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Fabrication of a versatile lignin-based nano-trap for heavy metal ion capture and bacterial inhibition

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Abstract

Diverse functional nanomaterial with minimal environmental impact and reduced production cost is currently greatly needed because of the growing environmental awareness and shortage of petroleum resources. Herein we reported the creation of a lignin-based nano-trap (LBNT) through functionalizing one of the most abundant biomass on Earth, lignin, with both soft and borderline bases facilitating the coordination of different types of heavy metal ions. The resultant LBNT exhibited remarkable removal efficiencies of > 99% toward both soft (Ag(I), Hg(II), Cd(II)) and borderline (Pb(II), Cu(II), Zn(II)) ions, of which the residual concentrations were diminished from 5 mg/L to 3–9 μg/L that were below the permission values of drinking water regulated by the World Health Organization (WHO). Moreover, the produced nanomaterial could be adopted to load metal ions in atomic-level dispersion for preparing advanced nanocomposite. This was evidenced by the high bactericide rate of the silver-loaded nanocomposite (Ag@LBNT) as an antimicrobial toward Escherichia coli (99.68%) and Staphylococcus aureus (99.76%). This work may pave a way for the
production of cost-effective and biomass-based nanomaterial that could be applied in the field of separation and antimicrobial.

**Keywords**: Lignin; Nanomaterial; Functionalization; Adsorption; Antimicrobial

**Introduction**

Heavy metal ion contaminated water is one of the key environmental issues that is dramatically growing because of civilization, population, and industrial development during the past decades [1]. Heavy metal ions, for instance, copper, zinc, lead, silver, cadmium etc., can last for a long time in the environment and threaten human health and aquatic life [2]. Nowadays, the promising nanotechnology has provided enormous opportunities for the design and development of advanced nanomaterial with high surface-volume ratio, high chemical activity, and versatile functionalities for the cleanup of wastewaters [3, 4]. With growing environmental concerns and shortage of fossil-based resources, renewable biomass has received increasing attentions in fabrication of new eco-friendly nanomaterials, because of the distinctive features such as abundance, low-in cost, biocompatibility and renewability [5-7].

Lignin, one of the most abundant natural polymer existing in lignocellulosic biomass, is underused for now [8]. It is an amorphous phenolic polymer cross-linked by three precursors including p-hydroxyphenyl, guaiacyl, and syringyl [9, 10]. The technical lignin is produced in large scale as a byproduct from pulping or bio-refinery industries [11]. Lignin has been reported as a valuable component in different fields, for instance, adhesives, lubricants, dispersants, coatings, plasticizers, and adsorbents [12, 13]. Recently, lignin attracts more and more interests in adsorbing heavy metal ions from
aqueous media, in consideration of its distinctive macromolecular structure, i.e., the hydrophobic polymer chain with hydrophilic carboxyl groups and hydroxyl groups which serve as active sites for binding heavy metal ions [14-18]. Unfortunately, the adsorbing materials derived from lignin reported so far presented relatively low adsorption capacity and poor affinity for specific heavy metal ions. For examples, the alkaline lignin, reported by Albadarin et al. [19], only showed an adsorption capacity of 31.6 mg/g for Cr(VI); although the lignin extracted from Eucalyptus, reported by Mohan et al. [20], had a high adsorption capacity of 137.14 mg/g for Cd(II), it was less effective for Cu(II) (87.05 mg/g); similar results could also be found in [21] that reported a carboxymethylated formic lignin with a good adsorption capacity of 107.5 mg/g for Pb(II), whereas a poor adsorption capacity of 67.7 mg/g for Cd(II); and a lignin-based gel [22] presented a high adsorption capacity of 370.8 mg/g for Pb(II), whereas a low adsorption capacity of 43.6 mg/g for Co(II). This might be owing to their small surface areas (large size) and lack of functionalities, which rendered lignin-based materials at a disadvantage in adsorption of heavy metal ions [12]. In addition, reusability of adsorbents after adsorption is very important in view of practical applications. Extensive literatures [22-25] have clearly indicated the possibility of regenerating lignin-based adsorbents with kinds of chemicals such as hydrochloric acid, nitric acid and ethylenediamine tetraacetic acid, etc. Unfortunately, this traditional regeneration method always consumes numerous chemicals/solvents and will cause “secondary pollution” [18]. The weakness and disadvantages associate with those reported lignin-based adsorbing materials compel the design of novel lignin derivatives
with excellent adsorption capability toward different kinds of heavy metal ions in aqueous media as well as new strategies for reuse of the adsorbents.

To this end, a novel nanoscale heavy metal ion capture, i.e., functionalized lignin-based nano-trap (LBNT) was created by means of a simple inverse-emulsion copolymerization method. The LBNT is expected to possess the following features: reduced particle size for enhancing diffusion and contacting frequency, and strong metal binding groups on the surface affordable to different kinds of heavy metal ions with excellent adsorption capability, and the surface-dispersed binding sites in control of loading heavy metal ions facilitating further multiple use. Accordingly, the as-obtained LBNT could function as a versatile adsorbent for different types of heavy metal ions capture and could also function as a new host for metal ions loading and thereafter explore new applications, for example, in the aspect of antibacterial. This might establish a new approach for the design and creation of lignin-based advanced nanocomposite as well as value-added utilization of lignin derivatives in an eco-friendly and effective way, which is superior to the traditional method for the regeneration of adsorbents that usually consumes numerous solvents and produces “secondary pollution”.

To fulfill this goal, reduced particles size with high surface-volume ratio and strong functional groups are needed, for which dithiocarbamate (DTC), because of its multi-active groups: soft thiol groups and relatively softer (borderline) amine/imine groups, is an ideal choice [26]. The nanoscale feature of modification and expanded adsorbing capability originated from both soft and borderline bases make LBNT
coordinate to different heavy metal ions species (including soft and borderline acids), as shown in Figure 1A. In this work, LBNT was created by grafting diethylenetriamine (DETA) onto lignin under moderate reaction conditions through inverse-emulsion copolymerization followed by esterification with CS$_2$ (Figure 1B). The resultant LBNT showed good adsorption performance for soft acid (Ag(I), Hg(II), Cd(II)) and borderline acid (Pb(II), Cu(II), Zn(II)), and the removal degree was $>99\%$ for all cases, of which the residual concentration was reduced below the permission values of drinking water regulations by the World Health Organization (WHO). More importantly, the LBNT could be used as a novel host to load target heavy metal ions to produce efficient antimicrobial material, as evidenced by the outstanding antibacterial efficiency of the silver loaded LBNT, i.e., Ag@LBNT, toward the representative bacterial: Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) for their occurrence in aquatic environment and threat to the human beings. Due to the large portion of ionic silver on the surface of LBNT which could release into the culture media directly and interact immediately to the bacterial through binding to the cell walls or even penetrating the cells, the proposed Ag@LBNT exhibited excellent bactericide rates of 99.68$\%$ and 99.76$\%$ toward E. coli and S. aureus respectively.
Figure 1. (A) Illustration of creating the multifunctional lignin-based nano-trap for heavy metal ions capture; (B) synthesis diagram of the functionalized lignin nanoparticles.

Materials and Methods

Chemicals. Alkaline lignin was provided by Nanpu Pulp Mill, Nanning, China. Other chemicals including AgNO$_3$, HgCl$_2$, CdCl$_2$, Cu(NO$_3$)$_2$, Pb(NO$_3$)$_2$, ZnCl$_2$, NaOH, HCl, CS$_2$, formaldehyde, diethylenetriamine (DETA), and liquid paraffin were purchased from Guanghua Co., Ltd, Guangzhou. Double distilled water was used in all experiments.

Synthesis of Lignin-based nano-trap (LBNT). For the synthesis of lignin-based nano-trap, an inverse-emulsion copolymerization method was adopted: Lignin dissolved in distilled water, with an amine, and a cross linker (CH$_2$O) emulsified in liquid paraffin by a surfactant (Span80), then heated to 90°C for 3 h. After that it was
cooled down to 30°C, adding CS₂ for esterification of 2 h, centrifugation, washing and freeze drying to obtain LBNT (Figure 1B, under optimum conditions the product had a water content of 3.8 wt. %).

**Characterizations.** Particle size distribution of the LBNT was determined with a laser particle size analyzer (Malvern Mastersizer 3000). FT-IR spectra were measured by a Nexus 470 spectrometer with a KBr method in the range of 400 ~ 4000 cm⁻¹. Surface morphology was observed by a scanning electron microscopy (SEM, SU8020, Hitachi). Chemical components were analyzed by a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) using monochromatic Al Ka (1486.6 eV) X-ray under 10⁻⁹ torr. Brunauer-Emmett-Teller surface area (S_BET, m²/g) of the samples were determined from N₂ adsorption/desorption isotherms by a Quadrasorb SI analyzer (Quantachrome, USA). Analyzing the residual ion concentration was carried out by an ICP-OES, optima 5300DV, Perkin-Elmer, USA.

**Adsorption Studies.** LBNT (0.2 g/L) was contacted with different concentration of Ag(I)/Pb(II)/Cu(II) solutions under stirring at 25±0.5°C for a certain time. After adsorption completed the sample was filtered by a 0.22 μm membrane, and the ion concentration was determined by ICP-OES. Effect of pH, contacting time, initial concentration and temperature on the adsorption performance of silver, copper and lead ions by the LBNT was fully studied. Besides, the adsorption performance of LBNT toward multiple heavy metal ions in water was also conducted. All measurements were taken in triplicate and the average values were adopted.

**Antibacterial Test.** Ag@LBNT was obtained through adsorption of Ag(I) with LBNT
(500 mg/L, dosage 0.2 g/L, 12 h) followed by filtration, washing with deionized water and drying under vacuum at 65°C of 12 h. The bactericidal activity of Ag@LBNT, LBNT, and lignin or without antimicrobial on E. coli (ATCC2592) and S. aureus (ATCC6538), both purchased from Institute of Microbiology Chinese Academy of Science, Beijing, was measured by plate count method [27, 28]. Briefly, the bacterial were cultured in LB broth for 18 h under 37°C with shaking speed of 200 r/min. Then the culture was diluted to 10⁷ CFU (Colony-Forming Units) /mL. 25 mL of the sample was incubated with or without the antimicrobials (1.5 mg/mL). A certain amount of sample was taken out and placed on plates with broth for bacteria growing under 37°C. After 24 h, the quantity of bacterial cells was counted. The bactericidal rate (%) was calculated according to the CFU with and without antimicrobial. Measurements were taken in triplicate.

Results and Discussion

Synthesis of LBNT. The LBNT was created by means of a simple inverse-emulsion copolymerization process. The reaction parameters including phase ratio (liquid paraffin: water, v/v), surfactant (Span 80) dosage, CH₂O dosage, and stirring speed impacted the final LBNT diameter in different manner. First, the phase ratio demonstrated a pronounced effect on the diameter of lignin particles. Increasing phase ratio created smaller nanoscale particles, as shown in Supplementary Figure S1A, with a phase ratio of 6:1 the lignin particles had an average particle diameter of 160.1±5.6 nm. Secondly, increasing dosage of Span80 in liquid paraffin resulted in a reduction of particle size, with an optimum dosage of 5 mL Span80, the average particle size was
much smaller (161.8±5.7 nm) (Supplementary Figure S1B). Thirdly, the stirring speed had a distinct influence on the particle diameter of lignin. Under an optimum stirring speed of 800 rpm the average particle diameter was 162.5±5.7 nm (Supplementary Figure S1C). While the dosage of CH$_2$O had a negative effect on the particle diameter, which might be due to the condensation copolymerization with more CH$_2$O, resulting in the formation of micro-scale particles during production (Supplementary Figure S1D).

Based on the above observations, the fabrication of lignin-based nano-trap was proposed as “Lignin emulsion-copolymerization-stabilization”: as an aromatic biopolymer, lignin has strong hydrophobicity and intrinsic π-π stacking that makes it being easy to agglomerate and assemble to large blocks in water. During the inverse-emulsion copolymerization process, lignin firstly dissolved in water owing to the phenolic hydroxyl and carboxyl groups and accordingly emulsified as droplets in liquid paraffin with surfactant. Then, the lignin macromolecules and DETA copolymerized by crosslinking of CH$_2$O under elevated temperature. After that, the large amount of amine/imine groups in DETA provided positive surface charges and accordingly stabilized the particles by the electrostatic repulsion forces. While the intra- and intermolecular hydrogen bonds could enhance the toughness of the nanoparticles.

**Morphology.** The morphology of the original lignin and the as-obtained LBNT was characterized by SEM (Figure 2). A large amount of functionalized lignin-based nanoparticles were produced in nanoscale within 100 ~ 400 nm, and the average
particle size was around 160 nm (Figure 2B, C). On the other side, lignin presented as irregular blocks with rough surfaces in micrometer scale (Figure 2A). An obvious reduction of particle size of lignin after the inverse-emulsion polymerization process was observed. This might be due to the formation of H-bonding from O-H in lignin and –NH₂ in DETA moieties, which further contributed to the stabilization of the nanoparticles. Besides, the incorporation of nitrogen/sulfur elements into the LBNT was strongly confirmed by the EDS results (S: 2.31 keV, N: 0.39 keV, Figure 2D). As known from the Hard and Soft (Lewis) Acids and Bases (HSAB) concept [29], the thiol groups belong to soft base while the amine/imine groups belong to borderline base which has a strong affinity to soft acid, for example, silver ions, and borderline ions, for examples, lead and copper ions, respectively. Besides, the LBNT showed a 12 times higher BET surface area of 23.7 m²/g than the original lignin (1.8 m²/g). Such an increases in surface area of LBNT was due to the reduction in particle size, which could enhance the diffusion and contacting frequency between the adsorbents and adsorbates and accordingly benefit the capture of heavy metal ions in water [30, 31].
Figure 2. SEM images of (A) lignin and (B, C) LBNT with different magnification and (D) their EDS spectra.

XPS and FT-IR Spectra. The chemical components of the LBNT were further analyzed by XPS and FT-IR measurements. The survey XPS spectra were shown in Figure 3A, which clearly presented three new peaks in LBNT with binding energies at 164.3 eV (S 2p), 228.2 eV (S 2s), and 400.8 eV (N 1s), demonstrating the existence of S and N element in LBNT. High-resolution XPS signals were also presented in Figure 3B, C. The N 1s peaks centered at 400.34, 401.77 and 403.04 eV could be attributed to N–C=S(S), N–H and N–C, respectively in LBNT (Figure 3B) [32, 33]. The S 2p$_{1/2}$ peak centered at 165.21 eV could be attributed to C=S, while the S 2p$_{3/2}$ peak located at 163.62 eV could be attributed to and C-S (Figure 3C) [34]. FT-IR spectra were presented in Figure 3D, the broad band at 3430 cm$^{-1}$ was due to hydroxyl groups and amine/imine stretching vibration in lignin chain and DETA moieties. The bands at 2930
cm$^{-1}$ was due to H-C tensile vibration in methylene. The benzene ring stretch shifted from 1600 cm$^{-1}$ to 1650 cm$^{-1}$ after modification that was due to the replacement of H by -NCSS$^-$ groups [32]. The bands at 1500 cm$^{-1}$ was due to the aromatic ring skeletal vibrations and C-OH deformation vibration. The bands at 1380 and 1330 cm$^{-1}$ were attributed to the C-O stretching. It could also be found that the LBNT exhibited additional absorption bands at 960, 1110 and 1430 cm$^{-1}$ that was attributed to the respective stretching vibrations of C-S, C=S and C-N [35]. These results strongly proved the successful incorporation of DTC groups into LBNT.

**Figure 3.** (A) XPS survey spectra, (D) FT-IR spectra of the lignin and LBNT.

**Effect of pH on adsorption.** The effect of solution pH on the removal of heavy metal ions by LBNT is shown in Figure 4. As could be seen, the adsorption efficiencies of the
heavy metal ions were much pH-dependent. At pH 2, the adsorption efficiencies were low, \( \sim 31\%\), 39\%, 72\%, for Pb(II), Cu(II) and Ag(I), respectively. Under acidic conditions, the competition adsorption onto the adsorption sites between a large amount of \( \text{H}^+ \) and heavy metal ions occurred [25]. Meanwhile, the functional groups, \(-\text{NCSS}^-\) and \(-\text{NH}_2/-\text{NH}^-\) in this case, were protonated and thereafter the LBNT was positively charged. As the pH value rising, the \(-\text{NCSS}^-\) and \(-\text{NH}_2/-\text{NH}^-\) groups gradually deprotonated; thus, the removal efficiencies of these heavy metal ions were enhanced. It should be noted that, even at the same pH value of 2, the removal efficiency of Ag(I) by LBNT was much higher than Pb(II) and Cu(II). This situation could be explained by the hard and soft acids and bases concept which states that the soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and from stronger bonds with hard bases [29, 36]. Therefore, in this case, the soft thiol groups had stronger binding affinity to the soft silver ions rather than the borderline base lead and copper ions as well as the hard protons. Moreover, when pH \( \geq 7\), insoluble M(OH)_x would be formed. Accordingly, the following adsorption experiment was carried out under pH 6.

![Graph showing removal efficiency vs pH for Ag(I), Pb(II), and Cu(II)]
**Figure 4.** Effect of pH on the removal efficiency of silver, lead and copper ions by LBNT. (10 mg/L, 25 ± 0.5 °C, dosage 0.2 g/L, 180 min).

**Effect of Adsorption Time and Adsorption Kinetics.** The influence of adsorption time on the adsorption of heavy metal ions on LBNT is shown in Figure 5. Clearly, the adsorption amounts increased with adsorption time for all cases. The adsorption amounts increased dramatically at early stage and then increased slowly to equilibrium which was around 30 min in all cases. After 180 min of exposure, over 99% of silver, lead and copper ions had been removed by LBNT. The residual content of silver, lead and copper ions was determined to be 6 ppb, 7 ppb and 4 ppb, respectively (Figure 5 Right Y axis). Owing to the fact that LBNT had both soft and borderline bases as well as reduced particle’s size which facilitated the diffusion and binding of the metallic ions to the coordination sites in LBNT [31], it exhibited fast response and excellent adsorption capability to these metallic pollutants.

**Figure 5.** Effect of contact time on adsorption amount and the residual heavy metal ions concentration. (Dosage 0.2 g/L, 10 mg/L, pH= 6, 25 ± 0.5 °C).

The adsorption kinetics were further analyzed with pseudo-first order [37] and pseudo-second order [38] models by equations:
Pseudo-first-order: \( \log(Q_e - Q_t) = \log Q_e - \left(\frac{k_1 t}{2.303}\right) \)  

Pseudo-second-order: \( \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \)

where \( k_1 \) (1/min), \( k_2 \) [g/ (mg·min)] are the kinetic rate constants, \( Q_e \) and \( Q_t \) are the adsorption amounts (mg/g) at equilibrium and time \( t \) (min), respectively. The fitting results and the regression coefficients \( (R^2) \) are tabulated in Table 1. According to the higher values of \( R^2 \) with the pseudo-second order model than the pseudo-first order model, the adsorption of silver, lead and copper ions by LBNT followed the pseudo-second order model. This suggested that the controlling mechanism in binding silver, lead and copper ions by LBNT was mainly chemical interactions [25].

Table 1. Adsorption kinetics parameters of the pseudo-first order and pseudo-second order models.

| Heavy metal ions | Pseudo-first order | Pseudo-second order |
|------------------|--------------------|---------------------|
|                  | \( Q_e \) (mg/g)   | \( k_2 \) (l/min)   | \( R^2 \)            | \( Q_e \) (mg/g) | \( k_2 \) (g/(mg·min)) | \( R^2 \) |
| Ag(I)            | 48.85              | 0.078               | 0.9711               | 57.48           | 0.0015               | 0.9941 |
| Pb(II)           | 47.69              | 0.141               | 0.8516               | 50.70           | 0.0050               | 0.9363 |
| Cu(II)           | 49.85              | 0.159               | 0.9298               | 52.82           | 0.0055               | 0.9976 |

Effect of Initial Ion Concentration and Adsorption Isotherms. The adsorption isotherms were also investigated and the results are shown in Figure 6. As seen, the adsorption amounts increased with increasing initial ion concentrations. This was because of that as the metallic ion concentration increasing, more metallic ions being available and could be adsorbed by more vacant binding sites on LBNT. The maximum adsorption amount of Ag(I) by the LBNT was determined to be 1057.95 mg/g. Apparently, the LBNT exhibited too much higher silver ions adsorption capacity than
traditional adsorbents (Table 2), such as activated carbon (152.1 mg/g) [39], carbon nanotube (~49 mg/g) [4], mesoporous silica (46 mg/g) [40], and zeolite (61 mg/g) [41]. In addition, LBNT also had high adsorption capacities toward Pb(II) (282.51 mg/g) and Cu(II) (209.70 mg/g) than other heavy metal-adsorbing materials, including carbon nanotube (Pb: 101 mg/g) [42], lignin-grafted carbon nanotubes (Pb: 235 mg/g), activated carbon (Pb: 27 mg/g) [43], microwave treated activated carbon (Cu: 97.8 mg/g) [44], and silica gels (Pb: 83 mg/g) [45]. The high adsorption capacity of LBNT toward these target heavy metal ions could be attributed to its nanoscale size and plenty of surface functional groups [30, 31].

![Figure 6](image_url)

**Figure 6.** Effect of initial ion concentration on adsorption amount of (A): Ag(I), (B): Pb(II) and Cu(II), and Fitting with the Langmuir and Freundlich models. (Dosage 0.2 g/L, 12 h, 25 ± 0.5°C).

**Table 2.** Comparison of the maximum adsorption capacities for heavy metal ions of LBNT and other reported adsorbents.

| Adsorbent          | Adsorption capacity (mg/g) | Reference |
|--------------------|----------------------------|-----------|
|                    | Ag(I) | Pb(II) | Cu(II) |
| LBNT               | 1057.95 | 282.51 | 209.70 | This work |
| Activated carbon   | 152.1 | - | - | [39] |
The adsorption isotherms were further fitted by Langmuir and Freundlich models. The Langmuir model assumes a monolayer adsorption takes place on a homogeneous surface [49]. The Freundlich model is empirical and the adsorption surface is heterogeneous [50]. They can be given by the following equations:

\[ Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (3) \]

\[ Q_e = K_F C_e^{1/n} \quad (4) \]

where \( Q_m \) is the theoretical adsorption capacity (mg/g), \( C_e \) is the equilibrium ion concentration, and \( b \) is the Langmuir constant (L/mg). \( K_F \) is the Freundlich constant [(mg/g) (L/mg)^{1/n}], and \( n \) is a constant indicating the adsorption intensity.

The fitting results were presented in Figure 6 and Table 3. The theoretical adsorption capacities (\( Q_m = 1079.96, 324.43, 214.71 \) mg/g for Ag(I), Pb(II), Cu(II), respectively)

| Material                          | Capacity (mg/g) | Parameter | Reference |
|----------------------------------|-----------------|-----------|-----------|
| Carbon nanotube                  | 49              | -         | [4]       |
| Mesoporous silica                | 46              | -         | [40]      |
| Zeolite                          | 61              | -         | [41]      |
| PAM-TL                           | 145.2           | -         | [46]      |
| Fe3O4/PPy nanocomposite          | 143.3           | -         | [47]      |
| Fe3O4@SiO2-HO-S                  | -               | 178.2     | 51.2 [48] |
| Carbon nanotube                  | -               | 101       | -         |
| Lignin-grafted carbon nanotubes  | -               | 235       | -         |
| Activated carbon                 | -               | 27        | -         |
| Microwave treated activated carbon | -            | -         | 97.8 [44] |
| Silica gels                      | -               | 83        | -         |

The adsorption isotherms were further fitted by Langmuir and Freundlich models. The Langmuir model assumes a monolayer adsorption takes place on a homogeneous surface [49]. The Freundlich model is empirical and the adsorption surface is heterogeneous [50]. They can be given by the following equations:

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\[ Q_e = K_F C_e^{1/n} \quad (4) \]

where \( Q_m \) is the theoretical adsorption capacity (mg/g), \( C_e \) is the equilibrium ion concentration, and \( b \) is the Langmuir constant (L/mg). \( K_F \) is the Freundlich constant [(mg/g) (L/mg)^{1/n}], and \( n \) is a constant indicating the adsorption intensity.

The fitting results were presented in Figure 6 and Table 3. The theoretical adsorption capacities (\( Q_m = 1079.96, 324.43, 214.71 \) mg/g for Ag(I), Pb(II), Cu(II), respectively)
calculated by the Langmuir model were consistent with the experimental saturation amounts \((Q_e=1057.95, 282.51, 209.70 \text{ mg/g for Ag(I), Pb(II), Cu(II), respectively})\) with high values of \(R^2\), which indicated the adsorption could be described well with the Langmuir model, and accordingly the adsorption was a monolayer coverage [49]. On the contrary, Freundlich model was not suitable for describing the adsorption process due to the lower \(R^2\) values. In spite of this, the values of \(n\) were all greater than 1 that meant the binding of these heavy metal ions by LBNT was favorable to silver ions followed by lead ions and then copper ions [32].

**Table 3.** Adsorption isotherms fitting results by the Langmuir and Freundlich models.

| Heavy metal ions | Experimental (mg/g) | Langmuir model | Freundlich model |
|------------------|---------------------|----------------|------------------|
|                  | \(Q_m\) (mg/g)      | \(b\) (L/mg)  | \(R^2\)          |
| Ag(I)            | 1057.95             | 1079.96        | 0.9546           |
| Pb(II)           | 282.51              | 324.43         | 0.9473           |
| Cu(II)           | 209.70              | 214.71         | 0.9670           |

\(K_F\) \(n\) \(R^2\)

Ag(I) | 458.60 | 6.55 | 0.8268 |
Pb(II) | 107.55 | 3.73 | 0.8285 |
Cu(II) | 61.83 | 3.39 | 0.9665 |

**Adsorption thermodynamics.** Adsorption thermodynamic parameters are necessary to determine the process is spontaneous or endothermic or not. Accordingly, the adsorption of Ag(I), Pb(II) and Cu(II) by LBNT was conducted at 25, 35, 45 and 55 °C (with initial concentrations of Ag(I): 350 mg/L, Pb(II) and Cu(II): 100 mg/L, pH 6, dosage 0.2 g/L, contacting time 180 min). The Gibbs free energy change \((\Delta G^\circ, \text{kJ/mol})\), enthalpy change \((\Delta H^\circ, \text{kJ/mol})\) and entropy change \((\Delta S^\circ, \text{J/K mol})\) could be determined with the following equations [51]:

\[
\Delta G^\circ = -RT \ln k_d \tag{5}
\]
\[ \ln k_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]  

(6)

where \( k_d \) is the distribution coefficient \( (k_d = Q_e/C_e) \), \( Q_e \) is the adsorption amount \( (\text{mg/g}) \) and \( C_e \) is the equilibrium concentration \( (\text{mg/L}) \), \( R \) is the gas constant \( (8.314 \text{ J/mol K}) \). A plot of \( \ln(k_d) \) versus \( 1/T \) will be linear with the slope and intercept giving the values of \( \Delta H^\circ \) and \( \Delta S^\circ \) respectively.

**Figure 7.** (A) Effect of temperature on the adsorption of Ag(I), Pb(II) and Cu(II) on LBNT; (B) Plots of \( \ln(k_d) \) versus \( 1/T \) for the adsorption of Ag(I), Pb(II) and Cu(II) on LBNT.

As could be seen from Figure 7A, as the temperature increased from 25 to 55 ℃, the adsorption amounts of Ag(I), Pb(II) and Cu(II) on LBNT all increased. This might be due to the mobility of the ions in solution increased with increasing temperature [52]. The plots of \( \ln(k_d) \) versus \( 1/T \) were shown in Figure 7B. The values of \( \Delta H^\circ \) and \( \Delta S^\circ \) could be determined from the slope and intercept by linear fitting of the plots, which were tabulated in Table 4. As seen, the values of \( \Delta G^\circ \) were found to be all negative in these cases, which indicated the spontaneity and feasibility of the adsorption of Ag(I)/Pb(II)/Cu(II) onto LBNT. Moreover, a decrease in the value of \( \Delta G^\circ \) with
increasing temperature indicated the adsorption was more easier under higher temperature [53]. The positive values of $\Delta H^\circ$ implied that the adsorption of Ag(I)/Pb(II)/Cu(II) onto LBNT was endothermic [54]. The magnitude of $\Delta H^\circ$ gives information about the type of adsorption. In general, the value of $\Delta H^\circ$ below 4.18 kJ/mol implies a physical adsorption, while in a range of 80-200 kJ/mol implies a chemisorption [55]. Therefore, as known from Table 4, the value of $\Delta H^\circ$ was 21.86 kJ/mol, 21.18 kJ/mol and 18.46 kJ/mol for adsorption of Ag(I), Pb(II), and Cu(II), respectively, which indicated the adsorption process did not belong to a single physical or chemical adsorption but a physic-chemical adsorption. Furthermore, the positive values of $\Delta S^\circ$ for adsorption of Ag(I), Pb(II) and Cu(II) on LBNT implied an increase in the degree of randomness at the solid-solution interface [56].

**Table 4.** Thermodynamic parameters for the adsorption of Ag(I), Pb(II) and Cu(II) onto LBNT.

| Metal ion | $C_0$ (mg/L) | $T$ (K) | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/K mol) |
|-----------|--------------|---------|--------------------------|--------------------------|---------------------------|
| Ag(I)     | 350          | 298     | -22.00                   | 21.86                    | 146.97                    |
|           |              | 308     | -23.30                   |                          |                           |
|           |              | 318     | -24.83                   |                          |                           |
|           |              | 328     | -26.40                   |                          |                           |
| Pb(II)    | 100          | 298     | -21.54                   | 21.18                    | 143.25                    |
|           |              | 308     | -22.91                   |                          |                           |
|           |              | 318     | -24.27                   |                          |                           |
|           |              | 328     | -25.87                   |                          |                           |
Adsorption Mechanism

Figure 8. High resolution XPS spectra of (A) S2p, (B) N1s, (C) Ag3d in Ag@LBNT; (D) S2p, (E) N1s, (F) Pb4f in Pb@LBNT; and (G) S2p, (H) N1s, (I) Cu2p in Cu@LBNT.

To disclose the adsorption mechanism between these heavy metal ions and LBNT, the high resolution XPS spectra of S2p, N1s and Ag3d, Pb4f, Cu2p of Ag@LBNT,
Pb@LBNT and Cu@LBNT were recorded and the results were shown in Figure 8. The S2p binding energies of C=S and C-S bonds of dithiocarbamate group in Ag@LBNT shifted to higher values of 166.23 and 164.12 eV (Figure 8A) than that of LBNT (165.21 and 163.62 eV, respectively). And the N1s binding energies of N-CSS- and N-H in Ag@LBNT were 401.19 and 402.55 eV (Figure 8B) which were also higher than that in LBNT (400.34 and 401.77 eV, respectively). These results confirmed the chemical interaction of silver with dithiocarbamate group through sharing the electrons between dithiocaramate group and Ag ions. Besides, the Ag 3d spectrum (Figure 8C) was composed of two peaks at 368.65 (3d5/2) and 374.64 eV (3d3/2) indicating the state of silver in Ag@LBNT was ionic Ag(I) [46, 57]. In the case of Pb@LBNT, the S2p binding energies of C=S and C-S were 165.33 and 163.75 eV (Figure 8D), respectively which were almost the same to that in LBNT (165.21 and 163.62 eV, respectively), indicating the S moieties were scarcely involved in binding with Pb ions. By comparing the N1s binding energies of N-CSS-, N-H and N-C in Pb@LBNT (400.29, 402.65 and 403.09 eV, respectively, Figure 8E) to those values in LBNT (400.34, 401.77 and 403.04 eV), the binding energy of N-H increased 0.88 eV, which strongly indicated the complexation between –NH groups and Pb(II) ions. Besides, the Pb4f7/2 (Figure 8F) could be decomposed into two peaks, the peak at 136.72 eV was characteristic of the divalent ion from and the peak at 135.95 eV was assigned to the complexation between –NH and Pb(II) ions [58]. These results further confirmed the chemical interactions of Pb(II) and LBNT. The S2p and N1s spectra of Cu@LBNT were almost the same with that of Pb@LBNT, and the Cu2p3/2 could be decomposed
to two peaks at 934.69 and 933.21 eV, respectively, corresponding to divalent copper ion and complex of amine and copper. Similar results could also be found in literatures [59, 60]. Accordingly, the S moiety and a portion of N moiety (N-H) in dithiocarbamate groups both contributed to the complexation with the silver ions, whereas only the N moiety accounted for the coordination of Pb(II) and Cu(II), that was the reason why adsorption capacity of LBNT toward Ag(I) was much higher than Pb(II) and Cu(II). Besides, the size reduction of lignin increased the specific surface area of LBNT, and increased the diffusion rate and the contacting frequency between the metallic ions and the nano-trap, which accordingly greatly enhanced the responding rate and adsorption capacity [30, 31]. Moreover, silver ion belongs to a monovalent ion which only chelated with one electron-donating functional groups in LBNT, while the divalent ion (lead and copper) need to complex with two functional groups. The synergistic effects of the functional groups, large surface area as well as ions characteristics undoubtedly played a crucial role in the capture of different heavy metal ions. Considering lignin is a by-product from pulp & paper industry and bioethanol industries which is underused, the production of LBNT from lignin for water decontamination gives great advantages of abundance, cost-effectiveness, strong adsorption capability, as well as environmentally compatibility contrasted to other adsorbing materials including MOF, CNTs and ACs [61, 62].

**Adsorption performance for multiple heavy metal ions.** The adsorption efficiency of LBNT toward multiple heavy metal ions in water simultaneously was further investigated. LBNT (0.10 g) was added into a 10 mL solution containing both soft acids
(Ag(I), Hg(II), Cd(II)), and borderline acids (Pb(II), Cu(II), Zn(II)) with each metal concentration of 5 mg/L. The mixture was kept at 25 ± 0.5 °C for 12 h, after the adsorption completed it was filtered and the filtrate was measured by ICP-OES. As shown in Figure 9, LBNT was very efficient for the adsorption of all these tested heavy metal ions with excellent adsorption efficiency of >99%. The residue concentrations of these heavy metal ions was in the range of 3-9 μg/L, which were all below the permission values of drinking water regulations of WHO. These results further demonstrated the effectiveness of LBNT for capturing different types of heavy metal ions.

![Figure 9](image_url)

**Figure 9.** Adsorption performance of LBNT in a multiple heavy metal ions solution.

**Antibacterial activity.** The above results demonstrated the creation of LBNT from lignin was promising as a heavy metal adsorbent. Since the surface functional groups of LBNT had strong coordination toward heavy metal ions which was proved to be a single-layer (atomic-level) adsorption by the fitting results of Langmuir model. This unique feature of the proposed LBNT with atomic-level loaded metal ions make it great potential in other applications. As is known to all, heavy metal-loaded adsorbents are
commonly regenerated by solvent elution, which always consumes numerous solvents and will produce “secondary pollution” [2]. Considering lignin and silver has some sort of bactericidal ability [63-65], the obtained LBNT could not only be used as an efficient heavy metal ions capture, but also could be explored in other application fields, for example, antibacterial. Thus, we proposed a new route for the value-added usage of the metal loaded LBNT, exemplified by silver-load LBNT, i.e., Ag@LBNT, as an antimicrobial which could provide a new platform for reusing adsorbents and overcome the aforementioned limitations.

The growth of E. coli with or without antimicrobial was shown in Supplementary Figure S2. As could be seen, most of the bacterial were killed after interaction with LBNT and Ag@LBNT (Supplementary Figure S2 B, D). In contrast, a few bacterial colonies were observed on the plate with lignin (Supplementary Figure S2 C). This highlighted excellent antimicrobial activity of LBNT and Ag@LBNT toward the bacterial. Furthermore, the bactericidal rate of the samples toward E. coli and S. aureus was assessed and presented in Figure 10, from which the Ag@LBNT showed a much higher killing efficiency toward E. coli (99.68%) and S. aureus (99.76%) bacterial than the other two. This result strongly confirmed the important contribution of silver component in the Ag@LBNT nanomaterial for killing bacterial. This could be attributed to the silver loaded on the surface of LBNT in ionic state, as proven by the XPS results (Figure 8C), exhibited a single layer occupation (as proven by the fitting with Langmuir isotherm model) and a large portion of the silver ions could release into the culture media and interact directly with the bacterial through binding to the cell walls or even penetrating the cells, thus restrained the cell viability until killing [63, 66]. As known, ionic silvers are more effective against bacterial growth compared to silver nanoparticles due to their immediate and direct interaction to bacterial, while silver nanoparticles require time to conversion to silver ions [63]. Thus, the Ag@LBNT exhibited excellent bactericide rate to E. coli and S. aureus. It should also be noted that
the killing efficiency of LBNT toward E. coli and S. aureus remained 93.17% and 93.35%, respectively, which was better than the lignin (66.37% and 68.26%, respectively). The inhibition of lignin against bacterial growth, as reported in literatures [67, 68], was correlated with the phenolic components of lignin. The side chain structure and nature of the functional groups of the phenolic moieties are major determinants of the antimicrobial effects of lignin. In general, phenolic components with functional groups containing oxygen (such as hydroxyl groups, carbonyl groups) in the side chain are less inhibitory, whereas the presence of double bonds and methyl groups increases the biocide effect of phenolics [67]. Thus, the introduction of DTC moieties [-CH$_2$-N-C(=S)S, as shown in Figure 1B] onto the side chain of lignin enhanced the antibacterial activity of LBNT. Besides, nanoparticles through their small size can penetrate into the bacterial cell and change the intracellular environment that accordingly causing the death of bacterial [69].

![Figure 10](image)

**Figure 10. Bactericidal rates of lignin, LBNT, and Ag@LBNT toward E. coli and S. aureus.**

**Conclusions**

A multifunctional lignin-based nano-trap (LBNT) was developed for efficiently capture of different types heavy metal ions in water. LBNT was designed to have both soft and borderline bases which accordingly showed very high adsorption efficiency (>99%) toward target heavy metal ions, i.e. soft acid (silver, mercury and cadmium ions)
and borderline acid (lead, copper and zinc ions). Especially, it showed a remarkable adsorption capacity to silver ions ($Q_e = 1057.95$ mg/g). The adsorption kinetics followed well with the pseudo-second order model that indicated the chemical involves between the heavy metal ions and LBNT which were also confirmed by XPS analysis. The adsorption isotherms followed well with the Langmuir model indicating a single layer occupation on the LBNT surface. The adsorption thermodynamics parameters suggested the adsorption process of Ag(I), Pb(II) and Cu(II) onto LBNT was spontaneous and endothermic. The atomic-level dispersion of metal ions on LBNT inspired a new approach for the production of novel lignin-based nanocomposite. As proved by the high antibacterial efficiency of Ag@LBNT toward the representative E. coli and S. aureus. Since lignin is one of the most abundant biomass on the Earth and was produced as a by-product from pulping and bioethanol industry, the fabrication of lignin-based nanomaterials is promising. The LBNT has great prospect in wastewater treatment and antibacterial applications.

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Highlights

- A lignin-based nano-trap (LBNT) with various functional groups was synthesized.
- Multifunctionality endows it with adsorption versatility for different heavy metal ions.
- 6 kinds of heavy metal ions could be reduced from 5 ppm to quite low levels (3~9 ppb).
- It showed a high adsorption capacity of 1057.95 mg/g for silver ions in water.
- The Ag@LBNT showed excellent bactericide rate to E. coli (99.68%) and S. aureus (99.76%).
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