfonation in a certain region of spruce wood fiber coincides with the high concentration of coniferaldehyde group at that region. Consequently, the evidence indicates that sulfonic acid groups are introduced into juniper wood by the reaction with coniferaldehyde group during the chemical treatment.

3.5. Production of heavy metal binding sites

The carboxyl groups in biosorbents were proven to be directly responsible for heavy metal sorption onto biosorbents (Fourest and Volesky, 1996; Romero-Gonzalez et al., 2001; Yun et al., 2001; Min et al., 2004). Hydrolysis with sodium hydroxide increased the sorption capacity of biosorbents, whereas esterification in biosorbents decreased their removal ability because of the loss of surface carboxyl groups (Tiemann et al., 1999; Min et al., 2004). Phenolic groups are believed to be accountable for the formation of complexes with heavy metals (Gaballah and Kibertus, 1998; Bailey et al., 1999). Sulfonic acid groups also are binding sites for heavy metals (Schiewer and Volesky, 1995; Fourest and Volesky, 1996).

Sulfonation was conducted in a milder extent compared to acid sulfite pulping (Peng and Westermarck, 1997). Nevertheless, the mild condition of sulfonation can also produce the reactions occurring in acid sulfite pulping. Two basic reactions occur in acid sulfite pulping, sulfonation and hydrolysis. Hydrophilic sulfonic acid groups in the hydrophobic lignin polymer are generated by sulfonation, whereas breakage of ether bonds between the phenylpropane units through hydrolysis creates free phenolic hydroxyl groups (Sjöström, 1993). Katz et al. (1984) determined the contents of sulfonic and carboxylic acid groups on sulfonated wood pulp. More than 120 mmol kg^{-1} of sulfonic acid group and more than 90 mmol kg^{-1} of carboxylic acid group were detected on the sulfonated wood pulps, though the amounts of acidic sites produced by sulfonation depended on the condition of the treatment.

The change in the juniper wood surface by sulfonation can be explained from the mechanisms proposed for acid sulfite pulping. Gellerstedt (1976) suggested the reaction mechanisms that occur in lignin during acid sulfite pulping. Fig. 7 shows the mechanism of sulfonation of coniferaldehyde end group and β -substituted structures containing α -carbonyl groups (ketones) during acid sulfite pulping (Sjöström, 1993). In the reaction mechanism for the structure containing a ketone

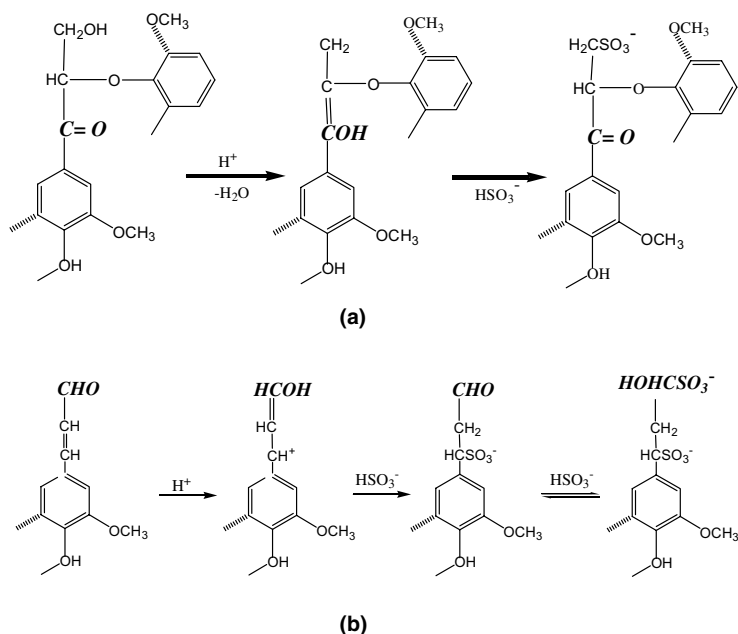


Fig. 7. Sulfonation of substituted structures containing α -carbonyl groups (a) and coniferaldehyde end groups (b) (Gellerstedt, 1976).

(Fig. 7a), the carbonyl group remains in the ketone form even after sulfonation. Instead, an alcohol functional group is substituted with a sulfonic group. In short, the ketone functional group is not modified during the sulfonation process. In contrast, in Fig. 7b, an aldehyde end group is changed into a sulfonic group after sulfonation, indicating the disappearance of aldehyde groups. Even at low temperature, coniferaldehyde end groups can bind sulfur dioxide as a result of the formation of α -hydroxysulfonic acid (Sjöström, 1993). Therefore, the decrease in the IR band around 1660 cm^{-1} is due to the sulfonation of the aldehyde end groups in the lignin of juniper wood.

In summary, sulfonic acid groups can be produced by the reaction with coniferaldehyde groups by the mechanism depicted in Fig. 7b. Despite a lack of direct evidence for the existence of the sulfonic acid sites in SJW, all the data discussed in this work indicate that such sites were produced by the sulfonation of the coniferaldehyde groups. Additionally, the concentration of carboxylate groups can be increased. The slight increase in the height of the band at 1605 cm^{-1} indicates the production of new carboxylate groups that are well-known binding sites for heavy metals.

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