Adsorption of Toxic Zinc by Functionalized Lignocellulose Derived from Waste Biomass: Kinetics, Isotherms and Thermodynamics

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Abstract: Heavy metals pollution receives worldwide attention due to great toxicity, significant bio-accumulation and non-biodegradability. Adsorption is a promising technique for removing heavy metals from wastewater. Adsorption of zinc (Zn(II)) from aqueous solution was investigated by functionalized lignocellulose derived from fallen leaves. Alkalized lignocellulose (AC), xanthated lignocellulose (XC) and carboxylated lignocellulose (CC) were characterized by Fourier transform infrared spectrum (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The effect of sorbent dosage, solution pH, sorption time and initial Zn(II) concentration on Zn(II) sorption was investigated by single-factor experiment. Sorption kinetics, isotherms and thermodynamics were examined to reveal sorption mechanism. The sorption capacity and removal rate remarkably depend on experimental variables. Zn(II) sorption onto AC, XC and CC is well described by the pseudo second order kinetics and Langmuir isotherm. The sorption process is fast, reaching sorption equilibrium at 30 min. The maximum sorption capacity of Zn(II) onto CC is 46.49 mg/g, higher than that onto AC, XC and other reported sorbents. Thermodynamic parameters indicate that Zn(II) sorption is a spontaneous process. Sorption mechanism is majorly attributed to surface complexation. This work shows the feasibility of removing toxic Zn(II) from aqueous solution by locally available biomass, providing a sustainable approach for wastewater treatment.

Keywords: adsorption; chemical modification; heavy metals; waste biomass; wastewater treatment

1. Introduction

Heavy metals (HMs) cause a serious threat to ecological system and public health, due to great toxicity, significant bio-accumulation and non-biodegradability [1,2]. HMs in water can be easily taken in by organism and accumulated in animals and human beings via food chain. The accumulated HMs in living tissues and organs results in serious diseases and disorders [3]. Therefore, HMs should be strictly controlled to meet the safe discharge standards. Various techniques are proposed for management of HMs pollution [4,5]. Among these techniques, adsorption is very promising because of the advantages of easy operation, low cost and possibility of metal recovery.

Adsorbents are the key material for adsorption process. Great efforts have been conducted to develop effective adsorbents for HMs. Various advanced materials, such as carbon nanotubes [6], graphene oxide nanocomposites [7] and biopolymer nanofiber membranes [8], have attracting performance for HMs adsorption, but the cost and preparation process significantly limits their real application. The common commercial adsorbents, such as activated carbon and ion exchange resins, are relatively expensive for application [9]. Recently, sorption of HMs by lignocellulosic biomass (LCB) has been the focus of
considerable studies, and adsorbents derived from waste biomass have been proved to be effective to promote sustainability owing to the renewability, eco-friendliness and low cost of biomass [10,11]. Natural LCB is mainly composed of cellulose, hemicelluloses and lignin, containing various polar groups involving alcohol, aldehyde, carboxylic and ether groups. These groups have ability to donate an electron pair to form complexes with HMs. Most of the adsorption studies have been focused on untreated LCB including persimmon leaf [12], Landoltia punctata and Spirodela polyrhiza [13], Cinnamomum camphora [14] and orange peel [15].

However, natural LCB shows low adsorption capacity and causes negative effects on water such as high chemical oxygen demand, due to the release of soluble organic compounds contained in the materials [16]. Chemical modifications are proposed to reduce soluble organic compounds and/or increase functional groups, which enhances complexation ability to HMs. Biosorption of Cd(II), Cu(II) and Zn(II) was examined using sodium hydroxide immersed Cymbopogon schoenanthus L. Spreng [17]. Introduction of xanthate and carboxylate groups on porous starch improved Pb(II) sorption [18]. Modifications of olive tree pruning with nitric acid, sulfuric acid and sodium hydroxide were compared for Pb(II) sorption, and sodium hydroxide modification gave best performance [19]. Removal of Pb(II) ions from aqueous solution was investigated using nitric acid pretreated Tephrosia purpurea leaf [20]. Microwave-assisted modification of jute fiber was reported for HMs removal, and the modification removed non-cellulose substances and introducing carboxyl groups [21]. Ultrasound-assisted xanthation of Cinnamomum camphora is optimized for Pb(II) sorption [22]. Previous studies have proven the effectiveness of modification of LCB for HMs adsorption.

Zinc, as an essential trace element for human health, is vital for physiological functions of tissues and organs. However, excessive zinc causes serious health problems including anemia, nausea, skin irritations and stomach cramps [23]. Zn(II) was used as target toxic metal to evaluate sorption efficiency of the prepared sorbents. To the best of our knowledge, Zn(II) sorption by chemically modified LCB from waste biomass is investigated in this work. The main objective of this study is to examine the sorption behavior and mechanism of Zn(II) ion on modified lignocellulose from LCB, specifically (1) to characterize the physicochemical properties of sorbents; (2) to determine the effect of experimental factors including sorbent dosage, solution pH, sorption time and initial Zn(II) concentration; (3) to reveal sorption mechanism by studying sorption kinetics, isotherms and thermodynamics.

2. Materials and Methods
2.1. Materials
Samples of waste biomass were locally obtained fallen leaves in Changsha city, China. The samples were washed, dried and ground into 0.3–0.076 mm. All used chemicals were analytical grade. Zn(II) solution of 1000 mg/L was prepared by dissolving zinc nitrate hexahydrate in a 1 L volumetric flask. Zn(II) solutions with different concentration were prepared by serial dilutions. Visual MINTEQ 3.1, a chemical equilibrium freeware for the calculation of metal speciation, solubility equilibria, etc., was used to examine the zinc ion species in aqueous solution.

2.2. Preparation of Functionalized Cellulose
Alkali treatment of the waste biomass with 1.0 mol/L NaOH solution was conducted to obtain alkalized lignocellulose (AC). Xanthation of AC assisted by ultrasound was carried out to obtain xanthated lignocellulose (XC). Experimental conditions were NaOH concentration 1.3 mol/L, ultrasonic time 72 min and CS2 dosage 1.5 mL. Carboxylated lignocellulose (CC) was gained by carboxylation modification of AC. Briefly, AC (5 g) was reacted with succinic anhydride (15 g) under pyridine reflux (50 mL) for 24 h. The yield of the prepared sorbents was calculated via \( \frac{M}{M_0} \times 100 \), where M and is the final and initial mass of cellulose, respectively.
2.3. Characterizations

Fourier transform infrared spectra were recorded using a Nicolet Avatar 360 FTIR spectrometer (Nicolet Magua Corporation, USA) to characterize the functional groups of the sorbents. The surface elements were determined by an ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS; Thermo Electron Corporation, USA), and binding energies were referenced to the Cls peak at 284.6 eV. A Quanta FEG 250 scanning electron microscopy (SEM; FEI, USA) was used to determine surface morphology of sorbents.

2.4. Sorption Experiments

Zn(II) sorption was evaluated in an SHA-B thermostatic oscillator (Changzhou Aohua Instrument Co. Ltd., China) at stirring speed of 150 rpm. Experimental conditions were fixed at 200 mg/L Zn(II) solution, sorption time 30 min and room temperature (30 ± 2 °C). The effect of sorbent dosage (2–32 g/L), pH (1–7), sorption time (0–90 min) and initial concentration (50–1200 mg/L) on Zn(II) sorption was investigated. After sorption, Zn(II) concentration was determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES, Perkin Elmer Optima 5300 DV). The removal rate and sorption capacity of Zn(II) were calculated by Equations (1) and (2).

\[
R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)
\]

\[
Q = \frac{(C_0 - C_e)V}{m} \quad (2)
\]

where \( R \) is the removal rate, %; \( Q \) is the sorption capacity, mg/g; \( C_0 \) and \( C_e \) is the initial and equilibrium concentration of Zn(II), mg/L; \( V \) is the volume of solution, L; \( m \) is the mass of sorbent, g.

To provide better understanding of sorption process, sorption kinetics, isotherms and thermodynamics were investigated employing multiple models. The pseudo first order, pseudo second order and Weber–Morris kinetic models are shown as Equations (3)–(10).

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)
\]

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)
\]

\[
Q_t = k_i t^{0.5} + C_i \quad (5)
\]

where \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg min)) are the rate constant of pseudo first order model and pseudo second order model; \( t \) is the contact time; \( Q_i \) (mg/g) and \( Q_e \) (mg/g) are the sorption capacity of Zn(II) at time \( t \) and equilibrium sorption capacity.

The Langmuir and Freundlich isotherm models are shown as Equations (6) and (7).

\[
\frac{C_e}{Q_e} = \frac{b}{Q_m} + \frac{C_e}{Q_m} \quad (6)
\]

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)
\]

where \( C_e \) (mg/L) is the equilibrium concentration of Zn(II); \( Q_e \) (mg/g) is equilibrium sorption capacity of Zn(II); \( Q_m \) (mg/g) is the maximum sorption capacity; \( b \) (L/mg) is a constant that relates to the sorption heat; \( K_F \) and \( n \) are Freundlich constants indicating sorption capacity and sorption intensity, respectively.

To examine sorption thermodynamics, the Gibbs free energy change, enthalpy change and entropy change were calculated based on Equations (8)–(10).

\[
\Delta G = -RT \ln K_c \quad (8)
\]

\[
\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)
\]
\[ K_c = \frac{Q_e}{C_e} \]  
(10)

where \( \Delta G \) (kJ/mol) is the Gibbs free energy change; \( \Delta H \) (kJ/mol) is the enthalpy change; \( \Delta S \) (J/(mol K)) is the entropy change; \( K_c \) is the equilibrium constant; \( Q_e \) (mg/g) is the equilibrium sorption capacity; \( C_e \) (mg/L) is the equilibrium concentration of Zn(II); \( R \) (8.314 J/(K mol)) is the gas constant; \( T \) (K) is the temperature in Kelvin.

3. Results and Discussion

3.1. Characterizations

Preparation of functionalized lignocellulose is shown in Figure 1. Major ingredients of raw biomass are cellulose, hemi-cellulose and lignin [24]. Alkali treatment is conducted to extract cellulose by partly removing hemi-cellulose, lignin and low molecular weight matters. The reactivity and accessibility of hydroxyl groups in cellulose molecules can be improved [25]. Xanthation and carboxylation of AC are carried out to further modify cellulose derived from biomass, and they induce more functional groups for metal sorption [26,27]. It should be noted that complete extraction of cellulose from LCB using the alkalization process is not possible, and therefore functionalization reaction with hemicellulose and lignin cannot be completely ruled out. The yield of AC, XC and CC is 81.7%, 94.2% and 97.6%, respectively. The properties of AC, XC and CC are studied by FTIR, XPS and SEM analysis.

![Figure 1. Preparation of functionalized lignocellulose from waste biomass.](image)

In Figure 2a, characteristic peaks of AC, XC and CC are observed in FTIR spectra. The broad peak at 3426 cm\(^{-1}\) attributes to stretching vibrations of -OH. The peaks at 2851 and 2920 cm\(^{-1}\) assign to asymmetric and symmetric vibrations of \(-\text{CH}_2\) groups [27]. The peaks at 1000–1200 and 1635 cm\(^{-1}\) are due to vibrations of C-O and C=O bonds [28]. As to XC, C=S and C-S groups are determined by the peaks at 582 and 1024 cm\(^{-1}\), verifying the creation of xanthate groups after xanthation modification [22]. As to CC, the peak at 1735 cm\(^{-1}\) corresponds to C=O groups, revealing the presence of carboxyl groups after carboxylation modification. FTIR analysis manifests the introduction of more surface groups through modifications.

As shown in Figure 2b, the XPS survey spectra show that major elements of AC, XC and CC are carbon and oxygen, which agrees well with the major ingredients of cellulose. The increase of sulfur content in XC and high resolution S2p spectra verify the presence of xanthate groups [22]. After carboxylation, the O/C ratio increases from 0.1880 to 0.3367, implying that more carboxyl groups are introduced on the surface. SEM micrograph of XC and CC is similar to that of AC, showing the porous and uneven surface morphology. Additionally, XC and CC have more pore structures, which favor metal sorption [14].
3.2. Sorption Studies

3.2.1. Effect of Sorbent Dosage on Zn(II) Sorption

In Figure 3, the sorption capacity of Zn(II) onto AC, XC and CC reduces with an increase of sorbent dosage. The phenomena can be attributed to unsaturation sorption and particle aggregation [18]. On the contrary, the removal rate increases significantly with increasing AC, XC and CC dosage, which attributes to more sorption sites derived from more sorbents [14]. The sorption behavior is consistent with Zn(II) sorption onto modified lemon grass [17]. Taking sorption capacity and removal rate into consideration, the optimal dosages for Zn(II) sorption are chosen as 24 g/L AC, 12 g/L XC and 12 g/L CC, respectively.
3.2.2. Effect of Solution pH on Zn(II) Sorption

Solution pH affects metal species in aqueous solution and functional groups on sorbent surface [29]. Figure 4 shows that Zn(II) free ions are the predominant species in aqueous solution at pH below 7 [30]. The effect of solution pH on Zn(II) sorption is examined at pH below 7, and alkaline solution is not used to avoid the formation of hydroxide precipitation. Figure 5 reveals that Zn(II) sorption is dependent on solution pH. The sorption capacity and removal rate increase with an increase of pH, especially at pH below 3.5. The results are similar to the study reported by Nasernejad et al. [31].

In sorption process, besides surface complexation, ion exchange may occur due to the negatively charged oxygen or sulfur atoms (−O−Na+, −COO−Na+ and −CSS−Na+) [22]. At low pH, abundant H+ or H3O+ leads to protonation of surface groups, causing fewer sites being available for Zn(II) sorption. Additionally, the binding H+ or H3O+ ions restricts the approach of Zn(II) cations by electrostatic repulsion [32]. It is expected that there is a competition between H+ or H3O+ and Zn(II) ions for the free sorption sites at low pH. By contrast, CC has higher sorption capacity and is more sensitive to solution pH. The difference in sorption behavior of Zn(II) onto AC, XC and CC is mainly ascribed to the functional groups.

3.2.3. Effect of Sorption Time on Zn(II) Sorption

In Figure 6, the sorption capacity and removal rate of Zn(II) increase sharply with increasing sorption time at the initial stage, mainly attributing to abundant vacant sorption sites on sorbent surface. Sorption equilibrium is achieved at sorption time over 30 min due to saturation sorption. Compared with other reports [33,34], Zn(II) sorption in this work
is faster. At equilibrium, the removal rate of Zn(II) onto AC, XC and CC is $99.04 \pm 0.3\%$, $99.20 \pm 0.4\%$ and $98.68 \pm 0.9\%$, respectively. The larger sorption capacity of XC and CC proves that xanthation and carboxylation modifications improve the performance for Zn(II) sorption.

### 3.2.4. Effect of Initial Concentration on Zn(II) Sorption

The effect of initial Zn(II) concentration on sorption process is shown in Figure 7. The sorption capacity rises remarkably with increasing initial concentration. The concentration gradient provides the driving force for overcoming diffusion resistances of Zn(II) ions [29]. At high concentration, the sorption sites on sorbent surface are made full use for Zn(II) uptake, and thus the sorption capacity gradually reaches a plateau due to saturation sorption [30]. The removal rate drops significantly with increasing Zn(II) concentration. By contrast, CC shows higher sorption capacity at high concentration, which can be due to the presence of abundant carboxyl groups. For a given dosage, AC, XC and CC are suitable for managing wastewater with low Zn(II) concentration.

![Figure 6. Effect of sorption time on Zn(II) sorption (AC 24 g/L, XC 12 g/L, CC 12 g/L, pH 5.5 ± 0.2, and Zn(II) concentration 200 mg/L).](image)

**Figure 6.** Effect of sorption time on Zn(II) sorption (AC 24 g/L, XC 12 g/L, CC 12 g/L, pH 5.5 ± 0.2, and Zn(II) concentration 200 mg/L).

### 3.3. Sorption Kinetics

Sorption kinetics is studied by pseudo first order (PFO), pseudo second order (PSO) and intraparticle diffusion (IPD) models [35–37]. The parameters for kinetics models are listed in Table 1. The correlation coefficients suggest that PFO and IPD models cannot describe the sorption process, especially for IPD model. This indicates that Zn(II) sorption is not controlled by internal diffusion. Figure 8a shows that PSO model exhibits well-fitting of sorption data. The rate constant of PSO model manifests that Zn(II) sorption onto AC is
faster than that onto XC and CC. Generally, HMs sorption in aqueous solution involves (i) bulk diffusion, solute diffuses from the bulk solution to the liquid film surrounding sorbent surface; (ii) film diffusion, solute transports from the liquid film to sorbent surface; (iii) internal diffusion, solute moves from the surface to active intra-sites, and (iv) interactions between solute and sorption sites on internal surfaces [36]. One or more steps dominate metal sorption onto porous sorbents, and generally bulk diffusion is fast. The sorption behavior as a function of sorption time suggests that Zn(II) sorption onto AC, XC and CC is fast.

Table 1. Parameters for sorption kinetics.

| Sorbents | PFO Model | PSO Model | IPD Model |
|----------|-----------|-----------|-----------|
|          | $Q_i$ (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ | $Q_i$ (mg/g) | $k_2$ (g/(mg min)) | $R^2$ | $C$ | $k_i$ | $R^2$ |
| AC       | 0.0566 | 0.0596 | 0.8982 | 8.4947 | 3.5262 | 1.0 | 8.4083 | 0.0109 | 0.4656 |
| XC       | 0.7183 | 0.0861 | 0.8923 | 18.4060 | 0.2934 | 1.0 | 17.2527 | 0.1486 | 0.4151 |
| CC       | 0.5192 | 0.0553 | 0.9580 | 21.2811 | 0.4029 | 1.0 | 20.6397 | 0.0795 | 0.6050 |

Figure 8. (a) PSO kinetics plots and (b) Langmuir isotherms for Zn(II) sorption onto AC, XC and CC.

Mechanism for HMs adsorption generally involves physical adsorption, ion exchange, surface precipitation, surface complexation and electrostatic interaction [38]. The porous structure of AC, XC and CC is mainly derived from raw biomass, and thus physical adsorption due to porous structure contributes little to Zn(II) sorption. Due to the functional groups caused by modifications, Zn(II) sorption onto XC and CC can be explained by surface complexation or ion exchange. The well-fitting PSO reveals that Zn(II) sorption onto AC, XC and CC is dominated by chemisorption that involves transferring or sharing of electrons [27,32].

3.4. Sorption Isotherms

Zn(II) sorption onto AC, XC and CC is examined by Langmuir and Freundlich isotherms (Wang et al., 2018a). Parameters for Langmuir and Freundlich models are shown in Table 2. The sorption process can be well described by Langmuir and Freundlich models. The Freundlich parameter, $n$ ($2 < n < 10$), reveals that Zn(II) sorption on the sor-
bents is favorable. Figure 8b shows good linear fitting to sorption data by Langmuir model. Owing to high correlation coefficient and consistency between calculated and experimental values of \( Q_m \), Zn(II) sorption onto AC, XC and CC follows Langmuir isotherm.

Table 2. Parameters for sorption isotherms.

| Sorbents | Langmuir Model | Freundlich Model |  
|----------|----------------|------------------|  
|          | \( Q_m \) (mg/g) | \( b \) (L/mg) | \( R^2 \) | \( K_F \) (mg/g)/(mg/L)^{1/n} | \( n \) | \( R^2 \) | \( Q_{m,exp} \) (mg/g) |  
| AC       | 20.1248        | 0.1544           | 0.9990 | 5.4587 | 4.2439 | 0.9445 | 20.04 |  
| XC       | 36.5898        | 0.2979           | 0.9998 | 14.3757 | 6.0890 | 0.9491 | 36.54 |  
| CC       | 46.4912        | 0.1030           | 0.9660 | 15.9181 | 5.8889 | 0.8988 | 47.10 |  

Langmuir model is based on these assumptions: monolayer adsorption, homogeneous sorption sites, initially free sites, ideal behavior of surface and bulk phases and equal molar surface areas of solute and solvent [39]. Langmuir constant, \( b \), relates to the bond energy of sorption reaction between metal ion and sorbent [40]. It is a simple fitting parameter rather than Langmuir sorption constant since the system does not meet with all the assumptions of Langmuir model [41]. However, \( b \) is useful to determine the sorption affinity of sorbents. XC shows larger \( b \) value for Zn(II) sorption, suggesting the bond energy between ligands of XC and Zn(II) is larger than CC. This can be explained by different ligands of XC and CC, namely –CSS\(^-\) and -COO\(^-\).

The maximum sorption capacity of Zn(II) onto unmodified biomass is 12.39 mg/g, and modifications obviously improve the sorption capacity. CC and XC is 2.3 and 1.8 times higher than that onto AC, implying that functionalized lignocellulose remarkably enhances Zn(II) sorption. The higher sorption capacity onto CC is related to abundant carboxyl groups on CC indicated by high oxygen content. Due to the difference in experimental materials, methods and conditions, direct comparison of sorption capacity from different reports is difficult. As listed in Table 3, the sorption capacity of Zn(II) onto CC is higher than that of other sorbents. It should be noted that process cost and sorption efficiency should be considered for removal HMs using LCB.

Table 3. Maximum capacity for Zn(II) sorption onto different sorbents.

| Sorbents                  | References | Capacity (mg/g) | Solution pH | Sorption Time (min) | Initial Concentration (mg/L) | Temperature (°C) |  
|---------------------------|------------|-----------------|-------------|---------------------|-------------------------------|------------------|  
| Lemon grass               | [17]       | 15.87           | 6.0         | 180                 | 10                            | 25               |  
| Carrot residues           | [31]       | 29.61           | 4.5         | 1440                | 20–500                        | 25               |  
| Tectona grandis           | [33]       | 16.42           | 5.0         | 180                 | 20                            | 30               |  
| Spirodea polyrhiza        | [34]       | 28.50           | 6.0         | 120                 | 5–35                          | 30               |  
| Corn straw biochar        | [42]       | 11.00           | 5.0         | 1440                | 6–260                         | 22               |  
| Hardwood biochar          | [42]       | 4.54            | 5.0         | 1440                | 6–260                         | 22               |  
| Coconut shell-based       | [43]       | 9.43            | 7.0         | 1200                | 5–50                          | 32               |  
| activated carbon          |            |                 |             |                     |                               |                  |  
| Fallen leaves             | This study | 12.39           | 6.0         | 30                  | 50–1000                       | 30               |  
| AC                        | This study | 20.12           | 6.0         | 30                  | 50–1000                       | 30               |  
| XC                        | This study | 36.59           | 6.0         | 30                  | 50–1000                       | 30               |  
| CC                        | This study | 46.49           | 6.0         | 30                  | 50–1000                       | 30               |  

3.5. Sorption Thermodynamics

The calculated Gibbs free energy change (\( \Delta G \)), enthalpy change (\( \Delta H \)) and entropy change (\( \Delta S \)) for Zn(II) sorption are displayed in Table 4. The negative value of Gibbs free energy change suggests that Zn(II) sorption onto AC, XC and CC is spontaneous [44]. Zn(II) sorption onto AC and CC is exothermic due to \( \Delta H < 0 \), revealing that increasing temperature goes against Zn(II) sorption [33]. However, it is endothermic for Zn(II) sorption onto XC owing to the positive value of \( \Delta H \). The negative values of \( \Delta S \) for Zn(II) sorption
onto AC and CC manifests that the adsorbed Zn(II) ions are more ordered than Zn(II) ions near sorbent surface. As indicated by the positive value of $\Delta S$, Zn(II) sorption onto XC decreases the randomness at the solid–solution interface [33]. The difference in Zn(II) sorption onto CC and XC can be explained by different binding model between Zn(II) and surface groups containing oxygen or sulfur. Combined with analysis of sorption kinetics, isotherms and thermodynamics, it can be concluded that CC is very promising for Zn(II) sorption with respect to wastewater treatment.

### Table 4. Thermodynamic parameters for Zn(II) sorption onto AC, XC and CC.

| Sorbents | $\Delta G$ (kJ/mol) | $\Delta S$ (J/(mol·K)) | $\Delta H$ (kJ/mol) | $R^2$ |
|----------|---------------------|------------------------|---------------------|-------|
|          | 303 K               | 313 K                  | 323 K               |       |
| AC       | −3.5171             | −3.3848                | −3.2856             | −11.6121 | −7.0304 | 0.9964 |
| XC       | −5.6069             | −6.0788                | −6.4772             | 43.5929 | 7.5903 | 0.9849 |
| CC       | −5.5008             | −4.3984                | −3.6653             | −92.1694 | −33.3705 | 0.9802 |

4. Conclusions

Waste biomass was modified by alkalization, xanthation and carboxylation for Zn(II) sorption. FTIR and XPS verify the introduction of functional groups on sorbent surface, and SEM show porous structure of sorbents. Zn(II) sorption is highly dependent on process parameters including sorbent dosage, solution pH, sorption time and Zn(II) concentration. The sorption capacity of Zn(II) onto AC, XC and CC declines with an increase of sorbent dosage and Zn(II) concentration and increases with increasing solution pH and sorption time. Optimal parameters of Zn(II) sorption are obtained considering sorption capacity and removal rate. The sorption process obeys PSO kinetic model and Langmuir isotherm. Maximum sorption capacity of Zn(II) onto AC, XC and CC is 20.12, 36.59 and 46.49 mg/g, respectively. Zn(II) sorption onto CC is fast and spontaneous, and the sorption capacity is higher than other reported sorbents. Sorption mechanism is majorly attributed to surface complexation. This work reveals the enhancement of Zn(II) sorption by functionalized cellulose, providing effective modifications of LCB for preparation of sorbents. Additionally, conversion of locally available waste biomass into sorbents of HMs will find promising application in China.

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