



Article Extraction of Humic Acid from Lignite by KOH-Hydrothermal Method

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Abstract: Humic acid (HA) was extracted by a hydrothermal method from Huolinhe lignite from Inner Mongolia. The effects of the alkali-to-carbon mass ratio, water-to-coal mass ratio, reaction temperature, and reaction time on the HA yield were investigated. The physicochemical characterization of the products was performed, and the reaction mechanism was explored. Raw coal, HA, and residual coal were characterized using Fourier-transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–VIS), elemental composition, and X-ray diffraction (XRD) analyses and compared to each other. The maximum HA yield (90.2%) was obtained from the 0.250–0.180 mm size fraction of the coal sample at a reaction temperature and time of 190 °C and 7 h. Proximate analysis proved that the ash and sulfur of lignite can be removed by hydrothermal treatment. Elemental analysis showed that the O/C and H/C ratios were highest for HA, followed by those for residual coal and raw coal, indicating an increase in the oxygen and hydrogen content of HA. FTIR and UV–VIS analyses showed that hydrothermal extraction destroyed the macromolecular structure of lignite. Moreover, the organics were degraded and hydrolyzed during the reaction process.

Keywords: humic acid; hydrothermal; lignite; XRD; FTIR

1. Introduction

Humic acid (HA) is a complex mixture in which there can be small, large, and polydisperse molecules formed and accumulated through the decomposition and transformation of microorganisms and a series of geochemical reactions [1,2]. Schulten and Schnitzer [3] proposed a structure for HA formed by alkyl benzene moieties attached through covalent bonds. Piccolo [4] proposed that it is a self-assembled superstructure with relatively small heterogeneous molecules held together primarily by hydrophobic dispersive forces and hydrogen bonds. Many authors thought that HA had no precise structures, which depend on the source that generated them and the specific extraction conditions [5].

HA contains a high number of active groups such as carboxyl groups, phenolic hydroxyl groups, carbonyl groups, sulfonic acid groups, and methoxy groups, which have a crucial influence on the acidity, ion exchange properties, colloidal properties, and complexation properties [6]. HA is widely used in agriculture, medicine, health, wastewater treatment [7,8], and other applications. The existence of carboxylic and phenolic groups results in HA carrying a predominantly negative charge in aqueous solutions under normal environmental conditions [9,10]. Humic acid can efficiently purify metal ions

and improve water quality [11,12]. In addition, HA can also be used as surfactants, flocculants, ceramic additives, battery cathode expansion agent, boiler anticrustator, water-soluble fertilizer, compound fertilizer, soil remediation agent, etc. [13,14]. High functionality of the surface ensures that HA is a good adsorbent with an excellent capacity for treating the pollution caused by waste gases [15,16].

HA widely exists in lakes, marsh, soils [17], peat, lignite, oxidized bituminous coal, weathered coal, shale, and flora/fauna residues [18–20]. Lignite has attracted considerable attention, as its reserves account for nearly 45% of global coal reserves [21–23]. However, its abundant oxygen functional moieties, low calorific value, and high moisture content have critically restricted its direct and wide use [24–27]. Compared to HAs originating from soil and peat, lignite HAs are characterized by higher carbon content and biochemical activity, lower oxygen and nitrogen content, more aromatic moieties, and fewer carboxylic groups. Lignite HA is characterized by the presence of methylene and ethylene bridges between the aromatic rings. In contrast to soil humic acids, lignite humic acids were shown to contain saturated long chain alkanoic acids with a strong predominance of even numbered homologues [28].

Humic acids are insoluble under acidic conditions, but become soluble and extractable in alkaline solutions. Multiple approaches can be used to extract HA from lignite, including physical, chemical (alkaline [29] and acid), and biological methods [30]. Stefanova et al. [31] extracted HA from Bulgarian lignite using a NaOH dissolution and HCl precipitation, obtaining 83% HA content. Cihlář et al. [32] first dissolved South Moravian lignite with a NaOH (0.5 mol/L) and Na₄P₂O₇ (0.1 mol/L) solution, followed by pickling with a 0.5% HCl-HF solution, and HA was finally obtained by H₂O₂/HNO₃ oxidation treatment. Drosos et al. [33] prepared a water-soluble humic acid-like polycondensate (HALP) that mimicked the fundamental physicochemical and spectroscopic properties of natural HA. The polymerization procedures were as follows; a gallic acid and protocatechuic acid (mass ratio is 1:1) suspension liquid (0.5 L) was adjusted to pH 1 using HCl and continuously stirred for 12 h at 25 °C in a closed glass jar, and the pH was then adjusted to 10.5 with NaOH. Khemakhem et al. [34] isolated a water-soluble HA and melanin-like polymer complex from olive mill waste waters (OMWW) by using ammonium sulphate as a natural additive.

Compared to the above methods, the hydrothermal method [35] is an effective approach for obtaining higher HA yields. Hydrothermal extraction is based on the theory that subcritical water can dissolve organic matter. The reaction is carried out in a special closed container with hot-compressed water above 100 °C [36], and undissolvable/insoluble substances are dissolved in aqueous medium [37]. Elemental analysis and spectroscopic methods including UV-VIS and FTIR spectroscopy are usually used for the characterization of HAs. Huang et al. [38] examined the effects of water content and particle size on the yield and reactivity of lignite char. A thermogravimetric analyzer (TGA) was used for measuring the reactivity of the chars after pyrolysis and gasification. For the $<75 \mu m$ coal particles, the high water content decreased the char yield; for the 0.9–2.0 mm coal particles, the high water content contributed to the increase in char yield. Liu et al. [39] studied the structural changes in lignite during hydrothermal treatment. The weak bonds in lignite were broken, and the oxygen functional groups decreased gradually during hydrothermal treatment below 240 °C. The covalent bonds began to break above 240 °C. Liu et al. [40] and Chang et al. [41] modified lignite by the hydrothermal method. The carboxyl and carbonyl content decreased significantly with an increase in the temperature after hydrothermal treatment. Wang et al. [42] studied the effects of hydrothermal treatment on the swelling, extraction, and liquefaction performances of Shenhua coal. The results showed that hydrothermal treatment could hydrogenate, deash, and devolatilize lignite. The IR spectra showed that the forms of noncovalent bonds (hydrogen bonds) were changed by hydrothermal treatment, the weak covalent bonds (e.g., ether bonds and ester bonds) hydrolyzed, and the side-chains of the aromatic rings broke. The hydrothermal temperature had a strong influence on the reaction process. Zhang et al. [43] extracted fulvic acid from weathered coal using hydrothermal catalytic oxidation with nano-copper oxide as the catalyst and hydrogen peroxide as a green oxidant. The maximum total HA and fulvic

acid contents were 73.23% and 8.98%, respectively. HA could be broken up into two soluble and two insoluble fractions by successive dissolution in deionized water at near-neutral pH [44].

The above analyses showed that hydrothermal pretreatment destroys the macromolecular structure of lignite and increases the content of oxygen-containing functional groups. In the present study, KOH solution was adopted to extract HA from lignite. The reaction equation is given by

$$R - (COOH)_{n} + nKOH \rightarrow R - (COOK)_{n} + nH_{2}O$$
(1)

In this study, the extraction process of HA from lignite was optimized by evaluating the effects of different factors, i.e., alkali-to-carbon mass ratio, reaction time, reaction temperature, water-to-coal mass ratio, and coal size. Characterization of the extracted humic acid was also done to further evaluate its composition and structure through proximate analysis by UV–VIS, FTIR, XRD, etc. This study will further the economic value and application of lignite [45].

2. Materials and Methods

2.1. Materials

Chemicals of analytical reagent grade or better as well as deionized water were used in the experiments. Hydrochloric acid and potassium hydroxide were purchased from Yantai Shuangshuang Chemical Industry Co. Ltd. and Tianjin Dalu Chemical Reagent Factory, respectively. Lignite was collected from Huolinhe in Inner Mongolia, China. After crushing and screening, the raw coal was divided into five size fractions, namely, 2–0.850 mm, 0.850–0.425 mm, 0.425–0.250 mm, 0.250–0.180 mm, and 0.180–0.150 mm. Finally, the prepared coal samples were tightly sealed.

2.2. Experimental Setup and Procedures

Hydrothermal tests were performed in a stainless steel reactor [46]. The detailed process is shown in Figure 1. The alkali-to-carbon mass ratio (mass ratio of potassium hydroxide to coal sample), water-to-coal mass ratio (mass ratio of water-to-coal sample), reaction time (3–11 h), and reaction temperature (130–190 $^{\circ}$ C) were studied to determine their effects on the HA yield.



Figure 1. Flow chart of humic acid (HA) extracted by the hydrothermal method.

The process was as follows.

Step 1: Coal samples were dried in a vacuum oven at 105 °C to constant weight [47]. An air-dried sample (20 g) was treated with potassium hydroxide (KOH) and deionized water in the reactor. Then, the reactor was placed into oven (130–190 °C). After the reaction was finished, the kettle was naturally cooled to room temperature [48].

Step 2: The supernatant was separated from residues by centrifugation. After centrifugation, the residuals were washed with distilled water until almost reaching neutral pH. Then, the residuals were filtered and dried in a vacuum oven at 105 °C.

Step 3: The supernatant and cleansing solution were acidized to pH < 2 with HCl, further separated by centrifugation, and dried in a vacuum oven at 60 °C. The obtained dried materials were HA.

The HA yield was calculated on an air-dried basis according to the following formula.

$$\varepsilon = \frac{M_{YM}(1 - M_{ad}) - M_{CY}}{M_{YM}(1 - M_{ad})}$$
(2)

where ε is the yield of HA, %; M_{YM} is the mass of lignite, g; M_{CY} is the mass of the residual coal, g; and M_{ad} is the water content in raw coal, %.

According to the GB/T212-2008 standard [49], the moisture content (M_{ad}), ash content (A_d), volatile content (V_{daf}), and fixed carbon content (FC_{daf}) were detected based on the air-dried samples. The elements C, H, O, N, and S were analyzed based on the air-dried samples by a TE-CHN700B Elemental Analyzer (Thermo Fisher Scientific, USA) in accordance with the GB/T476-2001 standard. The total HA content in raw coal was determined by the GB/T11957-2001 volumetric method, and the HA content of raw coal was 14.6%.

3. Results

3.1. Effect of Alkali-to-Carbon Mass Ratio

The effect of the alkali-to-carbon mass ratio (0.3:1–1.5:1) on the HA yield was analyzed for a hydrothermal temperature of 190 °C, water-to-coal mass ratio of 1:20, reaction time of 7 h, and coal sample size of 0.250–0.180 mm. The results are shown in Figure 2.



Figure 2. Effect of the alkali-to-carbon mass ratio on the HA yield.

As shown in Figure 2, as the alkali-to-carbon mass ratio increased, the HA yield increased rapidly from 35.5% to 80.8%, and then remained stable at 90.7%. The HA in raw coal forms a structurally stable

chelate complex with metal ions such as calcium, magnesium, and aluminum. The HA content in the raw coal was low, and the addition of KOH destroyed the chelating forces between HA and metal ions. Therefore, the HA was easier to dissociate from the coal. In addition, the increase in the OH⁻ concentration made HA more available for reaction (1) [50]. Because the amount of metal ions in the coal sample was fixed, the HA yield no longer increased even though the amount of KOH increased continuously. When the alkali-to-carbon mass ratio was 1.5, the HA yield reached a maximum of 90.7%, but the increase was not significant. Thus, 1:1 was selected as the optimal alkali-to-carbon mass ratio for HA extraction.

3.2. Effects of Reaction Time and Temperature

The effect of the reaction time on HA yield was further investigated after the optimal alkali-to-carbon mass ratio was determined. As shown in Figure 3, the HA yield increased from 54.4% to 90.2% as the reaction time varied from 3 to 7 h. At reaction times exceeding 7 h, the HA yield decreased from 90.2% to 84.7%. A short time resulted in an inadequate reaction, and HA easily decomposed at high temperatures and pressures. Therefore, 7 h was selected as the optimal time.



Figure 3. Effect of the reaction time on the HA yield.

After determining the optimal reaction time, the effect of the temperature $(130-190 \, ^\circ\text{C})$ was investigated (Figure 4). The HA yield increased sharply from 20% to 90.2% as the temperature increased from 130 to 190 $^\circ\text{C}$ and then increased slowly until the temperature rose to 210 $^\circ\text{C}$. Most of the intermolecular forces in coal are physical associations and are weak. A high temperature resulted in the destruction of the molecular structures, thereby releasing HA in the lignite. However, high temperatures also led to the breaking of noncovalent bonds (e.g., hydrogen bonds), the hydrolysis of weak covalent bonds (e.g., ether bonds and ester bonds), and the cleavage of side-chain bonds (e.g., aromatic rings and fat bonds). With increasing hydrothermal temperature, the permittivity and polarity of the water in the reactor decreased, the dissolving capacity of the intermediate polar and nonpolar organic compounds in the lignite was enhanced, and the amount of HA dissolved in lye increased. When the temperature corresponds to greater energy consumption and economic costs. Therefore, 190 $^\circ\text{C}$ was selected as the optimal reaction temperature.



Figure 4. Effect of the reaction temperature on the HA yield.

3.3. Effects of the Water-to-Coal Mass Ratio and Coal Size

The effect of the water-to-coal mass ratio (ranging from 5:1 to 25:1) was then investigated. As shown in Figure 5, an increase in HA yield was observed as the water-to-coal mass ratio increased. When the water-to-coal mass ratio increased from 20:1 to 25:1, the HA yield increased from 90.2% to 91.2%. The increase in HA yield was not obvious. Therefore, 20:1 was considered the optimal water-to-coal mass ratio.



Figure 5. Effect of the water-to-coal mass ratio on the HA yield.

The effect of different coal sizes on the HA yield is shown in Figure 6. When the coal sample size decreased from 2–0.850 mm to 0.850–0.425 mm, the HA yield slowly increased from 78.53% to 79.13%. The HA yield increased rapidly from 79.13% to 90.2% in the size range from 0.425–0.250 mm to 0.250–0.180 mm but did not increase thereafter. After the raw coal was ground, its specific surface area and pore structure increased [51], and the organic matter in the coal was mildly oxidized, leading to the breakage and deformation of weak chemical bonds and alkyl structure, the reduction of relative molecular mass, and an increase in the content of oxygen-containing functional groups [52]. Therefore, decreasing the coal sample size contributed not only to the contact between the KOH solution and the coal sample but also to the improvement in the HA yield.



Figure 6. Effect of coal size on the HA yield.

The observations above indicated that a satisfactory yield of HA (90.02%) was obtained from the 0.250–0.180 mm size fraction of the coal sample at a reaction temperature of 190 $^{\circ}$ C, reaction time of 7 h, alkali-to-carbon mass ratio of 1:1, and water-to-coal mass ratio of 20:1.

3.4. Physicochemical Characterization and Mechanism Analyses

The residual coal and HA obtained under the optimal conditions were characterized. Here, raw coal and residual coal are denoted by YM and CY, respectively. The proximate and ultimate analyses of raw lignite before and after the hydrothermal reaction are summarized in Table 1.

Products	Proximate Analysis/%				Ultimate Analysis/%				Atomic Ratios		
	M _{ad}	A _d	\mathbf{V}_{daf}	FC _{daf}	Nd	Cd	H _d	Od	O/C	N/C	H/C
YM	8.50	7.20	51.20	48.8	0.74	65.48	4.83	19.76	0.226	0.010	0.885
HA	0.96	4.92	40.09	59.91	1.68	55.44	6.02	21.28	0.288	0.026	1.303
CY	2.78	12.86	47.38	52.62	0.13	51.9	4.86	15.78	0.228	0.002	1.124

Table 1. Proximate and ultimate analyses of raw coal, residual coal, and HA.

As shown in Table 1, compared with YM, fixed carbon (FC) of HA increased, while the ash (A_d), volatiles (V_{daf}), and moisture (M_{ad}) of HA decreased to different extents. These results proved that the hydrothermal treatment could deash and devolatilize lignite, and are in good agreement with previous reports in the literature. The content of the elements N, H, and O was higher in HA than in YM and CY. The O/C and H/C atomic ratios were considered as an index for the measurement of aromaticity, with higher O/C and H/C atomic ratios corresponding to lower aromaticity [53]. Thus, the aromaticity of HA was lower than those of YM and CY. The N/C atomic ratio reflected the amount of nitrogen in the organic material. The N/C ratio of HA was higher than that of YM and CY because nitrogen is mainly present in coal as organic pyridine or pyrrole [54]. The macromolecular structures of coal were destroyed, and the amount of oxygen-containing functional groups increased after the hydrothermal treatment.

The variations in the organic functional groups present in the YM, HA and CY samples were evaluated by FTIR analysis [55,56]. FTIR spectra were recorded in the range of 4500–400 cm⁻¹ (2 cm⁻¹ resolution) using an infrared spectrometer (VERTEX 70, Germany). The results are shown in Figure 7.



Figure 7. Fourier-transform infrared (FTIR) spectroscopy of YM, HA, and CY.

In the region of \sim 3500 cm⁻¹, the hydrogen bonding interactions from free hydroxyl groups and between the hydroxyl groups and π bonds were weakened, indicating that hydrothermal treatment could change the hydrogen bond distribution of the raw coal [57]. In the 3600 to 3300 cm^{-1} range, the HA molecules had strong and broad absorption peaks. Because lignite contains almost no alcohols [58], these peaks should be attributed to the hydrogen bond-associated -OH stretching or -NH stretching vibration absorption peaks in phenolic and carboxylic acid structures [59]. This result showed that the hydrothermal reaction led to the hydrolysis of oxygen-containing functional groups such as ether bonds and ester bonds in raw coal and increased the content of carboxyl groups and phenolic hydroxyl groups in HA molecules. The stretching vibration absorption bands of aliphatic C-H bonds were in the 3000 to 2700 cm⁻¹ range. Among these wavenumbers, 2923 cm⁻¹ and 2853 cm⁻¹ were the symmetrical and asymmetric stretching vibrational peaks of the C-H bonds in the saturated hydrocarbon groups -CH₃ and -CH₂, respectively. Within this range, the intensity of the absorption peak of CH_3 at 2923 cm⁻¹ was higher for HA than for the residual coal. However, the intensity of the -CH₂ absorption peak at 2853 cm⁻¹ was somewhat diminished, probably because the hydrothermal reaction broke the CH₂–CH₂ bond of the long-chain aliphatic macromolecular compounds in the raw coal and increased the $-CH_3$ content. The peaks in the 1900 to 1000 cm⁻¹ range were mainly attributed to the oxygen-containing functional groups in HA. The peak at 1696 cm^{-1} represented the sharp C=O stretching vibration peak of carboxylic acids, aldehydes, and ketones. The peak at 1604 cm^{-1} may be attributed to C=O in amides (amide I band), quinones, or ketones. The peaks in the broad frequency range of 1550 to 1790 cm⁻¹ could be mainly attributed to protonated carboxylic acid (-COOH), carboxylate anion (-COO-), and ester carbonyl (-COOR) groups, as well as to some other functional groups. The peak at 1440 cm⁻¹ was assigned as the out-of-plane stretching vibrational absorption peak of C–H in aliphatic CH₃. The peak at 1371 cm⁻¹ was attributed to the deformation of the hydroxyl group, the C–O stretching vibration of a phenolic hydroxyl group, the C–H deformation of a methyl or methylene group, or the asymmetric stretching vibration of COO-. Aromatic structures had an absorption band within the range of 900 to 700 cm⁻¹, which may be a deformation vibration of the aromatic ring out of the CH plane, indicating that the groups around the aromatic ring are substituted. HA showed significantly higher absorption band at 1040 cm⁻¹ than YM and CY, indicating that HA had higher carbohydrate contents than YM and CY, since the absorption band at 1040 cm⁻¹ was found to represent the C-O asymmetric stretch vibration of carbohydrates. The element analytical result showed that O/C ratios of HA was slightly higher than those of YM and CY, this verified the conclusion that HA contain more carbohydrates than YM and CY [60]. The characteristic peaks at 1150 cm^{-1} , representing asymmetric stretching of the C–O–C bridge. The peak observed at 1253 cm⁻¹ can be assigned to the -COO (ester) group [61].

UV–VIS is an important method for detecting the molecular structure of HA. The location and intensity of the peaks are closely related to the unsaturated bonds and substituent groups of the molecule. UV–VIS (TU-1810SPC, Beijing Purkinje General Instrument Co., Ltd., China) analysis of the extracted HA solution was performed by recording the spectra from 200 to 900 nm and determining the absorbance variation of HA. Briefly, 20 mg of dry HA sample was added to 70 mL of a NaHCO₃ solution, and the pH was adjusted to 8.0 with 1% NaOH solution or 0.1 mol/L HCl solution. Another sample without HA was used as the blank sample.

As shown in Figure 8, the absorption signal of HA decreased monotonically in the visible light region (400–700 nm). For the near-ultraviolet region (200–400 nm), there was a weak absorption plateau (aromatic structure) at approximately 300 nm. A higher coal rank corresponds to deeper aromatization and a more pronounced absorption plateau [62]. It was inferred that the aromatized structure of the raw coal may have been destroyed by the hydrothermal reaction; there was a large absorption peak at 240 nm, indicating the presence of conjugated carbonyl groups with two double bonds in the HA molecule. The absorption peaks at 240 nm represented the unsaturated thiol, aldehyde and hydrazine carbonyl groups [63]. This result was consistent with the results of the infrared spectrum analysis and indicated that HA contained more oxygen-containing functional groups than YM or CY.



Figure 8. Ultraviolet–Visible (UV–VIS) spectra of HA.

The mineralogical compositions of YM, HA, and CY were determined by XRD, and the XRD patterns were recorded with an X-ray diffractometer (D/max-rA) over scanning angles (2θ) with a step of 0.02°, as shown in Figure 9.

Figure 9 shows the XRD crystal phase analyses of YM, CY, and HA. The diffraction peaks at 20.85°, 26.65°, 36.54°, 39.45°, 40.28°, 42.46°, 45.81°, 50.14°, 59.95°, and 68.32° were the absorption peaks of SiO₂ and the diffraction peaks at 12.37°, 19.8°, 20.36°, 24.9°, and 34.99° were kaolinite Al₂Si₂O₅(OH)₄. Comparison of the crystal phases of YM, CY, and HA showed that there were many diffraction peaks in YM, but most of them had no obvious peak shape, which was related to the complex mineral structure of lignite. The qualitative analysis of the diffraction peaks energy spectrum indicated that the inorganic elements existed mainly in the form of oxides or hydroxides. Almost no inorganic compound existed in HA. Compared to YM, the diffraction peaks of the SiO₂ and kaolinite crystal planes in CY were very sharp. This difference was due to the destruction of chelation interactions between HA and metal elements after the hydrothermal treatment, which effectively reduced the metal element content. Furthermore, the addition of HCl during the acidification process also ionized the hydroxide precipitates produced by the reaction with KOH, thereby reducing the inorganic element content in the HA. Therefore, the hydrothermal extraction of HA yielded a low-ash product than no treatment.



Figure 9. X-ray diffraction (XRD) patterns of the samples.

4. Conclusions

A KOH-hydrothermal method was used to extract HA from Inner Mongolia lignite. The maximum HA yield (90.2%) was obtained from the 0.250–0.180 mm size fraction of the coal sample at a reaction temperature and time of 190 °C and 7 h. The ash content of residual coal was highest, followed by that of raw coal and HA, indicating that hydrothermal reaction can deash coal. The O/C and H/C ratios of HA were highest, followed by those of residual coal and raw coal, indicating an increase in the oxygen and hydrogen content of HA. Analysis of the FTIR and UV–VIS spectra showed that the macromolecular structure of the raw coal was destroyed and that the organics were degraded and hydrolyzed during the reaction process.

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