Chemical, Electrochemical and Spectral Characterization of Water Leachates from Biomass

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ABSTRACT: To develop pretreatment strategies for better industrial utilization of biomass materials, six types of biomass were washed with deionized water at 303, 333, and 363 K, and the leachate was characterized by chemical, electrochemical, and spectral analysis. The results show that K⁺ is the most abundant cation in the leachates. An increase in the washing temperature leads to an increase in the cation concentration mainly because of the increment of K⁺. The chemical oxygen demand (COD) and the charge difference between inorganic cations and anions for leachate suggest that, in addition to inorganic ions, a few organic compounds and organic anions are released from biomass during washing. Fourier transform infrared (FTIR) spectra of the dry leachate samples reveal that carbohydrates and carboxylates are the major components of the organic compounds and organic anions, respectively. Except for the leachate of rice straw, the charge difference and COD increase with increasing washing temperature because of the increment of carboxylates for all of the other leachates.

1. INTRODUCTION

Biomass-fired boilers have been experiencing great problems with deposition and high-temperature corrosion, which are the critical limitations in the design and operation of biomass power plants.¹⁻⁴ Biomass fuels contain high amounts of K and Cl and a modest content of S.¹ It seems that the problems in operation can be effectively mitigated by reducing the contents of these elements through fuel pretreatment, such as pyrolysis and char washing.⁵,⁶ and water washing.⁷⁻⁹ Washing will produce large amounts of leachate for disposal or further treatment.⁸ The leachate can be used to irrigate fields, or it can be recovered by distillation or reverse osmosis techniques.⁹⁻¹¹ Jenkins et al.⁷ investigated the removal of troublesome elements in biomass by washing the fuel with water. The electrical conductivity (EC) of the leachate was measured, and the concentrations of ions in the leachate were determined by high-performance liquid chromatography (HPLC). The detected inorganic ions included Na⁺, K⁺, Mg²⁺, Ca²⁺, HCO₃⁻, Cl⁻, and SO₄²⁻. The anion–cation balance showed that the cation concentration was unusually high, which was assumed to be caused by improper calibration of the chromatograph or contamination of the column. In subsequent investigations, Jenkins et al.⁸ provided a biomass leachate treatment using reverse osmosis on leachates from rice straw and assessed the rejection of ions and chemical oxygen demand (COD, an indicator of the organic content of leachate) by the membrane. During the reverse osmosis trial, samples of permeate and retentate were collected for analysis of inorganic ions, organic acids, sugars, and COD. The experimental results showed that recovery of water by reverse osmosis could be expected to exceed 80%, and COD rejection and rejection of ions other than carbonate were above 90% for the membrane used when processing the leachate from rice straw.

Inorganic elements and organic compounds in soil are essential for plant growth and development.¹⁰ Leachate can be disposed into fields, thereby recycling valuable nutrients to the soil. Wu et al.¹¹ reported the removal and recycling of inherent inorganic species in mallee biomass and its derived biochars by water leaching. Experiments showed that water leaching could recycle almost all of K, Na, and Cl, as well as large proportions of S, P, and Mg for biomass samples. The overall recycling of the nutrient species was substantially reduced through biomass pyrolysis followed by biochar leaching. Water leaching also removed a small amount of organic matter from biochar. He et al.¹² characterized plant-derived water-extractable organic matter (WEOM) by multiple spectroscopic techniques to achieve a better understanding of the relationship between WEOM composition and behavior in soil environments. It was found that all plant-derived WEOM samples were primarily composed of significant soluble carbohydrates, organic acids, amino acids, and phenolic compounds.

In the pulp and paper industry, the accumulation of lipophilic extractives (nonpolar extractives, composed mainly of free fatty and resin acids, sterols, waxes, steryl esters, and so on) during pulping and papermaking can cause significant technical and economic problems.¹³ Sun et al.¹⁴ pointed out that treatment of biomass materials (including pulping and papermaking) can cause significant technical and economic problems.¹³ Sun et al.¹⁴ pointed out that treatment of biomass materials (including pulping and papermaking) can cause significant technical and economic problems.
Significant abundances of organic compounds (e.g., carbohydrates, lipids, proteins), large amounts of inorganic ions (e.g., K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻), and modest amounts of organic anions (e.g., carboxylate anions, phytate anion, glucosinolate anions) are present in biomass. During washing, a fraction of organic compounds and inorganic ions enter the water. Meanwhile, a few organic anions, which occur as accompanying anions for the cations in biomass, can also enter the water. Previous studies showed that water washing treatment of biomass can effectively remove the troublesome elements in biomass fuels, return the mineral elements and organic compounds to the soil, and mitigate the technical and economic troubles in the pulp and paper industry. In any case, characterization of the leachate should be performed in advance. Much attention has been focused on inorganic ions; however, there have been only a few analyses of organic compounds. To date, less attention has been devoted to organic anions. The removal of metallic elements is closely related to the bonding mode of organic anions to metallic cations in biomass. Furthermore, organic anions can increase the availability of phosphorus in the soil and contaminate the process effluent. Therefore, comprehensive analysis of the leachate is essential to understand the washing process and develop an effluent treatment method.

In addition, inorganic ions in the leachate were characterized by HPLC or ion chromatography (IC) in prior research. However, organic compounds in the leachate can cause contamination of the chromatographic column, and thus, the measured concentrations of inorganic elements should be considered only semiquantitative. Many researchers have investigated the effects of water washing treatment of biomass on mineral element removal at a certain temperature. Their experimental data indicate that water temperature is an important factor for the removal of inorganic nutrient species. Moreover, water temperature is closely related to the economy of the washing pretreatment system. However, the effect of water temperature on element removal has seldom been studied.

To avoid the defects in quantification of inorganic ions encountered in prior studies, in this work, the leachate produced during water washing treatment of biomass was characterized by chemical analysis (gravimetric method and titration method), electrochemical analysis (potentiometry), and spectral analysis (spectrophotometric method, atomic absorption spectrophotometry and Fourier transform infrared spectroscopy). The release of inorganic salts, organic salts (composed of inorganic cations and organic anions, such as carboxylate), and organic compounds from biomass was discussed. A novel test setup was designed to provide well-controlled conditions for water washing. Six types of biomass were investigated. The effect of water temperature was examined in detail.

2. EXPERIMENTAL SECTION

2.1. Materials and Water Washing Treatment. The six types of biomass selected for investigation were wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood, and rice hull. All of the biomass materials were collected from rural areas of Xi'an, Shaanxi Province, China. After being allowed to air dry in the field, all samples were cut with a herb shredder and then sieved to 280 μm. These six types of biomass are representative of typical biomass materials in northwestern China. Wheat straw, rice straw, corn stalk, and cotton stalk are herbaceous materials, whereas candlenut wood is a woody material. Rice straw and rice hull are different parts of the rice crop. The former is the stem and leaf, whereas the latter is the fruit shell.

An experimental setup was constructed to perform water washing under different conditions, as shown in Figure 1. The cuboid frames were made of stainless steel wires. Each frame, with a height of 9 cm and a square bottom of 6 × 6 cm², contained a biomass sample of approximately 12.5 g. To facilitate the complete collection of the washed sample, the frame was wrapped by a piece of nylon sieve cloth, with holes of about 98 μm in diameter. When the frame was submerged in the water, the sample could be washed thoroughly. A sample of 12.5 g was submerged and soaked in 1.0 L of deionized water for 3 h. Regulation of the electric power of the water bath allows water washing to be carried out at a constant temperature. For each sample, washing tests were performed at 303, 333, and 363 K. After being washed, the wet samples were air-dried at 378 K for 24 h and then deposited at room temperature to absorb moisture in the atmosphere to a constant weight. Weight measurements for the original sample and the washed sample were carried out using an electronic balance (Sartorius, BS210S). The weights of the original sample and the washed sample were both based on wet mass. All washing experiments were performed at least twice for reliability purposes. The mean difference between duplicate weight measurements for the washed sample was 0.08%. All of the original and washed samples were analyzed for proximate analysis, ultimate analysis, and ash composition (see section 2.3 in the Supporting Information).

The leachates produced during water washing treatment of wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood, and rice hull are denoted as LWS, LRS, LCS, LCCTS, LCW, and LRH, respectively. All of the leachates were withdrawn through a 0.45-μm hydrophilic polytetrafluoroethylene (PTFE) filter and then prepared for determination of inorganic ion concentrations, pH, EC, and COD and analysis of Fourier transform infrared (FTIR) spectra.

2.2. Quantification of Inorganic Ions in the Leachate. A series of analysis methods were used to determine the concentrations of inorganic ions in the leachate. K⁺ and Na⁺ concentrations were analyzed by atomic absorption spectroscopy.
photometry. Measurements were performed on a WYX-9003A atomic absorption spectrophotometer (Shenyang Yitong Analytical Instrument Co. Ltd., Shenyang, China). Ca²⁺ and Mg²⁺ concentrations were quantified using titration method with disodium salt of ethylenediaminetetraacetic acid (EDTA). PO₄³⁻ and NO₃⁻ concentrations were determined by a spectrophotometric method with ammonium molybdate and phenol disulfonic acid, respectively. Determinations were carried out on an ultraviolet–visible spectrophotometer (UV-1800, Shimadzu). Cl⁻ and HCO₃⁻ concentrations were measured using silver nitrate titration and acid–base titration, respectively. The SO₄²⁻ concentration was analyzed using a gravimetric method. All ion concentration measurements were performed at least twice following the standard methods, and the uncertainties of the analysis (expressed as one standard deviation) were calculated (see section 1.2 in the Supporting Information). The discrepancy between the experimental data obtained from duplicate measurements was within the repeatability limit.

2.3. Quantification of pH, Electrical Conductivity, and Chemical Oxygen Demand of the Leachate. The pH was determined using potentiometry, on a PHS-3C pH meter (Shanghai Rex Instrument Factory, Shanghai, China). The EC was quantified on a DDSJ-308A conductivity meter (Shanghai Rex Instrument Factory, Shanghai, China). The COD was measured using a fast digestion-spectrophotometric method. Measurement was performed on a SB-3C COD determining apparatus (Lianhua, China). Measurements of pH, EC, and COD were performed following the standard methods, and the uncertainties of these measurements (expressed as one standard deviation) were calculated (see section 1.2 in the Supporting Information). For the leachates produced during water washing treatment of wheat straw and rice straw, these measurements were performed twice for repeatability, and the discrepancy between the experimental data was within the repeatability limit.

2.4. Fourier Transform Infrared Spectroscopy Analysis. Drying of the leachate was performed in an air oven, prior to FTIR spectroscopy analysis. Leachate samples in beakers were air-dried at 378 K for 24 h to evaporate the water and then kept in a desiccator at room temperature until use. Even though the temperature of the air in the oven was 378 K, it could be observed that the temperature of the leachate was only about 345 K. Through the air-drying treatment of wheat straw and rice straw, these measurements were performed twice for repeatability, and the discrepancy between the experimental data was within the repeatability limit.

3. RESULTS AND DISCUSSION

3.1. Inorganic Ions in the Leachate. The inorganic ion concentrations in the leachates are listed in Table SI-2 (see section 2.1 in the Supporting Information). The leachate samples collected from water washing treatment with water temperatures of 303, 333, and 363 K are denoted as 1, 2, and 3, respectively. It can be seen that, in all of the leachates, K⁺ was the most abundant cation, HCO₃⁻ was the main anion, and no NO₃⁻ was detected. SO₄²⁻ was more abundant in LWS than in the other leachates. High concentrations of SO₄²⁻ and Cl⁻ were found in LRS, LCS, and LCTS, whereas SO₄²⁻ was not detected in LRH. The concentrations of inorganic ions in the leachate sample varied significantly with ion species and biomass species. The mode of occurrence of an element in biomass is of great importance for it to enter the water during washing.

Potassium is assimilated in the form of K⁺ ions, and it occurs also in the form of K⁺ ions in biomass. Potassium is not metabolized, and it forms only weak complexes with organic acid anions. It is the most abundant cation in the cytosol.¹⁰,¹⁹ The mode of occurrence of sodium in biomass is similar to that of potassium.¹⁰ Both calcium and magnesium are taken up in ionic form. In the apoplasm, part of the calcium is present as a structural or regulatory component of macromolecules because of its capacity for coordination, another part is bound to R–COO⁻ groups in readily exchangeable form, and the other part is precipitated as calcium oxalate or calcium carbonate. Most of the water-soluble calcium is accumulated in the vacuoles, accompanied by organic anions or inorganic anions.¹⁰ Magnesium tends to form complexes with organic counterions, and a substantial proportion of the total magnesium in the cell is present in free ionic form to regulate the cellular pH and the cation–anion balance.¹⁰,¹⁹ According to the modes of occurrence of the four metallic elements, it seems that, during washing, most of the potassium and sodium, a modest fraction of the magnesium, and only a small amount of the calcium in the biomass would enter water. All six biomass samples had high contents of potassium, modest contents of calcium and magnesium, and extremely low contents of sodium (see Table SI-3 in the Supporting Information). Therefore, the concentration of K⁺ was much higher than that of the other three cations in the leachate. These results are consistent with earlier findings.⁷,⁸

Most of the sulfur is assimilated in the form of SO₄²⁻ by the roots, whereas the rest of it is taken up in the form of SO₄ by the aerial parts of higher plants. Sulfur can be stored in the form of sulfate, metabolized and incorporated into essential organic structures, or utilized without reduction as sulfolipids and polysaccharides.¹⁰,¹⁹ SO₄²⁻ was not detected in LRH, which indicates that almost all of the sulfur in rice hull occurs in organic form. Chlorine is taken up in the form of Cl⁻. In plants, chlorine occurs mainly as a free anion or is loosely bound to exchange sites. A fraction of chlorine might also occur in chlorinated organic compounds.¹⁰,¹⁹ Cl⁻ is the main counter-ion for K⁺ in biomass.¹⁰ During washing, Cl⁻ might still occur as an accompanying anion when K⁺ enters water. Nitrogen can be taken up in the inorganic forms of NO₃⁻ and NH₄⁺ or in the organic forms of amino acids and urea. NO₃⁻ can be stored in the vacuoles of roots, shoots, and storage organs or reduced to NH₄⁺. Most of the NH₄⁺ can normally be incorporated into organic compounds in the roots.¹⁰ NO₃⁻ was not detected in all of the leachates, which suggests that nearly all of the nitrogen in the six biomass samples occurred as organic N compounds. In biomass, carbon is stored mainly in the form of organic carbon. Inorganic carbon occurs only in the form of carbonate and bicarbonate.¹⁰ Phosphorus is assimilated mainly in the form of H₂PO₄⁻ in the physiological pH range. After uptake, phosphorus remains as inorganic phosphate or is esterified as a simple phosphate ester or attached to another.
phosphorus. According to the range of pH observed in the leachate samples and the modes of occurrence of carbon and phosphorus in the biomass, it can be concluded that, during washing, inorganic carbon entered water mainly in the form of HCO$_3^-$ in all of the leachates and inorganic phosphorus entered water mainly in the form of H$_2$PO$_4^-$ in most of the leachate samples. In contrast, HPO$_4^{2-}$ was the main inorganic phosphorus form in LCS2 and LCS3. It should be noted in Table SI-2 (Supporting Information) that the inorganic phosphorus form in all of the leachates was represented as H$_2$PO$_4^-$ for convenience.

Figure 2 shows the K balances for the six biomass samples at different water temperatures. The error bars represent one standard deviation (see section 2.4 in the Supporting Information). The original and washed samples were analyzed for proximate analysis and ash composition (see section 2.3 in the Supporting Information), and the element removal was quantified on the basis of mass balance in the system. The light gray column represents the calculated value of the weight of K removed from a 12.5-g biomass sample, and the gray column represents the measured value of K in 1.0 L of leachate. It can be seen that, in general, the calculated values agree well with the measured values, and they show the same trend. The weight of K in the leachate increased for all six biomass samples as the water temperatures rose. It is likely that more K$^+$ ions that form weak complexes with organic acid anions enter water as the water temperature increases. To determine whether washing treatments at different temperatures make sense, statistical significance tests were performed for the K$^+$ concentration in the leachate (see section 2.5 in the Supporting Information). The results show that the K$^+$ concentrations at the three temperatures were statistically significantly different at $P = 0.05$, $P = 0.01$, and $P = 0.001$.

It is believed that, during washing, Na, Ca, Mg, and Cl enter water only in the inorganic form of ions. Although the calculated weight losses of these elements, which can be obtained from section 2.4 in the Supporting Information, were of the same order of magnitude as the measured values in the leachates, the element balances were poor for the six biomass samples at different water temperatures (see Figure SI-1 in the Supporting Information). Compared with proximate analysis, ultimate analysis and ash composition measurements for the original and washed samples, concentration determination of inorganic ions for the leachate is more believable. Low contents of Na, Ca, Mg, and Cl were found in the six biomass samples. After washing, these element contents were even lower in the washed samples. Some of them were lower than the method detection limits. This might introduce experimental uncertainty to the results of proximate analysis, ultimate analysis, and ash composition. According to the modes of occurrence of C, S, and P in biomass, these elements can enter water in both inorganic form and organic form. When these elements that were removed by water washing in this study. As suggested by these researchers, the mode of occurrence of critical ash-forming elements in biomass structure is important for the release behavior. That is, the amount of water-soluble ash-forming elements is of great importance for the design and operation of biomass boilers. According to Davidsson et al. and Dayton et al., water washing was sufficient for a lowering in the measured alkali and chlorine release of over 90%. Therefore, it seems that water washing is a prospective pretreatment process to mitigate deposition and high-temperature corrosion problems in straw-fired stoker boilers.

![Figure 2](image-url) **Figure 2.** Potassium balance for the six biomass samples at different water temperatures.

![Figure 3](image-url) **Figure 3.** Cation–anion balances for all of the leachates at different water temperatures.
The cation–anion balances for all of the leachates, which were calculated using the data in Table SI-2 (Supporting Information), are shown in Figure 3. The error bars represent one standard deviation (see section 2.7 in the Supporting Information). It can be seen that the cationic charge concentration was larger than the anionic charge concentration in all of the leachates. Similar results were obtained by Jenkins et al. They ascribed the charge difference to improper calibration of the chromatograph or contamination of the column. However, these defects in quantification of inorganic ions were avoided in this study. Therefore, the charge difference between cations and anions is believed to be attributed to the presence of organic anions in the leachate samples. It can be seen from Table SI-2 (Supporting Information) that, during washing, fewer cations entered water for candlenut wood and rice hull than for the other biomass samples. A possible reason is that fewer organic anions occur as accompanying anions whenever cations enter water for candlenut wood and rice hull. Thus, the charge differences between cations and anions were smaller for LCW and LRH, as shown in Figure 3.

From Figure 3, it can also be noted that the cation concentration increased for all of the leachates as the water temperature increased. As shown in Table SI-2 (Supporting Information), the increment in the K⁺ concentration made the main contribution to the increase in cation concentrations as the water temperature rose. Except for LRS, the charge difference between cations and anions in the leachate increased with increasing water temperature. This suggests that, during washing, an increasing fraction of organic anions entered the water as the water temperature increased. For LRS, the largest charge difference was observed at the water temperature of 333 K. Sun et al. discussed the competition between fatty acids and lipids for entry to water during hot-water treatment of wheat straw. Similarly, when the water temperature reached 363 K, the organic anion concentration could decrease, because of the increment of other organic compounds in water in the present study.

### 3.2. Electrical Conductivity, Chemical Oxygen Demand, and pH of the Leachate

EC, COD, and pH of all of the leachates are also listed in Table SI-2 (Supporting Information). It can be seen that all of the leachates were generally acid–base neutral. The pH values of most of the leachates were in the range of 6–8. Both EC and COD were high for LRS. The lowest EC and COD were found for LCW and LRH, respectively.

EC is a measure of the ability of a solution to carry an electric current. Electrons cannot flow freely, but must be carried by ions in the solution. All of the ions present in the solution contribute to the conductivity measurement. Therefore, the EC value can be used as a measure of the concentrations of the salts (inorganic and organic salts) in the leachate. Because each ion has its own specific ability to conduct current, EC is only an estimate of the total ion concentration. An apparatus called a conductivity meter that consists of a conductivity cell and a meter is usually used to measure the EC of a solution.

As discussed in section 3.1, during washing, both inorganic and organic salts will be extracted. Thus, all of the leachates have the capacity to conduct electricity. EC balances were carried out for all of the leachates at different water temperatures investigated in this work. The measured value of EC was compared to a calculated value that was determined from the inorganic ion concentrations in the leachate. The calculated value of EC can be obtained from

$$\text{EC} = \sum C_f$$

where \(i\) represents the ion species, \(C_i\) is the concentration of ion species \(i\) in the leachate (see Table SI-2, Supporting Information), and \(f_i\) is the conductivity factor for the same species. The values of \(f_i\) are listed in Table 1.

#### Table 1. Conductivity Factors of Ions

<table>
<thead>
<tr>
<th>ion</th>
<th>(f_i) ((\mu S) cm⁻¹ L mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cations</td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>1.84</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.13</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.60</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3.82</td>
</tr>
<tr>
<td>Anions</td>
<td></td>
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<tr>
<td>HCO₃⁻</td>
<td>0.72</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1.54</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.14</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>0.37</td>
</tr>
<tr>
<td>HPO₄³⁻</td>
<td>1.11</td>
</tr>
</tbody>
</table>

The EC balances are shown in Figure 4. The error bars represent one standard deviation (see section 2.8 in the Supporting Information). The EC measured values for LRS, LCS, LWS, and LCTS were much higher than those for LCW and LRH. The maximum value even reached 794 \(\mu S\) cm⁻¹. The EC of the leachate sample was found to vary with biomass species. It can be seen that the cationic charge concentration and the EC of the leachate sample follow similar trends with biomass species in Figures 3 and 4. The reason for this might be that, in all of the leachates, the higher the concentration of cationic charge, the higher the concentrations of inorganic and organic salts.

From Figure 4, it can also be seen that the measured values of EC were greater than the calculated values for all of the leachates. Because cations, inorganic anions, and organic anions in the leachate all contribute to EC, the neglect of the contribution of organic anions will lead to such a deviation. The tiny EC differences for LCW and LRH indicate that there were only small numbers of organic anions in these leachate samples. Figure 3 also supports this inference. Except for LRS, the total charge concentration of all of the organic anions in the leachate sample increased with increasing water temperature (see section 3.1). However, it is possible that, during washing, different species of organic anions could enter the water at different concentrations. According to eq 1, different species of ions make different contributions to EC. Therefore, the EC difference did not increase monotonically as water temperature rose for LWS, LRS, LCS, LCTS, and LCW, as shown in Figure 4.

COD is a measure of the pollution degree of reducing matters (mainly organic matters) in water. In this study, COD value can be used as a measure of the total concentration of organic compounds in the leachate. During measurements, the leachate sample was first mixed with \(H_2SO_4\), \(Ag_2SO_4\), \(HgSO_4\), and \(K_2Cr_2O_7\) in a digestion tube. Then, the mixture solution was heated to 438 K and held for 15 min. The organic compounds will be oxidized by the \(K_2Cr_2O_7\). After being cooled to room temperature, the solution was determined for COD value using the spectrophotometric method.
According to Sun et al., more organic compounds enter the leachate. The COD value reflects the total concentrations of organic compounds and organic anions in the leachate. According to Sun et al., more organic compounds enter the water as the temperature increases. Likewise, more organic anions entered water at the higher water temperature for LWS.

Figure 5 presents measured COD results for all of the leachates. The error bars represent one standard deviation (see section 1.2 in the Supporting Information). The CODs of LCS, LCTS, LRS, and LCWS were much higher than those of LCW and LRH. The maximum COD value was 787 mg L\(^{-1}\) for LCS. The COD value reflects the total concentrations of organic compounds and organic anions in the leachate. According to Sun et al., more organic compounds enter the water as the temperature increases. Likewise, more organic anions entered water at the higher water temperature for LWS, LCS, LCTS, LCW, and LRH, as discussed in section 3.1. Thus, the CODs of these leachate samples increased with increasing water temperature. However, it was observed that the COD of LRH3 was lower than that of LRH2. It seems that the decrement of organic anions (see section 3.1) was larger than the increment of organic compounds in the leachate when the water temperature was increased from 333 to 363 K.

### 3.3. Fourier Transform Infrared Spectra

When an infrared light source irradiates a sample, molecules in the sample can absorb certain wavelengths of light, so that absorption bands appear in FTIR spectra. In general, the infrared spectrum interval is divided into three areas: (1) near-infrared region, 12800–4000 cm\(^{-1}\); (2) mid-infrared region, 4000–400 cm\(^{-1}\); and (3) far-infrared region, 400–10 cm\(^{-1}\). In the mid-infrared region (mostly between 4000 and 1330 cm\(^{-1}\)), vibration frequencies of some functional groups always appear in narrow regions. They have high absorption strengths and can be separated from other vibration frequencies in FTIR spectra. Such a frequency is defined as the fingerprint frequency. Based on the combined analysis of the two types of vibration frequency, the FTIR spectra of samples can be interpreted.

Figure 6 shows FTIR spectra of all of the leachates. During washing, a fraction of inorganic salts, organic salts, and organic compounds that are inherent in the biomass sample would enter the water. It is obvious that the FTIR spectra of all of the leachates showed several similar absorption bands. The absorption band around 3400 cm\(^{-1}\) is due to the O–H bond stretching. He et al. and Jenkins et al. have reported that significant sugars are extracted during washing. Sun et al. demonstrated that treatment of wheat straw with hot water released minor amounts of sterols and diglycerides. It appears that the absorption peaks of the O–H stretching of carbohydrates, sterols, and diglycerides in the dry leachate samples overlapped and resulted in a broad band, as shown in Figure 6. By comparing the N content of the original sample with that of the washed sample (see Table SI-3, Supporting Information), it can be concluded that a fraction of N entered the water for LRS, LCS, LCTS, LCW, and LH during washing. However, no NO\(_3^-\) was detected in any of the leachates (see section 3.1). Thus, a few organic N compounds existed in these leachate samples. N–H bond stretching might also make a contribution to the absorption band around 3400 cm\(^{-1}\).

A relatively strong band around 2930 cm\(^{-1}\) and a minor band around 2850 cm\(^{-1}\) appeared in the FTIR spectra of all of the dry leachate samples, as shown in Figure 6. These two bands are attributed to the antisymmetric and symmetric stretching, respectively, of CH\(_2\). Both of them were inconspicuous in the FTIR spectra, as they were partially masked by the absorption peaks of O–H and N–H bond stretching.

Two characteristic absorption bands were observed in the region between 1650 and 1380 cm\(^{-1}\) in the FTIR spectra of all of the dry leachate samples. As Figure 6 shows, the two bands appeared at about 1580 and 1400 cm\(^{-1}\) for LWS and LRH, at about 1640 and 1395 cm\(^{-1}\) for LRS, at about 1621 and 1390 cm\(^{-1}\) for LCS, at about 1628 and 1395 cm\(^{-1}\) for LCTS, and at about 1616 and 1395 cm\(^{-1}\) for LCW. Similar results were found in the FTIR spectroscopy analysis of eight WEOM fractions by He et al. In their study, a strong peak associated with COO\(^-\) groups did not appear at about 1720 cm\(^{-1}\) in the FTIR spectra, which indicates that there were no large amounts of organic acids. Moreover, because of the relatively less polyvalent ions, it was unlikely that there existed lots of carboxylates. As a result, they suggested that there was no significant abundance of COO\(^-\) groups in the WEOM samples. Finally, they assigned those two bands to aromatic compounds and phenolic OH and aliphatic C–H groups, respectively. In this study, the weight of
the dry leachate sample can be obtained from section 2.9 in the Supporting Information. The contents of polyvalent ions (Ca$^{2+}$, Mg$^{2+}$) in the dry leachate sample were of the same order of magnitude as those reported by He et al.$^{12}$ However, there was an abundance of K$^+$ in the leachate samples, and the cationic charge concentrations were larger than the anionic charge concentrations (see section 3.1). Therefore, the two bands are most probably attributable to the antisymmetric and symmetric stretching of COO$^-$ group in the samples. Moreover, the surplus cations occurred mainly as carboxylates in the dry leachate samples. From Figure 6, it can also be seen that the peak positions of the two bands varied with the leachate species. One reason for this could be the different cation species in carboxylates in the dry leachate sample.$^{31}$ All the four metallic cations can form carboxylates, but only Ca$^{2+}$ and Mg$^{2+}$ can form complexes with carboxylic anions. Another reason for the different peak positions could be the different coordination modes.$^{31}$ For LWS and LRH, the coordination mode of carboxylate is bridging coordination, whereas for LRS, LCS, LCTS, and LCW, the coordination mode is unidentate coordination.

Previous work$^{12,14,21}$ has reported that, during washing of biomass samples, substantial amounts of carboxylic acids enter the water. A characteristic absorption band at 1719 cm$^{-1}$, which was attributed to the C=O stretching of carboxylic acids, was observed in the FTIR spectra of water-soluble lipophilic extractives from wheat straw by Sun and Tomkinson. However, the corresponding absorption band did not appear in the FTIR spectra in this study (see Figure 6) or the study of He et al.$^{12}$ This suggests that the contents of carboxylic acids were extremely low in all of the dry leachate samples in this work. In this study and the study of He et al.,$^{12}$ after water washing, the leachate samples were immediately dried and then analyzed by FTIR spectroscopy, whereas in the study of Sun and Tomkinson,$^{21}$ the leachate sample was extracted twice with methyl tert-butyl ether (MTBE) prior to drying process. During the extraction process, the carboxylic anions that occurred as accompanying anions for K$^+$ and Na$^+$ and the inorganic ions would show strong hydrophilic characters. Most of them would

Figure 6. FTIR spectra of all of the leachates at different water temperatures.
not enter MTBE, and therefore, the contents of carboxylic acids in the lipophilic extractives were much higher than those in the dry leachate samples in this study and in the WEOM samples in the study of He et al.12 Thus, the absorption band at 1719 cm⁻¹ was apparent in the spectra of the lipophilic extractives.

Composite bands around 1100 cm⁻¹ appeared in the FTIR spectra of all of the leachate samples, as shown in Figure 6. These bands arise from the C–O stretching of carbohydrates, sterols, and diglycerides and the C–O–C pyranose ring skeletal vibration of carboxydrates.12,33,35 Based on the analysis of the inorganic ions in the leachate (see section 3.1), sulfate and phosphate compounds might also contribute to the peaks around 1100 cm⁻¹.12,34

As shown in Figure 6, there were no strong characteristic absorption bands in the range between 900 and 650 cm⁻¹ in the FTIR spectra of any of the dry leachate samples. It seems that aromatic compounds hardly entered the water during washing. For all of the leachates, the absorption band around 615 cm⁻¹ was due to the OH out-of-plane bending of carbohydrates, sterols, and diglycerides.36,37

From Figure 6, it can also be noted that there are some differences among the FTIR spectra. For LCS and LCW, four absorption bands appear in the region between 1630 and 1450 cm⁻¹, and one absorption band is observed at about 1260 cm⁻¹ (see Figure 6c,e). According to He et al.,12 small amounts of amino acids or peptides enter the water during washing. Thus, there were carboxylic anions and amino cations in the dry leachate samples.31 Therefore, the two bands near 1645 and 1515 cm⁻¹ can be assigned to the antisymmetric and symmetric deformation of the NH₃⁺ group, and the two bands near 1550 and 1460 cm⁻¹ can be assigned to the antisymmetric and symmetric stretching of the COO⁻ group.38 According to Carmona et al.,39 the absorption band around 1260 cm⁻¹ can be attributed to the polypeptide amide III vibrational mode. For LCS, LRS, LCTS, and LRH, these five absorption bands were not apparent in the FTIR spectra, which might be caused by the extremely low contents of organic N compounds in these samples.

As shown in Figure 6b,d, an absorption band appears at about 1313 cm⁻¹ for LRS and at about 1333 cm⁻¹ for LCTS. This can be attributed to the twisting of CH₂ groups.38,39 Furthermore, the band for LRS is stronger than that for LCTS, which indicates that the CH₂ group is probably linked to a polar group in LRS.31

In the region between 900 and 700 cm⁻¹, the differences between the FTIR spectra lie in the weak absorptions at about 895, 834, and 780 cm⁻¹. For LWS and LCTS, the absorption band at 895 cm⁻¹ originates from β-glycosidic linkages between glucose units in carbohydrates,50,40,41 whereas for LCS, the absorption band at 834 cm⁻¹ originates from α-glycosidic linkages between glucose units in carbohydrates.42 As discussed in section 2.3 in the Supporting Information, the inherent Si in biomass seems to be dissolved into water as a hydrated form of amorphous silica during washing. The absorption band appearing at 786 cm⁻¹ for LRS, at 774 cm⁻¹ for LCTS, and at 790 cm⁻¹ for LRH might correspond to the symmetric stretching of Si–O–Si.43 In addition, according to He et al.44 phosphate could also contribute to these bands.

From Figure 6, it can be seen that the different dry leachate samples contained similar functional groups, including methylene, hydroxyl, acylamino, and carboxylic anions and amino cations. The FTIR spectra in Figure 6 confirm that carbohydrates and carboxylic anions were the major components of the organic compounds and organic anions, respectively, in the leachates.

For the same leachate species, the strengths of the characteristic bands varied with the water temperature. This indicates that different amounts of organic compounds and organic salts were extracted at different water temperatures. For LWS, LRS, LCS, LCTS, and LRH, the absorption band at about 1640 or 1580 cm⁻¹ is mainly due to the COO⁻ antisymmetric stretching of carboxylates, whereas the absorption band at about 1100 cm⁻¹ is mainly due to the C–O stretching and C–O–C pyranose ring skeletal vibration of carbohydrates. For these five leachates, the ratio of peak heights between the 1100 cm⁻¹ peak and the 1640 or 1580 cm⁻¹ peak increased with increasing water temperature, which indicates that more carbohydrates entered the water at higher temperature.

As shown in Figure 6c, the four absorption bands in the region between 1630 and 1450 cm⁻¹ were not apparent for LCS2 and LCS3. Because of the increment of carbohydrates and carboxylic acids in the leachate (see section 3.1), the contents of amino acids or peptides in the dry samples of LCS2 and LCS3 were lower than those in the dry sample of LCS1.

4. CONCLUSIONS

Using chemical, electrochemical, and spectral analyses, we characterized the leachates produced during water washing of six different biomass samples and examined the release of inorganic salts, organic salts, and organic compounds from biomass. The following conclusions can be drawn:

1. In all of the leachates, K⁺ was the most abundant cation, and no NO₃⁻ was detected. The inorganic C and P entered water mainly in the forms of HCO₃⁻ and H₂PO₄⁻, respectively. SO₄²⁻ was more abundant in the leachate of wheat straw than in the other leachates.

2. In addition to inorganic ions, a few organic anions and organic compounds were released from the investigated biomass during washing. The FTIR spectra of the leachates indicate that dry leachate samples were primarily composed of carbohydrates and carboxylates. For the leachates of wheat straw and rice hull, the coordination mode of carboxylate was found to be bridging coordination, whereas for the other leachates, the coordination mode was found to be unidentate coordination. Because of the neglect of the contribution of organic anions to the charge concentration and EC, the charge concentrations for inorganic cations were larger than those for inorganic anions, and the measured values of EC were greater than the calculated values for all of the leachates.

3. During washing of biomass, the water temperature was found to have an important influence on the release of inorganic salts, organic salts, and organic compounds from biomass. As the water temperature increased, more K⁺ entered water, and then the cation concentration increased. Except for the leachate of rice straw, the charge difference between inorganic cations and anions increased with increasing water temperature, as a result of the increment in the concentration of organic anions in the leachate. When the water temperature was increased from 333 to 363 K, the COD decreased for the leachate of rice straw. In this case, the decrement of organic anions was larger than the increment of organic...
compounds in the leachate. For the other leachates, the COD increased with increasing water temperature, as a result of the increments of both the organic compounds and the organic anions. For the leachates of wheat straw, rice straw, corn stalk, cotton stalk, and rice hull, more carbohydrates were found to enter the water as the water temperature increased.

■ ASSOCIATED CONTENT

Supporting Information
Details concerning data, methods, results, and discussion are presented in tables, figures, and text. This material is available free of charge via the Internet at http://pubs.acs.org.

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