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## **Abstract:**

### **Enhancement of Cadmium ion Sorption Capacity of Lignocellulosic Bio-sorbent by Sulfonation**

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## **Introduction**

Water contaminated by heavy metals remains a serious environmental and public health problem. Cadmium is a toxic heavy metal that not only causes choking, abdominal pain, anemia, renal dysfunction, and diarrhea, but also has been listed as a carcinogen by the EPA (Gaballah and Kibertus, 1998). Among current technologies used to reduce the amount of heavy metals in water, applications and studies of adsorption method with bio-sorbents have been expanded because of their low cost. (Gaballah and Kibertus 1998; Reddad et al., 2002).

Pinyon juniper and modified pinyon juniper have been used as sorbents for removal of heavy metal (Min et al., 2002). In general, raw lignocellulosic bio-sorbents were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic bio-sorbents is believed to take place through chemical functional groups such as carboxyl, amino, or phenolics. In this study, sulfonic sites were introduced into juniper wood as new binding sites for cadmium ions. Accordingly, the objectives of this study are 1) to assure that sulfonation enhances the cadmium ion sorption capacity of lignocellulosic bio-sorbents using sorption tests, and 2) to reasonably explain the improvement of sorption capacity by sulfonation by observing changes in functional groups on the surfaces of the sorbents.

## **Experimental studies**

Materials: Pinyon juniper trees were randomly collected from New Mexico, and shredded into small chips. Wood chips were separated from bark and then ground to pass through a 3-mm screen using a Wiley mill. This material was denoted JWP. Sulfonation of JWP was conducted under mild conditions as follows. 25.2 g of Na<sub>2</sub>SO<sub>3</sub> was dissolved into 200 mL of DI water. 20 g of JWP was added to the solution and the pH of

the solution was adjusted to 3 by adding 1M HNO<sub>3</sub> solution. The solution was stirred at 80 C for 1 day. After reaction, sulfonated juniper wood powder, denoted SJWP, was filtered, washed several times with DI water, and finally dried overnight at 60 C in an oven.

**DRIFT spectroscopy:** The 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).

**Sorption tests:** For both samples, adsorption kinetics experiments were performed in 1000 mL solution volume with 2.0 g of wood powder. The initial cadmium ion concentration of the solution was 20 mg/L. The pH of the solution was maintained at 5.0 using 1M HNO<sub>3</sub> and 1M NaOH solutions.

## Results and Discussion

In adsorption kinetics tests, the sorption capacity of SJWP was higher than that of JWP. To compare their sorption capacities quantitatively, a pseudo second order model was employed and the curve fitting results are presented in Table 1. Kinetic test results were well described by this model with correlation coefficients of over 0.996. The model showed 3.80 and 9.39 mg/g of q<sub>e</sub> (cadmium amount sorbed onto sorbents at equilibrium) for JWP and SJWP, respectively. The ratio of q<sub>e</sub> (SJWP) to q<sub>e</sub> (JWP) was 2.47, which implies that sorption capacity of the sorbent increased by 2.47 times after sulfonation.

Infrared spectra of both samples are shown in Figure 2. The characteristic IR bands can be divided into four regions: the broad hydroxyl bands (3200 - 3600 cm<sup>-1</sup>), the stretching bands of CH<sub>2</sub> and CH<sub>3</sub> (2800 - 3000 cm<sup>-1</sup>), the stretching bands of carbonyl groups (1600 - 1750 cm<sup>-1</sup>), and the fingerprint bands (below 1550 cm<sup>-1</sup>) in which the assignment of IR peaks is not clear because of their complexly interacting vibration systems. Unfortunately, since the characteristic IR bands of sulfonic groups (1163 and 1369 cm<sup>-1</sup>) are superimposed on the fingerprint bands, it is hard to show conclusively the increase of sulfonic groups on SJWP. In contrast, IR bands in the region of carbonyl groups changed remarkably after sulfonation, differing from IR bands of other regions. After sulfonation, the band at 1,738 cm<sup>-1</sup> and the band at 1664 cm<sup>-1</sup> decreased, while the band at 1602 cm<sup>-1</sup> increased slightly. Those IR bands are ascribed to carboxylic groups (1738 cm<sup>-1</sup>), aldehyde groups (1664 cm<sup>-1</sup>) and carboxylate (1602 cm<sup>-1</sup>), respectively. According to Gellerstedt (1976), aldehyde end groups in lignin are easily sulfonated during sulfite pulping. Therefore, the decrease in IR bands of aldehyde groups might be caused by sulfonation of the aldehyde groups in juniper wood. It is believed that the production of sulfonic groups on juniper wood enhanced the cadmium ion sorption capacity of JWP because sulfonic groups are negatively charged.

## Conclusions

Juniper wood powder (JWP), a lignocellulosic bio-sorbent, was modified by sulfonation to increase the sorption capacity for cadmium ion removal from water. In the sorption tests, sulfonated JWP showed 2.47 times higher sorption capacity for cadmium ions removal than did JWP. Based on infrared analysis, the enhancement of sorption capacity by sulfonation might be attributed to the production of sulfonic groups and the increase of carboxylate groups on juniper wood during the sulfonation process.

## References

- Gaballah, I., and G. Kibertus, "Recovery of Heavy Metal Ions through Decontamination of Synthetic Solutions and Industrial Effluents Using Modified Barks." *Journal of Geochemical Exploration*, 62, 241 (1998).
- Gellerstedt, G. "The Reactions of Lignin during Sulfite Pulping." *Svensk Papperstidn*, 79,537 (1976).
- Min, S. H., J. S. Han, E. W. Shin, and J. K. Park, "Improvement of Cadmium Ion Removal by Base Treatment of Juniper Fiber." submitted to *Water Research* (2002)
- Reddad, Z., C. Gerente, Y. Andres, and P. Cloirec, P. "Adsorption of Several Metal Ions onto a Low-cost Biosorbent: Kinetic and Equilibrium Studies." *Environmental Science and Technology*, 36(9), 2067 (2002).

Table 1. Parameters from the fit of sorption kinetics results to a pseudo second order equation<sup>a</sup>

Samples	R2	qe (mg/g)	k (g/mg/min)
JWP	0.996	3.80	0.0358
SJWP	0.999	9.39	0.0485

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$
 a;  $k$  is the equilibrium rate constant of the second order sorption and  $q_e$  is amount adsorbed at equilibrium.

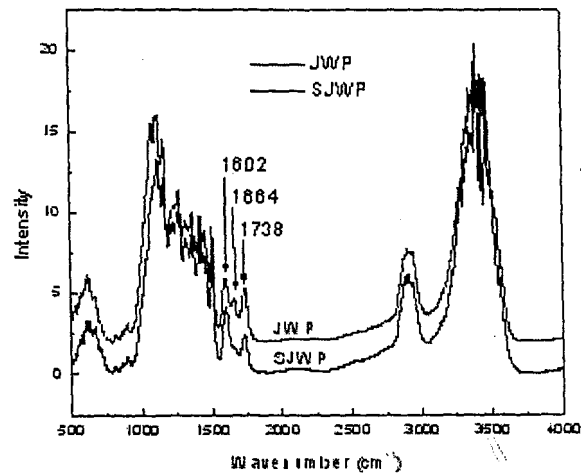
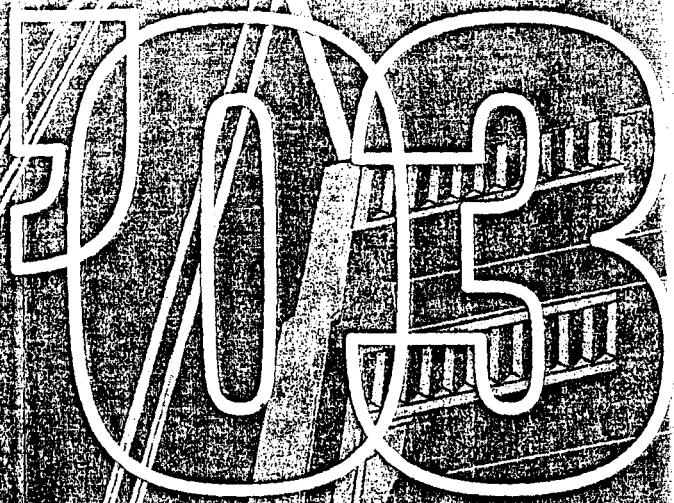


Figure 2. Infrared spectra of both sorbents.



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