Industrial lignins: the potential for efficient removal of Cr(VI) from wastewater

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Abstract
Cr(VI), a serious threat to human health, widely exists in the effluents of various industrial processes. In this paper, the potential of industrial lignin for efficient removal of Cr(VI) from wastewater was systematically investigated, including pulping black liquor lignin (BLN), enzymolysis lignin (ELN), and SPORL pretreatment spent liquor (FS). The structure characterizations of three lignins were investigated by thermogravimetry (TG), Fourier transform infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) surface area measurement, scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). Among these three lignins, BLN showed the highest adsorption amount of Cr(VI) and good selectivity in wastewater simulation. According to the Langmuir model, the calculated maximum adsorption amount of Cr(VI) on ELN, BLN, and FS was 801.57, 864.30, and 642.26 mg g⁻¹, respectively. The adsorption of Cr(VI) by industrial lignins was a chemisorption process, during which Cr(VI) was reduced to low-toxic Cr(III). This paper provided a promising application for the effective utilization of industrial lignins.

Keywords Industrial lignin · Cr(VI) removal · Mechanism · Industrial wastewater

Introduction
Cr(VI), as a common heavy metal ion, is highly toxic, carcinogenic, and non-degradable (Zhang et al. 2018). In the past few decades, Cr(VI) pollution has become a serious problem (Anirudhan et al. 2013). Cr(VI) not only pollutes water (Gan et al. 2015), it can also accumulate in fish and other aquatic animals, causing serious harm to humans (Ge and Li 2018). Hence, the removal of Cr(VI) has always been the focus of researchers’ attention. Among the various technologies of removing Cr(VI), adsorption is an efficient and economical technology, since different kinds of adsorbents with low cost can be prepared and used (Wang and Chen 2009), such as metal oxides (Pham et al. 2021; Pham et al. 2019), minerals (Pham et al. 2020), polymers (Truong et al. 2021), and biomass (Kwak et al. 2015). Using biomass as an adsorbent, also called biosorption (Kesaano and Sims 2014), will be an inexpensive alternative to existing commercial activated carbon.

Lignin, the second largest natural polymer after cellulose, is a highly branched and complex polymer (Ralph et al. 2019). It contains p-hydroxybenzene (H), guaiacyl (G), and syringyl (S) phenylpropane units (Terrell et al. 2020), while the composition and quantity of the units vary with the species of plants and industrial processes. In addition, the functional groups, such as methoxy, phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, non-cyclic phenyl ether, and carbonyl, have a significant influence on the reaction characteristics of lignin (Chen and Wan 2017, Ralph et al. 2019, Xu et al. 2006). At present, the major sources of lignin available for large-scale application are from the pulp and paper making industry and cellulosic ethanol industry (Lauwaert et al. 2019).

It is well known that pulping black liquor is a toxic and badly stained pulp wastewater. Its color and toxicity have a negative impact on water resources, and it contains a large amount of lignin, which is difficult to be degraded naturally (Fu et al. 2013; Gao et al. 2013). Lignin can be separated and purified from pulping black liquor by using its special performance in acid-base environment, which can not only treat black liquor friendly, but also bring secondary economic value. Biorefining of biomass for generating biofuels and high
valued chemicals has attracted increasing research interest (Zhou et al. 2016b). During the biorefining process, different lignin by-products are produced, such as enzymolysis lignin and lignins in pretreatment spent liquor (Liang et al. 2020). However, most of the industrial lignins are directly burned or wantonly discharged (Zhao et al. 2020b). After appropriate modification, industrial lignin can be used as adsorbent (Zhou et al. 2020), dispersant (Zhou et al. 2015), water-reducing agent (Zhou et al. 2016a), and rubber-reinforcing agent (Gregorová et al. 2006). Unfortunately, although the utilization of lignin is widely concerned, the comprehensive utilization ratio of lignin is less than 5% (Li et al. 2015).

Herein, three different types of industrial lignins were collected and characterized, including pulping black liquor lignin (BLN), enzymolysis lignin (ELN), and SPORL pretreatment spent liquor (FS). The potential of these three lignins for efficient removal of Cr(VI) from aqueous solution was investigated and compared. The structure characterizations were evaluated by TGA, FTIR, SEM, BET, and XPS. The removal efficiency and adsorption performance for Cr(VI) of these three lignins were systematically studied, including (i) the effect of adsorption time, original metal concentration, and temperature on adsorption process; (ii) adsorption isotherm, thermodynamics, and kinetics; and (iii) wastewater simulation, Cr species changes during adsorption, and potential adsorption mechanism.

Materials and methods

Materials

Pulping black liquor was come from a kraft pulping process. Enzymolysis lignin was kindly provided by Shandong Longlive Bio-technology Co., Ltd. (Shandong, China). Pulping black liquor lignin (BLN) and enzymolysis lignin (ELN) were purified using HCl precipitation method. Briefly, 10 g of samples was dissolved in 50 g deionized water at pH = 12 using NaOH adjustment. After stirring evenly, the mixture was filtered by vacuum to remove insoluble impurities. The filtrate was collected. After adjusting the pH to 2.0, the slurry was kept stirring at 75 °C for 2 h. Then, distilled water was used to wash the solid until the pH was stable. The BLN or ELN was obtained by filtration and then dried at 60 °C. Lignin sulfonate was produced from the SPORL pretreatment liquor of Douglas-fir, denoted as FS. The details of the pretreatment spent liquor (Liang et al. 2020).

Characterization

The surface area and pore structure of adsorbents were measured by a surface area analyzer (ASAP 2460, Micromeritics) at 77 K. Before the test, lignins were degassed for 10 h at 373 K under vacuum. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area ($S_{BET}$). The total volume ($V_{tot}$) was obtained by the liquid volumes of N$_2$ at $P/P_0 = 0.99$. The micropore volume ($V_{mic}$) was estimated by $t$-plot method. The extra volume ($V_{mic}$) was obtained via subtracting $V_{mic}$ from $V_{tot}$. The pore diameter ($D_p$) was estimated by the ratio 4 V/A by BET. A thermogravimetric analyzer (Mettler TGA 2, Swiss) was used to analyze the thermal stability of the lignins. High-purity N$_2$ of 50 mL min$^{-1}$ was used as the carrier gas. A total of 3.7 mg of lignins was added in an aluminum crucible, and then heated from room temperature to 900 °C at 20 °C/min. FTIR was investigated using a Nicolet iS50 FTIR. The sample disks were obtained by mixing 1 wt% of samples and KBr. The FTIR spectrum was taken in a wavelength between 400 and 4000 cm$^{-1}$. The surface characteristics of adsorbents were measured by a scanning electron microscopy (SEM) (Apreo, FEI, Hillsboro, USA), operated at the acceleration voltage of 2.0 kV. XPS was measured on a VG ESCALAB 250XI spectrometer (Thermo Electron) with an Al Kα (1486 eV) X-ray source. The details of XPS measurement could be found in our previous study (Wu and Zhou 2021).

Adsorption of Cr(VI)

Cr(VI) solutions with different concentrations were prepared from various weights of K$_2$Cr$_2$O$_7$. At pH ≈ 2, the HCrO$_4$ was the dominant species of Cr(VI) (Gupta et al. 2013; Memon et al. 2009). Except for HCrO$_4^-$, there were also some Cr$_2$O$_7^{2-}$ in the solution. For presentation purpose, the Cr(VI) oxides were presented as Cr(VI) in this work. The effects of adsorption temperature (25-45 °C), contact time (0-72 h), and Cr(VI) concentration (800-1600 mg L$^{-1}$) on the adsorption were investigated under pH = 2. HCl solution was used to adjust the pH of the solution. The ambient temperature and rotational speed during the adsorption process were controlled by a constant temperature shaker. A total of 50 mg of adsorbent was added into 50 mL Cr(VI) solution during all adsorption experiments. After a certain period of time, 1 mL of solution was taken out and centrifuged at 10,000 rpm for 3 min. The supernatant was collected and diluted. The concentration of the complex between Cr(VI) and 1,5-diphenylcarbazide was determined at 542 nm with a UV-2450 (Shimadzu Co.).

Removal efficiency ($R$) and adsorption quantity ($q_t$) (mg g$^{-1}$) can be calculated by the following formulas:

$$R(\%) = \frac{C_0-C_t \times n}{C_0} \times 100\%$$

$$q_t = \frac{C_0 - C_t \times n}{m}$$

(1)
where $C_0$ represents the original Cr(VI) concentration (mg L$^{-1}$), $C_t$ represents the Cr(VI) concentration (mg L$^{-1}$) after adsorption at time $t$, and $n$ represents the dilution multiple.

To understand the form of chromium in solution after adsorption, a flame atomic absorption spectrophotometer was used (TAS 986F, Beijing Purkinje General Instrument Co., Ltd.) to determine total chromium concentration. The difference between the total chromium and Cr(VI) concentration was the Cr(III) concentration. The adsorption process was performed at 35 °C with Cr(VI) initial concentration of 800 mg L$^{-1}$.

### Results and discussion

#### Structural characterization analysis

**BET analysis**

The $S_{BET}$, $V_{tot}$, and $D_p$ of the three adsorbents are listed in Table 1. Figure 1 shows the pore size distribution diagram measured by the DFT method. Among the three adsorbents, the $S_{BET}$ of ELN (29.78 m$^2$ g$^{-1}$) was the largest, and that of BLN and FS was 11.65 and 8.53 m$^2$ g$^{-1}$, respectively. As observed Fig. 1, all adsorbents almost had no micropores, which could be also demonstrated by the values of $V_{mic}$ (Table 1). Different from ELN, the pore width of BLN and FS was mainly concentrated in the mesoporous range, while ELN contained a large number of macropores. The $D_p$ of ELN was 36.23 nm, with the $V_{tot}$ of 0.2697 cm$^3$ g$^{-1}$. The $D_p$ of BLN was 4.44 nm with the $V_{mic}$ of 0.0129 cm$^3$ g$^{-1}$, while that of FS was 2.86 nm and 0.0061 cm$^3$ g$^{-1}$, respectively. In general, the high surface area and abundant pores are beneficial for the adsorption capacity of materials (Yi et al. 2019).

#### TGA analysis

The TGA and DTG curves of three lignins are illustrated in Fig. 2. As reported, the DTG curves of pure hemicellulose, cellulose, and lignin were different (Dhyani and Bhaskar 2018). Usually, hemicellulose began an early decomposition at 220-315 °C, while cellulose mainly decomposed in the range of 315-400 °C. Different with hemicellulose and cellulose, lignin decomposed slowly under a wide range of temperature from room temperature to 900 °C (Cha et al. 2020; Zhao et al. 2021). As displayed in Fig. 2b, the decomposition of lignins could be roughly divided into three stages. When the temperature increased from 30 to 158 °C (30-200 °C for FS), the mass of lignin decreased slightly, which was mainly attributed to the loss of water. The second stage of ELN, BLN, and FS occurred in the range of 158-295 °C, 158-278 °C, and 200-327 °C, respectively. This stage was mainly due to the decomposition of residual hemicellulose and cellulose in lignin. The last decomposition stage of ELN, BLN, and FS with the maxima for weight loss occurred at 377, 388, and 380 °C, respectively. The weight loss in this stage was mainly ascribed to the rapid decomposition of lignin polymer structure to form a variety of volatile compounds, such as aromatic hydrocarbons and phenols. This was the similar pattern of PCG lignin and ALM lignin reported by Zhang et al. (2012) and Nowakowski et al. (2010), respectively. The maximum decomposition rates of ELN, BLN, and FS were at 375 °C, 387 °C, and 299 °C, respectively. The terminal mass loss of ELN and BLN was 59.98% and 61.01%, while that of FS was 41.44%, indicating that the thermal stability of FS was the best among the three adsorbents.

#### FTIR

According to Fig. 3, the three lignins contained some of the same functional groups, such as O-H at 3422 cm$^{-1}$, symmetric and asymmetric C-H stretching vibrations of methyl and methylene at 2934, 2842, and 1458 cm$^{-1}$ (Popovic et al. 2020; Qi et al. 2016), and characteristic peaks of aromatic ring at 1510 and 1423 cm$^{-1}$ (Luo et al. 2018). All three lignins represented characteristic peaks of syringyl at around 1330, 1114, and 830 cm$^{-1}$, and guaiacyl at 1270 and 1150 cm$^{-1}$. The intensity of the syringyl ring breathing with C-O stretching at 1330 cm$^{-1}$ was highest for BLN (Dai et al. 2017; Zhao et al. 2020). The peak at 1700 cm$^{-1}$ was attributed to the carbonyl groups, the intensity of which in FS was lowest. The phenolic OH and ether could be founded at 1213 cm$^{-1}$ (Tejado et al. 2007). This peak in BLN was sharp, while it was inconspicuous in FS. The peak at 1040 cm$^{-1}$ was typical of primary alcohol C-O (Pan et al. 2016). After chromium ion was adsorbed, the spectra of the three lignins changed greatly. The C-H stretching vibrations, phenolic OH, C-O stretching,

### Table 1  Porous structure parameters of ELN, BLN, and FS

| Sample | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{tot}$ (cm$^3$ g$^{-1}$) | $V_{mic}$ (cm$^3$ g$^{-1}$) | $V_{ext}$ (cm$^3$ g$^{-1}$) | $D_p$ (nm) |
|--------|--------------------------|--------------------------|--------------------------|--------------------------|------------|
| ELN    | 29.78                    | 0.2697                   | -                        | 0.2697                   | 36.23      |
| BLN    | 11.65                    | 0.0129                   | -                        | 0.0129                   | 4.44       |
| FS     | 8.53                     | 0.0061                   | -                        | 0.0061                   | 2.86       |
and carbonyl groups almost disappeared. In addition, new peaks, assigned to the adsorbed chromium ions, appeared at 930 and 544 cm\(^{-1}\) (Das et al. 2008; Ko et al. 2002).

**SEM**

The SEM images of raw ELN, BLN, and FS were quite different (Fig. 4 (a, b, c)). The surface of the ELN exhibited honeycomb-like holes; therefore, it possessed the largest surface area among these three lignins. BLN had a smooth surface with multiple spheres without cracks. The FS surface was relatively flat with some ravines. The SEM images of the three adsorbents were in agreement with the \(S_{BET}\) data. The EDS spectra of the three lignins are shown in Fig. S1 and Fig. 4 (g, h, i). All three lignins contained C, H, and O elements. Except these elements, BLN and FS also contained S elements. After adsorption, there were significant Cr signals on all three lignin surfaces. However, there was no significant difference between the SEM images of ELN and BLN before and after Cr adsorption (Fig. 4(a) and (d), Fig. 4(b) and (e), respectively). However, the SEM image of FS after adsorption of Cr was different from the original FS. Plenty of particles were gathered on the surface of FS after Cr adsorption (Fig. 4(f)).

**XPS**

Figure 5 shows that the three adsorbents all contained elements of C and O. In addition, BLN and FS also contained S element. This phenomenon was consistent with the EDS results. After the completion of adsorption, Cr was detected on all three adsorbents. By comparing the C 1s and O 1s spectra before and after the adsorption (Fig. 6 and Fig. 7), it can be seen that functional groups related to C and O played a non-negligible role in Cr(VI) removal. Taking ELN as an example, the C 1s XPS spectrum of ELN (Fig. 6 (a)) exhibited three peaks (Chen et al. 2018; Djellabi et al. 2019; Ma et al. 2014), which were C-C (53.3%, graphite) at 284.7 eV, C-O (33.9%, alcohol, phenolic hydroxyl, and/or ether) at 286.2 eV, and C=O (12.8%, carbonyl and/or quinine) at 288.2 eV, respectively. After the adsorption of Cr, the proportion of C-O at 286.2 eV decreased to 24.6%, and the proportion of C=O at 288.2 eV increased to 17.2%. It indicated that C-O might be

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Fig. 1 Pore size distributions of ELN (a), BLN (b), and FS (c)

Fig. 2 TGA (a) and DTG (b) curves of ELN, BLN, and FS
oxidized to C=O during the adsorption process. Similarly, according to Fig. 6 (b) and (c), the proportion of C-O in BLN and FS decreased from 38.5% and 42.6% before adsorption to 21.1% and 28.8% after adsorption, respectively, while the proportion of C=O increased from 5.6% and 5.1% to 17.1% and 14.6%, respectively. The high resolution of O1s XPS spectrum proved this phenomenon. As shown in Fig. 7, the O1s spectrum before the adsorption was deconvoluted into three peaks, including C-O, O-C=O, and C=O at 533.5, 532.5, and 531.4 eV, respectively (Chen et al. 2020; Li et al. 2017). After Cr adsorption, the proportion of C=O in ELN, BLN, and FS changed from 12.7%, 13.7%, and 37.7% to 57.0%, 55.7%, and 56.8%, respectively. These changes might be due to oxidation of C-O, especially for ELN and BLN (Qi et al. 2016; Zhao et al. 2020a). The proportion of C-O in ELN and BLN decreased from 27.99% and 31.09% to 3.57% and 4.52%, respectively. Furthermore, the proportion of O-C=O was also decreased, which might be attributed to the complexation between O-C=O and Cr. A new peak at 529.9 eV assigned to Cr-

Fig. 3 FTIR of ELN, BLN, and FS

Fig. 4 SEM images of ELN, BLN, and FS before (a, b, c) and after (d, e, f) Cr(VI) adsorption, and Cr mapping images (g, h, i) after adsorption
O was detected (Shi et al. 2020). According to Fig. 8, the Cr 2p spectra after adsorption of all adsorbents indicated that Cr was existed in two forms: Cr(VI) and Cr(III) (Guo et al. 2017; Zhang et al. 2015). The existence of low-toxic Cr(III) suggested the reduction of highly toxic Cr(VI). In Cr 2p 3/2 and Cr 2p 1/2, the total proportions of Cr(III) adsorbed by ELN, BLN, and FS were 58.3%, 41.7%, and 62.7%, respectively. This indicated that the three adsorbents had a certain adsorption capacity of Cr(III).

### Adsorption of Cr(VI)

#### Effect of time

FS showed a rapid adsorption characteristic at the early moment of adding adsorbents to Cr(VI) solution (Fig. 9). After 30 min of adsorption, the removal efficiency of Cr(VI) by ELN and BLN reached 10.6% and 7.2%, and the adsorption capacity was 63.8 and 43.1 mg g\(^{-1}\), respectively. However, the removal efficiency of Cr(VI) by FS reached 19.2%; moreover, the adsorption quantity was 114.9 mg g\(^{-1}\). It indicated the important role of C-O functional groups on FS surface in the early stage of adsorption. With the extension of time, the removal efficiency gradually slowed down, which was related to the weakening of active sites and mass transfer impetus. The adsorption capacity of the three adsorbents gradually rose. After 4320 min of adsorption, the adsorption process reached adsorption equilibrium. The removal efficiency of ELN, BLN, and FS was 85.0%, 99.4%, and 63.2%, respectively. The adsorption capacity was 509.8, 596.7, and 379.7 mg g\(^{-1}\), respectively. Although ELN had the largest \(S_{BET}\) among these three adsorbents, the adsorption amount of ELN was smaller than that of BLN. It indicated that the role of functional groups was more important during Cr(VI) adsorption, such as phenolic hydroxyl groups.

#### Effect of initial metal concentration

According to Fig. 10, with increasing Cr(VI) concentration, the adsorption amount of the three adsorbents increased. When the concentration rose from 1000 to 1400 mg L\(^{-1}\), the adsorption capacity of ELN, BLN, and FS increased from...
589.2, 697.0, and 443.9 to 626.2, 758.8, and 482.8 mg g\(^{-1}\), respectively. The increased content of Cr(VI) in solution enhanced the driving force between adsorbates and adsorbents, and thus improved the adsorption capacity. Similarly, no matter at what concentration, the adsorption capacity of BLN was always the largest, while that of FS was the smallest. However, at the early moment of the adsorption, FS exhibited the fastest removal efficiency of Cr(VI). This result was in accordance with that in the previous section.

**Effect of temperature**

Fig. S2 shows the effect of temperature on adsorption at different concentrations. It could be seen that the increment of temperature contributed to the enhancement of adsorption capacity. When the adsorption temperature increased from 25 to 45 °C, the adsorption capacity of Cr(VI) on ELN, BLN, and FS increased from 610.6, 731.1, and 427.0 to 710.6, 774.7, and 582.1 mg g\(^{-1}\), with the increment of 100, 43.6, and 155.1 mg g\(^{-1}\), respectively. The adsorption quantity of BLN for Cr(VI) was almost independent of the adsorption temperature, while the adsorption quantity of ELN, especially FS, was highly dependent on the adsorption temperature. At higher temperature, the vibration frequency of Cr(VI) was enhanced, which was beneficial for the collision between lignins and Cr(VI). Moreover, the higher temperature might promote the transfer of electrons from lignins to Cr(VI), resulting in the reduction of Cr(VI) (Chi et al. 2020).

**Study of Cr species during adsorption**

Under 35 °C and pH 2.0, the variation trend of the total Cr, Cr(VI), and Cr(III) in solution with time was investigated at initial Cr(VI) concentration of 800 mg L\(^{-1}\). After 4320 min adsorption, the removal efficiency of Cr(VI) by ELN, BLN, and FS was 71.8%, 84.3%, and 52.1%, respectively (Fig. 11). The total chromium residual rate after ELN, BLN, and FS adsorption was 44.3%, 15.0%, and 62.4%, while the Cr(III) residual amount accounted for 36.4%, 33.0%, and 23.3% of the total chromium residual amount. The concentrations of Cr(III) in solution were 128.8, 39.6, and 116.1 mg L\(^{-1}\), after ELN, BLN, and FS adsorption, respectively (Fig. S3). This fully demonstrated that the three adsorbents could reduce Cr(VI) into Cr(III), although their reduction capacity was different. It was worth noting that Cr(III) was detected at 300 min and 600 min for FS adsorption process, with the content of 129.7 and 141.9 mg L\(^{-1}\), respectively. With the extension of adsorption time, the concentration of Cr(III) first decreased to 75.9 mg L\(^{-1}\) and then steadily increased to 116.1 mg L\(^{-1}\). It indicated that FS might have a strong adsorptive reduction
ability at the early stage of the adsorption, which effectively reduced Cr(VI) into less toxic Cr(III). This might result in the great influence of temperature change on Cr(VI) adsorption by FS. Cr(VI) and Cr(III) competed for limited active sites on the surface of FS, which might be one of the reasons for the weak adsorption ability of FS. In terms of ELN and BLN, especially BLN, no Cr(III) was detected in the solution at the initial adsorption stage.

Adsorption isotherm

The adsorption isotherm was used to provide insight into the affinity or driving force between the adsorbate and adsorbent (Mushtaq et al. 2016). Two of the most commonly used adsorption isotherm models, Langmuir and Freundlich, were used to study the adsorption process (Naushad et al. 2019).

Langmuir adsorption model presumes that adsorption occurs at a specific homogeneous adsorption site within the adsorbent (Tomczyk et al. 2020). Once a molecule occupies an adsorption site, no further equilibrium saturation point of adsorption will occur (Foo and Hameed 2010). In other words, the adsorption process is single-layer adsorption. Its expression is as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where $q_m$ means the maximum monolayer adsorption capacity of Cr(VI) (mg g$^{-1}$), and $K_L$ means the Langmuir constant, which has relation to the affinity between the adsorbate and adsorbent (L mg$^{-1}$). $C_e$ is the residual concentration of adsorbate in solution (mg L$^{-1}$), and $q_e$ means the quantity of adsorbate adsorbed by a unit mass of adsorbent at equilibrium (mg g$^{-1}$). Dimensionless constant $R_L$, also known as the separation factor, is often used to describe the basic features of the Langmuir adsorption model:

$$R_L = \frac{1}{1 + K_L C_e} \quad (4)$$

$R_L$ suggests the adsorption tendency: $R_L = 0$ (irreversible); $R_L > 1$ (unfavorable); $R_L = 1$ (linear); and $0 < R_L < 1$ (favorable) (Martins et al. 2015).
The Freundlich model is more comprehensive, which described multilayer adsorption on heterogeneous surfaces. Its assumption takes into account the molecular interaction between the adsorbate and the adsorbent (Antunes et al. 2017). Its expression is as follows:

\[ q_e = K_F \times C_e^\frac{1}{n} \]  

where \( K_F \) and \( n \) are the Freundlich rate constants designated as adsorption capacity (L g\(^{-1}\)) and adsorption intensity, respectively. The value of \( 1/n \) gives an indication of the favorability of adsorption. If \( 1 > 1/n > 0 \), it suggests that the removal of metal ions is beneficial (Li et al. 2018).

The adsorption isotherms at different temperatures of the three adsorbents were studied. The fitting results are illustrated in Fig. 12. The fitting parameters of the two isothermal models could be found in Table S1 and Table S2. The isotherms of the three adsorbents were in line with the Langmuir model, because their fitting correlation coefficient \( R^2 \) was closer to 1. It indicated that the Cr(VI) adsorption on all the three adsorbents was in single molecular layer. The \( R_L \) value was between 0 and 1, indicating that ELN, BLN, and FS were favorable for Cr(VI) adsorption. Besides, the smaller the \( R_L \) value is, the higher the affinity between lignin and Cr is (Ma et al. 2019). Among the three lignins investigated, BLN showed the smallest \( R_L \) values. At the range of investigated initial concentrations (700-2100 mg L\(^{-1}\)), the \( R_L \) values declined from 0.0017 to 0.0013, 0.0011 to 0.0006, and 0.0004 to 0.0004 at 25, 35, and 45 °C, respectively. At 45 °C and pH = 2, the maximum monolayer adsorption capacity of ELN, BLN, and FS was 801.57, 864.30, and 642.26 mg g\(^{-1}\), respectively.

**Adsorption thermodynamics**

Thermodynamic parameters can be calculated by the equilibrium constant as a function of temperature (Yadav et al. 2013). Gibbs free energy change (\( \Delta G^0 \)), entropy change (\( \Delta S^0 \)), and enthalpy change (\( \Delta H^0 \)) were calculated by the following equations:
\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

where \( K_d \) (mL g\(^{-1}\)) means the thermodynamic equilibrium constant, \( R \) means the gas constant (J mol\(^{-1}\) K\(^{-1}\)), and \( T \) (K) represents the absolute temperature. The plots of \( K_d \) versus \( 1/T \) is illustrated in Fig. S4. The calculated thermodynamic parameters are reported in Table 2. The \( \Delta G^0 \) of the three adsorbents was negative, indicating that the adsorption processes were spontaneous. Furthermore, the \( \Delta G^0 \) declined with increasing temperature, suggesting that the higher the temperature was, the better the adsorption efficiency was. The positive value of \( \Delta H^0 \) indicated the endothermic property of the adsorption process. It was proved that increasing temperature was conducive to the adsorption process (Yadav et al. 2013).

The \( \Delta S^0 \) value was positive, indicating that the randomness of the solid solution interface increased (Singha and Das 2011).

### Adsorption kinetics

For understanding the mass transfer and rate-controlling mechanism during the adsorption process, the kinetic data fitting was investigated by pseudo-first-order and pseudosecond-order kinetic model. Their expressions are as follows (Bhatti et al. 2020):

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) mean the adsorption capacity at equilibrium and time \( t \) (min), respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g
(mg min)$^{-1}$) are the pseudo-first-order and pseudo-second-order equilibrium rate constant, respectively.

The fitting curves of the two dynamics models are illustrated in Fig. 13 and Fig. 14. The kinetic parameters under different conditions are summarized in Table S3 and Table S4. By comparing the data in Table S3 and Table S4, no matter which adsorbent was used, the adsorption was more consistent with pseudo-second-order kinetic model, because the $R^2$ of the second-order kinetic model was larger ($R^2 > 0.995$). This results indicated that the process rate-controlling was mainly due to the chemisorption, in which the adsorbent and the absorbate were connected by electron sharing or electron exchange (Yadav et al. 2013).

**Wastewater simulation**

In wastewater treatment, coexisting ions might compete with Cr(VI) for active sites. Hence, it is necessary to investigate the competitive influence of coexisting anions and cations on Cr(VI). The influence of coexisting ion, including Cu$^{2+}$, Ni$^{2+}$, Al$^{3+}$, Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$, As(V), and As(III), on Cr(VI) removal, was investigated at a concentration of 600 mg L$^{-1}$.

As observed in Fig. 15, on the whole, the presence of coexisting ions had a certain inhibitory effect on Cr(VI) removal. The existence of cations had no influence on Cr(VI) removal by BLN, which was the best among the three lignins. In terms of ELN, Ni$^{2+}$ and Cu$^{2+}$ almost had no effect on Cr(VI) removal efficiency, while the addition of Al$^{3+}$ decreased the removal efficiency from 87.2 to 77.9% after 48 h adsorption. The cations also exhibited some inhibitory effect on FS performance, especially for Al$^{3+}$. As for anions, the effect of As(VI) was largest, especially for ELN. The removal efficiency of Cr(VI) dropped to 62.5% after 600 mg L$^{-1}$ As(VI) addition. As(VI) also exhibited some inhibition on Cr(VI) removal by BLN. The removal efficiency decreased from 99.6 to 78.1%. However, As(V) showed the smallest inhibition for FS. The removal efficiency of Cr(VI) by FS only dropped from 63.8 to 56.4%. However, As(VI) showed the smallest inhibition for all three lignins, which might be due to its similar ionic radius with HCrO$_4^-$. To sum up, BLN displayed the best selectivity for Cr(VI) without regard to As(VI) effect. ELN exhibited the worst selectivity among the three lignins investigated.

**Potential adsorption mechanism**

Based on the above discussion, the potential adsorption mechanism of Cr(VI) by three lignins is illustrated in Fig. 16.

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**Table 2** Thermodynamic constants for the adsorption of Cr(VI) on the three adsorbents at various temperatures

| Adsorbents | $T$ K | $K_d$ | $\Delta G^0$/kJ mol$^{-1}$ | $\Delta H^0$/kJ mol$^{-1}$ | $\Delta S^0$/J mol$^{-1}$ K$^{-1}$ | $R^2$ |
|------------|-------|-------|---------------------------|---------------------------|---------------------------------|-------|
| ELN        | 298   | 1.706 | $-4.229$                  | 36.581                    | 126.955                         | 0.9812 |
|            | 308   | 2.550 | $-6.533$                  |                           |                                 |       |
|            | 318   | 4.322 | $-11.433$                 |                           |                                 |       |
| BLN        | 298   | 4.928 | $-12.215$                 | 5.066                     | 30.263                          | 0.9459 |
|            | 308   | 5.363 | $-13.741$                 |                           |                                 |       |
|            | 318   | 5.601 | $-14.816$                 |                           |                                 |       |
| FS         | 298   | 0.886 | $-2.196$                  | 20.576                    | 67.842                          | 0.9613 |
|            | 308   | 1.089 | $-2.789$                  |                           |                                 |       |
|            | 318   | 1.495 | $-3.953$                  |                           |                                 |       |

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Fig. 13 Pseudo-first-order kinetic model fitting of Cr(VI) adsorption on adsorbents. a ELN. b BLN. c FS
lignins with abundant functional groups, such as carboxyl and hydroxyl groups, could effectively adsorb Cr(VI) from aqueous solution through electrostatic attraction or complexation. Then, Cr(VI) was reduced to Cr(III) with the assistance of electron-donor groups. The possible reduction is shown in Eqs. (10)-(11). The produced Cr(III) could be partially immobilized through complexation or precipitation.

\[ \text{HCrO}_4^- + 3e^- + 7H^+ \rightarrow \text{Cr}^{3+} + 4H_2O \quad (10) \]

\[ \text{Cr}_2\text{O}_7^{2-} + 6e^- + 14H^+ \rightarrow 2\text{Cr}^{3+} + 7H_2O \quad (11) \]

**Conclusion**

Removal efficiency of Cr(VI) by different industrial lignins were systematically compared in this study. Among
these three lignins, BLN exhibited the largest adsorption capacity of Cr(VI), while that of FS was smallest. According to the adsorption kinetics and thermodynamics study, Langmuir model and pseudo-second-order kinetic model could well explain the adsorption of Cr(VI) by the adsorbent. In this process, the increase of temperature was conducive to the improvement of adsorption capacity. According to the Langmuir model, the maximum monolayer adsorption amount of ELN, BLN, and FS was 801.57, 864.30, and 642.26 mg g\(^{-1}\) at 45 °C and pH = 2, respectively. During the wastewater simulation experiment, BLN showed the optimal selectivity of Cr(VI), and FS was the medium. The adsorption of Cr(VI) on three lignins was a chemisorption process, during which Cr(VI) was reduced to Cr(III) with low toxicity. Therefore, industrial lignin has a broad application prospect for heavy metal adsorption.

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Declarations

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References

Anirudhan TS, Nima J, Divya PL (2013) Adsorption of chromium(VI) from aqueous solutions by glycidylmethacrylate-grafted-densified cellulose with quaternary ammonium groups. Appl Surf Sci 279: 441–449

Antunes E, Jacob MV, Brodie G, Schneider PA (2017) Silver removal from aqueous solution by biochar produced from biosolids via microwave pyrolysis. J Environ Manag 203:264–272

Bhatti HN, Mahmood Z, Kauras A, Yakout SM, Shair OH, Iqbal M (2020) Biocomposites of polypyrrole, polyaniline and sodium alginate with cellulosic biomass: adsorption-desorption, kinetics and thermodynamic studies for the removal of 2,4-dichlorophenol. Int J Biol Macromol 153:146–157

Cha YL, Alam AM, Park SM, Moon YH, Kim KS, Lee JE, Kwon DE, Kang YG (2020) Hydrothermal-process-based direct extraction of polydispers lignin microspheres from black liquor and their physicochemical characterization. Bioresour Technol 297:122399

Chen Z, Wan C (2017) Biological valorization strategies for converting lignin into fuels and chemicals. Renew Sust Energ Rev 73:610–621

Chen S, Wang J, Wu Z, Deng Q, Tu W, Dai G, Zeng Z, Deng S (2018) Enhanced Cr(VI) removal by polyethyleneimine- and phosphorus-codoped hierarchical porous carbons. J Colloid Interface Sci 523:110–120

Chen W, Li K, Chen Z, Xia M, Chen Y, Yang H, Chen X, Chen H (2020) A new insight into chemical reactions between biomass and alkaline additives during pyrolysis process. Proc Combust Inst 38:3881–3890

Chi Z, Hao L, Dong H, Yu H, Liu H, Wang Z, Yu H (2020) The innovative application of organosolv lignin for nanomaterial modification to boost its heavy metal detoxification performance in the aquatic environment. Chem Eng J 382:122789

Dai G, Zou Q, Wang S, Zhao Y, Zhu L, Huang Q (2017) Effect of torrefaction on the structure and pyrolysis behavior of lignin. Energy Fuel 32:4160–4166

Das S, Mukherjee M, Guha A (2008) Interaction of chromium with resistant strain Aspergillus versicolor: investigation with atomic force microscopy and other physical studies. Langmuir 24:8643–8650

Dhyani V, Bhaskar T (2018) A comprehensive review on the pyrolysis of lignocellulosic biomass. Renew Energy 129:695–716

Djellabi R, Yang B, Wang Y, Cui X, Zhao X (2019) Carbonaceous biomass-titania composites with Ti O C bonding bridge for efficient photocatalytic reduction of Cr(VI) under narrow visible light. Chem Eng J 366:172–180

Fuu KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156:2–10

Fu K, Yue Q, Gao B, Sun Y, Zhu L (2013) Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation. Chem Eng J 228:1074–1082

Gan C, Liu Y, Tan X, Wang S, Zeng G, Zheng B, Li T, Jiang Z, Liu W (2015) Effect of porous zinc–biochar nanocomposites on Cr(vi) adsorption from aqueous solution. RSC Adv 5:35107–35115
Gao Y, Yue Q, Gao B, Sun Y, Wang W, Li Q, Wang Y (2013) Preparation of high surface area-activated carbon from lignin of papermaking black liquor by KOH activation for Ni(II) adsorption. Chem Eng J 217:345–353

Ge Y, Li Z (2018) Application of lignin and its derivatives in adsorption of heavy metal ions in water: a review. ACS Sustain Chem Eng 6: 7181–7192

Gregorová A, Košiková B, Moravčík R (2006) Stabilization effect of lignin in natural rubber. Polym Degrad Stab 91:229–233

Guo Z, Zhang J, Liu H, Kang Y (2017) Development of a nitrogen-functionalized carbon adsorbent derived from biomass waste by diammonium hydrogen phosphate activation for Cr(VI) removal. Powder Technol 318:459–464

Gupta VK, Pathania S, Sharma A, Agarwal S, Singh P (2013) Remediation of noxious chromium (VI) utilizing acrylic acid grafted lignocellulosic adsorbent. J Mol Liq 177:343–352

Kesaano M, Sims RC (2014) Algal biofilm based technology for wastewater treatment. Algal Res 5:231–240

Kwak HW, Kim MK, Lee JY, Yun H, Kim MH, Park YH, Lee KH (2015) Preparation of head-type biosorbent from water-soluble Spirulina platensis extracts for chromium (VI) removal. Algal Res 7:92–99

Lauwaert J, Stals I, Lancefield CS, Deschaumes W, Depuydt D, Vanlengerbe Ge, De Lamynck T, Brujinixx PCA, Verberckmoes A (2019) Pilot scale recovery of lignin from black liquor and advanced characterization of the final product. Sep Purif Technol 221:226–235

Li C, Zhao X, Wang A, Huber GW, Zhang T (2015) Catalytic transformation of lignin for the production of chemicals and fuels. Chem Rev 115:11559–11624

Li Z, Chen J, Ge Y (2017) Removal of lead ion and oil droplet from aqueous solution by lignin-grafted carbon nanotubes. Chem Eng J 308:809–817

Li Y, Zhang J, Liu H (2018) In-situ modification of activated carbon with ethyleneimine-aetraenic acid disodium salt during phosphoric acid activation for enhancement of nickel removal. Powder Technol 325:113–120

Liang Y, Duan W, An X, Qiao Y, Tian Y, Zhou H (2020) Novel betaine-amino acid based natural deep eutectic solvents for enhancing the enzymatic hydrolysis of corncob. Bioresour Technol 310:123389

Luo M, Lin H, Li B, Dong Y, He Y, Wang L (2018) A novel modification of lignin on corncob-based biochar to enhance removal of cadmium from water. Bioresour Technol 259:312–318

Ma X, Zhang F, Zhu J, Yu L, Liu X (2014) Preparation of highly developed mesoporous activated carbon fiber from liquefied wood using wood charcoal as additive and its adsorption of methylene blue from solution. Bioresour Technol 164:1–6

Ma H, Yang J, Gao X, Liu Z, Liu X, Xu Z (2019) Removal of chromium (VI) from water by porous carbon derived from corn straw: influencing factors, regeneration and mechanism. J Hazard Mater 369:550–560

Martins AC, Pezoti O, Cazetta AL, Bedin KC, Yamazaki DAS, Bandoch EF, Asefa T, Visentainer JV, Almeida VC (2015) Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: kinetic and equilibrium studies. Chem Eng J 260:291–299

Memon JR, Memon SQ, Bhaner MI, El-Turki A, Hallam KR, Allen GC (2009) Banana peel: a green and economical sorbent for the selective removal of Cr(VI) from industrial wastewater. Colloids Surf B: Biointerfaces 70:232–237

Mushtaq M, Bhatti HN, Iqbal M, Norreen S (2016) Eriobotrya japonica seed bio-composite efficiency for copper adsorption: isotherms, kinetics, thermodynamic and desorption studies. J Environ Manag 176:21–33

Naushad M, Ahamad T, Alothman ZA, Al-Muhtaseb AH (2019) Green and eco-friendly nanocomposite for the removal of toxic Hg(II) metal ion from aqueous environment: adsorption kinetics & isotherm modelling. J Mol Liq 279:1–8

Nowakowski DJ, Bridgwater AV, Elliott DC, Meier D, de Wild P (2010) Lignin fast pyrolysis: results from an international collaboration. J Anal Appl Pyrolysis 88:53–72

Pan Y, Cai P, Parmahini-Farahani M, Li Y, Hou X, Xiao H (2016) Amine-functionalized alkaline clay with cationic star-shaped polymer as adsorbents for removal of Cr(VI) in aqueous solution. Appl Surf Sci 385:333–340

Pham TD, Tran TT, Le VA, Pham TT, Dao TH, Le TS (2019) Adsorption characteristics of molecular oxytetracycline onto alumina particles: the role of surface modification with an anionic surfactant. J Mol Liq 287:110900

Pham TD, Pham TT, Pham MN, Ngo TMV, Dang VD, Vu CM (2020) Adsorption characteristics of anionic surfactant onto laterite soil with differently charged surfaces and application for cationic dye removal. J Mol Liq 301:301

Qi W, Zhao Y, Zheng X, Ji M, Zhang Z (2016) Adsorption behavior and mechanism of Cr(VI) using Sakura waste from aqueous solution. Appl Surf Sci 360:470–476

Ralph J, Lapierre C, Boerjan W (2019) Lignin structure and its engineering. Curr Opin Biotechnol 56:240–249

Shi X, Qiao Y, An X, Tian Y, Zhou H (2020) High-capacity adsorption of Cr(VI) by lignin-based composite: characterization, performance and mechanism. Int J Biol Macromol 156:1160–1173

Qi W, Zhao Y, Zheng X, Ji M, Zhang Z (2016) Adsorption behavior and mechanism of Cr(VI) using Sakura waste from aqueous solution. J Mol Liq 301:301

Tejado A, Pena C, Labidi J, Echeverria J, Mondragon I (2007) Physico-chemical characterization of limns from different sources for use in phenol-formaldehyde resin synthesis. Bioresour Technol 98:1655–1663

Terrell E, Carré V, Dufour A, Aubriet F, Le Brech Y, Garcia-Pérez M (2020) Contributions to lignomics: stochastic generation of oligomeric lignin structures for interpretation of MALDI-FT-ICR-MS results. ChemSusChem 13:4428–4445

Tomczyk A, Sokolowska Z, Boguta P (2020) Biomass type effect on biochar surface characteristic and adsorption capacity relative to silver and copper. Fuel 278:118168

Tnong TTT, Vu TN, Dinh TD, Pham TT, Nguyen TAH, Nguyen MH, Nguyen TD, Yusa S-i, Pham TD (2021) Adsorptive removal of cefixime using a novel adsorbent based on synthesized polycation coated nanosilica rice husk. Prog Org Coat 158

Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27:195–226

Wu W, Zhou H (2021) One-pot preparation of NaBiO3/PNMA composite: surface properties and photocatalytic performance. Appl Surf Sci 544:148910

Xu F, Sun J-X, Sun R, Fowler P, Baird MS (2006) Comparative study of organosol lignins from wheat straw. Ind Crop Prod 23:180–193

Yadav S, Srivastava V, Banerjee S, Weng C-H, Sharma YC (2013) Adsorption characteristics of modified sand for the removal of hexavalent chromium ions from aqueous solutions: kinetic, thermodynamic and equilibrium studies. Catena 100:120–127
Yi Y, Tu G, Zhao D, Tsang PE, Fang Z (2019) Biomass waste components significantly influence the removal of Cr(VI) using magnetic biochar derived from four types of feedstocks and steel pickling waste liquor. Chem Eng J 360:212–220
Zhang M, Resende FLP, Moutsoglou A, Raynie DE (2012) Pyrolysis of lignin extracted from prairie cordgrass, aspen, and Kraft lignin by Py-GC/MS and TGA/FTIR. J Anal Appl Pyrolysis 98:65–71
Zhang Y-J, Ou J-L, Duan Z-K, Xing Z-J, Wang Y (2015) Adsorption of Cr(VI) on bamboo bark-based activated carbon in the absence and presence of humic acid. Colloids Surf A Physicochem Eng Asp 481:108–116
Zhang X, Lv L, Qin Y, Xu M, Jia X, Chen Z (2018) Removal of aqueous Cr(VI) by a magnetic biochar derived from Melia azedarach wood. Bioresour Technol 256:1–10
Zhao Y, Jing S, Peng X, Chen Z, Hu Y, Zhuo H, Sun R, Zhong L (2020a) Synthesizing green carbon dots with exceptionally high yield from biomass hydrothermal carbon. Cellulose 27:415–428
Zhao Y, Tian Y, Zhou H, Tian Y (2020b) Hydrothermal conversion of black liquor to phenolics and hydrochar: characterization, application and comparison with lignin. Fuel 280:118651
Zhao Y, Zhang H, Zong P, Zhou H, Tian Y (2021) Evaluation of pyrolysis characteristics and product distribution of black liquor using Py-GC/MS and down tube reactor: comparison with lignin. Fuel 292:120286
Zhou H, Chang Y, Wu X, Yang D, Qiu X (2015) Horseradish peroxidase modification of sulfomethylated wheat straw alkali lignin to improve its dispersion performance. ACS Sustain Chem Eng 3:518–523
Zhou H, Qiu X, Yang D, Xie S (2016a) Laccase and xylanase incubation enhanced the sulfomethylation reactivity of alkali lignin. ACS Sustain Chem Eng 4:1248–1254
Zhou H, Chang Y, Zhu JY (2016b) Molecular structure of sodium lignosulfonate from different sources and their properties as dispersant of TiO2 slurry. J Dispers Sci Technol 37:296–303
Zhou H, Gleisner R, Zhu JY, Tian Y, Qiao Y (2018) SPORL pretreatment spent liquors enhance the enzymatic hydrolysis of cellulose and ethanol production from glucose. Energy Fuel 32:7636–7642
Zhou H, Shi X, Wu W, An X, Tian Y, Qiao Y (2020) Facile preparation of lignosulfonate/N-methylaniline composite and its application in efficient removal of Cr(VI) from aqueous solutions. Int J Biol Macromol 154:1194–1204

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