# Enhancing Lead Adsorption Capacity by Controlling the Chain Length of Alkyl Amine Grafted Lignin

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The adsorption capacity of lignin for lead can be controlled by varying the chain length of alkyl, attaching the amine to the lignin surface from C2 (ethyl) to C18 (octadecyl). Altering the chain length had a strong effect on the contribution of amine groups in the adsorption of lead ions by lignin. The adsorption capacity increased 105.0% as the chain length increased to butyl (C4); however, further chain lengths, up to C18, provided no additional benefit, and in some cases even hindered the adsorption capacity of lignin. A short-chain alkyl (C4) group enhanced the beneficial amine contributions for metal ion adsorption, which resulted from the efficient inductive effectiveness of the alkyl groups.

*Keywords: Adsorption; Alkyl group; Amine; Lignin; Heavy metal*

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## INTRODUCTION

Over the last few decades, there has been a significant increase in the accumulation of toxic heavy metals, including lead, cadmium, copper, and chromium, in the environment (Rascio and Navari-Izzo 2011; Fox *et al.* 2012). Heavy metals are potentially dangerous to both humans and the environment, as they are non-degradable, recirculating, and often accumulate in the environment (Sljukic *et al.* 2006). Adsorption is generally the preferred method for the removal of metallic ions because of its high efficiency, ease of handling, and the availability of a wide range of adsorbents, such as active carbon, zeolite, silica, and various biomasses (Rivera-Utrilla *et al.* 2011; Ge *et al.* 2014b; Ammar *et al.* 2014).

In recent years, lignin has drawn a significant amount of attention for its capability in removing heavy metals from aqueous media (Adebayo *et al.* 2014; Ge *et al.* 2014b; Li *et al.* 2015). There are many outstanding aspects of lignin; for instance, lignin is produced by delignification from plants, and, after cellulose, it is the most abundant biopolymer (Gosselink *et al.* 2004). Additionally, due to its origin as an essential component in the external protective structure of living systems, lignin shows excellent biodegradability and biocompatibility. Finally, lignin is a suitable polymer for the collection of heavy metal ions since the methoxy, aldehyde, keto, hydroxyl, and phenolic groups on the lignin chain can interact with heavy metal ions (Sciban *et al.* 2011). However, lignin is a 3-dimensional, non-linear polymer, and it is composed of easily formed intermolecular hydrogen bonds, which make it unable to uncoil in a solution and wrap around large particles to form large stable flocks. As a result, lignin exhibits fairly low adsorption capacity towards metallic ions (Demirbas 2004; Harmita *et al.* 2009; Sciban *et al.* 2011). Thus, modifying lignin to improve its adsorption capacity towards metallic ions may be beneficial. Amines are known to be very selective in regards to retaining metallic ions from an aqueous media, due to the strong chemical bonds formed in the chemisorption process (Perez-Quintanilla *et al.* 2006; Aguado *et al.* 2009). It has been reported that the adsorption capacity of lignin for heavy metals can be improved *via* amine functionalization onto the lignin surface (Dalimova 2006; Ge *et al.* 2014a).

However, research about the coordination of alkyl chain length on amine-functionalized lignin regarding heavy metals retention has not been forthcoming. Therefore in this work, the cooperative effect of alkyl chain and amine groups was investigated by systematically varying the alkyl chain length of the alkyl amine grafted onto alkaline lignin. The importance of amine-alkyl interactions during lead retention was also demonstrated, and structure-function trends for the adsorptions were elucidated.

## EXPERIMENTAL

### Materials

Alkaline lignin (AL) was obtained *via* precipitation from black liquor (Nanpu Pulp Mill, China) with $H_2SO_4$ at a pH level of 2.0 (Ge *et al.* 2014b). Ethylamine (C2), n-butylamine (C4), hexylamine (C6), dodecylamine (C12), and octadecylamine (C18) were purchased from Aladdin Industrial Corporation, Shanghai, China. All other chemicals, including $Pb(NO_3)_2$, NaOH, and formaldehyde, were of analytical reagent grade.

### Methods

*Synthesis of alkyl amine grafted lignin (AGL)*

The introduction of nitrogen-containing groups can be achieved by the Mannich reaction, which takes place between a compound that has reactive hydrogen atoms, such as phenol, lignin, with formaldehyde and a primary or secondary amine (Fig. 1). In a typical experiment, 20.0 g AL and 100 mL distilled water were poured into a flask equipped with an electric heating device, a motor stirrer, a thermometer, a dropping funnel, and a reflux condenser. The temperature was elevated to 50 °C, and the pH was adjusted to between 8 and 13 by NaOH. Secondly, different alkyl amines (0.11 mol) were added and the temperature was carefully elevated to 90 °C. Then, formaldehyde (0.15 mol) was added dropwise into the flask, and the reaction conditions were maintained for 6 h. After that, the mixture was precipitated by adding 0.1 M HCl to a pH level of 2.0. The residue was filtered and washed with distilled water to pH 6.8. Finally, the powders were ground after overnight drying under a vacuum at 65 °C. The products were denoted as AGL-C2, AGL-C4, AGL-C6, AGL-C12, and AGL-C18, respectively.

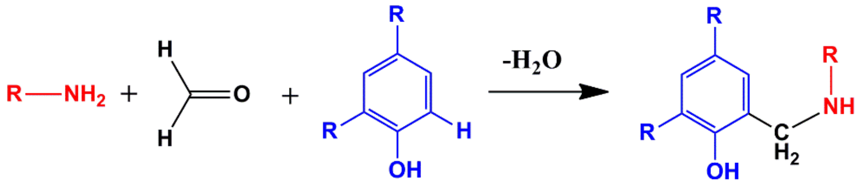

**Fig. 1.** Synthesis diagram of alkyl amine grafted lignin

### *Characterizations*

The samples were characterized using Fourier transform infrared (FT-IR) spectroscopy and element analysis (EA). The FT-IR spectroscopy was recorded on a FT-IR spectrophotometer (Thermo Nicolet 510, USA) using the KBr disk method. Elemental analysis (C, H, N, and S) was performed on a PE 2400 II (Perkin-Elmer, USA).

### *Adsorption experiment*

The batch adsorption lead ion test was conducted as follows. Using one set of sealed flasks, 0.02 g adsorbent was added into 50 mL of solution with different lead ion concentrations. The mixtures in the flasks were stirred to guarantee good adsorbent dispersion, and placed in a water bath at 25 ±1 °C for 24 h to allow for complete equilibration. The initial and residual ion concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, Perkin-Elmer). The adsorption capacity ($q$, mg/g) could be calculated as the difference between the initial and final metal concentrations in the solution.

# RESULTS AND DISCUSSION

## Characterization

The purpose of the FT-IR analysis was to find evidence of amines being grafted onto the lignin. Figure 2 showed the distinct absorption bands of the lignin and amino groups. In the figure, the broad bands at 3420 to 3470 cm$^{-1}$ could be attributed to the -OH or -NH stretching mode. The bands at 2850 and 2920 cm$^{-1}$ were mainly attributed to the C-H stretching of the methyl and methylene groups. Furthermore, the intensities were increased as the alkyl length increased to C12 and C18, as shown in Fig. 2 curves (e) and (f), respectively.

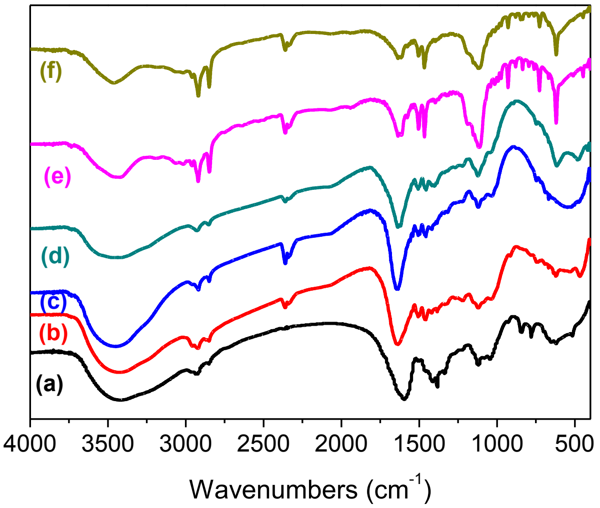

**Fig. 2.** FT-IR spectra of (a) alkaline lignin, (b) AGL-C2, (c) AGL-C4, (d) AGL-C6, (e) AGL-C12, and (f) AGL-C18

The bands at 1600 cm$^{-1}$, which contributed to the aromatic skeletal vibrations, indicated the aromatic structures of the lignin matrix (Hergert 1971). The bands at 1460 cm$^{-1}$, assigned to the C-N stretching mode of amino groups (Ge *et al.* 2014a), were distinctly observed in Fig. 2 curves (b) ~ (f), confirming the successful introduction of amine groups into the lignin matrix. The bands at 1120 cm$^{-1}$ were due to the C-H in-plane deformations, which were also enhanced after the grafting of long alkyl amines. The aromatic C-H deformation can be found at 850 cm$^{-1}$ (Ge *et al.* 2013). These results signify that the amines were successfully grafted onto the lignin.

The elemental contents of lignin grafted with different alkyl amines were also determined. The results were tabulated in Table 1, which includes the contents of nitrogen, carbon, hydrogen, and sulfur. The results indicated an increase in the percentage of nitrogen and carbon, which denotes the coupling of alkyl amines onto the surface of the lignin. The increase in the percentage of nitrogen can be attributed to the incorporation of the alkyl amines, which also explained the carbon content increase from 52.23% to 65.88%. As the alkyl chain length increases, the carbon content of the alkyl amine also increases as the nitrogen content decreases. Additionally, a small decrease in the nitrogen content in the AGLs was found, as expected.

**Table 1.** Elemental Analysis Results of the AGLs

| Materials | Element contents (%) | | | |
|---|---|---|---|---|
| | C | H | N | S |
| Alkaline lignin | 53.21 | 5.02 | 0.11 | 0.44 |
| AGL-C2 | 53.23 | 6.38 | 4.12 | 0.31 |
| AGL-C4 | 55.62 | 6.98 | 3.81 | 0.28 |
| AGL-C6 | 57.70 | 7.37 | 3.55 | 0.23 |
| AGL-C12 | 62.51 | 8.64 | 2.93 | 0.19 |
| AGL-C18 | 65.88 | 9.46 | 2.50 | 0.12 |

### *Adsorption performance*

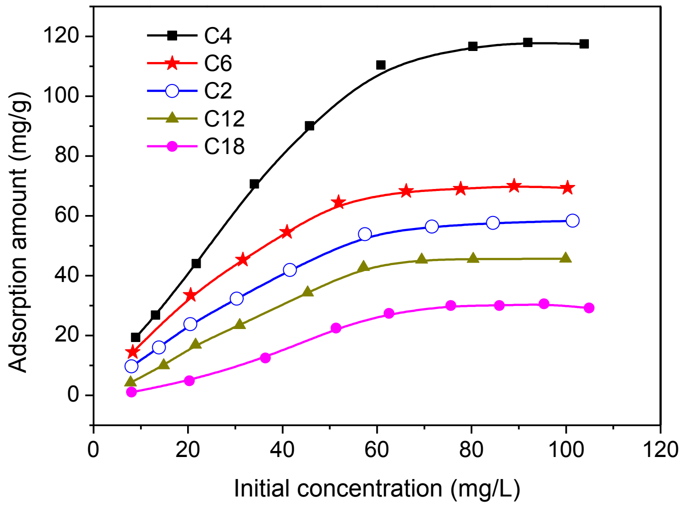

**Fig. 3.** Adsorption capacity of lead ions by AGLs having different chain length

The adsorption capacities of AGLs for lead ions are shown in Fig. 3. As can be seen, the higher the concentration of lead ions, the more lead ions were taken up for all the AGLs. Besides, the sharp increase in the adsorption capacity was observed at low concentrations, which can be attributed to the excessive active sites and the strong chelating force between AGL and lead ions for the mass transfer. As the lead ions concentration increased, more lead ions could be adsorbed onto the surface of the AGL, which caused biopolymer shrinkage, therefore lessening the increase in the adsorption amount (Pehlivan and Altun 2006). Additionally, the adsorption experiment data indicated that an increase in saturated adsorption capacity from 57.5 to 117.9 mg/g can be achieved by grafting alkyl amines onto lignin as the chain length increased from C2 to C4, which was an effective 105.0% increase in the adsorption capacity. However, further increased chain lengths were less effective in increasing the adsorption capacity, and even caused a decrease in the adsorption capacity. As a result, as the chain length increased from C6 to C18, the adsorption capacity decreased from 70.1 mg/g to 30.6 mg/g.

To elucidate the effect of the alkyl chain lengths on the adsorption efficiency towards lead ions, the adsorption capacities were calculated based on the nitrogen contents of the AGLs. The results are shown in Fig. 4, as expected, with the chain length increased from C2 to C4, the adsorption capacity sharply increased from 0.048 mmol/mmol N to 0.11 mmol/mmol N, indicating that the alkyl significantly contributed to the adsorption of lead ions. The increase can be explained by the inductive effect of the alkyl groups, which are electron-releasing groups that tend to give electrons (Huheey 1971; Tandon *et al.* 2013). After attaching the alkyl groups onto the amines, the overall electron density on the cluster increased, enabling the cluster to donate electrons for binding with lead ions, improving the adsorption of acidic heavy metal ions.

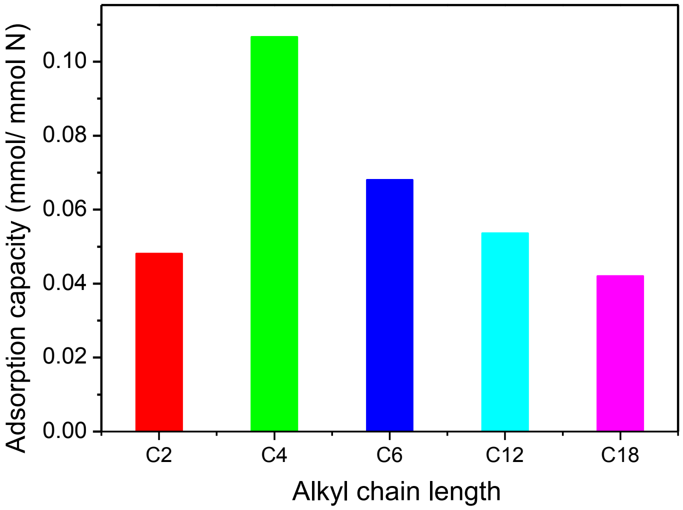

**Fig. 4.** Adsorption capacities for lead ions by AGLs, with different chain lengths

On the other hand, no further increase in the adsorption efficiency was observed with the additional increase in chain length to C6, C12, or C18. If the cooperation between the amines and alkyl was the dominant adsorption mechanism, an increase in the adsorption capacity would be expected with an increase in chain length. The fact that such an expectation was not realized suggests that some other reasons exist to account for the subsequent decease in adsorption capacity with chain length increasing beyond four. The strength of the inductive effect is also affected by the steric inhibition between the substituent group and the main group; the general rule is, the greater the steric inhibition, the weaker the effect (Benkeser *et al.* 1958; Schleyer and Woodworth 1968). As the chain length increased from C6 to C12 or C18, the electron-donating effect was weakened by the steric inhibition, and the basicity decreased as well. Thus, the reaction between amines and the acidic heavy metal ions was weak. Therefore, according to the experiment results, choosing the chain length of the alkyl amines presents a credible alternative for enhancing the adsorption capacity of lignin sorbents for heavy metals.

## CONCLUSIONS

1. Varying the chain length of the alkyl amines grafted onto lignin can control the adsorption capacity of lignin for lead ions.
2. The adsorption capacity increased from 57.5 mg/g to 117.9 mg/g as the chain length increased from C2 to C4, a significant 105.0% increase.
3. A further increase in chain lengths for the enhancement of the adsorption capacity was less effective, and even caused a decrease in the adsorption capacity. As the chain length increased from C6 to C18, the adsorption capacity decreased from 70.1 mg/g to 30.6 mg/g.
4. This work presents a cost-effective and eco-friendly alternative to the current modifications of improving lignin adsorption capacity for heavy metals.

## ACKNOWLEDGMENTS

We acknowledge the support from the National Natural Science Foundation of China (21264002, 21464002). The authors are also grateful for the support of Haina Project of Guangxi University and the Training Program for Outstanding Young Teachers of Guangxi Higher Education Institutions.

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Article submitted: December 23, 2014; Peer review completed: February 16, 2015; Revised version received and accepted: February 25, 2015; Published: March 2, 2015.
DOI: 10.15376/biores.10.2.2425-2432