



Research Article

Influence of addition of KOH on the yield and characteristics of humic acids extracted from lignite using NaOH

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Abstract

In this study, humic acids (HAs) were extracted from Chinese lignite by adding KOH to a NaOH solution. The extraction yield of HAs was found to improve because of the synergistic effect imparted by the alkali mixture of sodium hydroxide (NaOH) and potassium hydroxide (KOH). The maximum yield was obtained at 150 min by adding the mixture of 0.750 M NaOH + 0.710 M KOH to Xianfeng lignite at 80 °C. The potassium (K), sodium (Na), nitrogen (N), oxygen (O), and iron (Fe) contents were determined by X-ray diffraction, scanning electron microscopy, and proximate and ultimate analysis. The oxygen-containing functional groups in HAs were identified by Fourier transform infrared spectroscopy. The addition of KOH resulted in higher oxygen/carbon and nitrogen/carbon ratios and oxygen-containing functional groups, as compared with that in NaOH alone. The extractants containing KOH could release HAs with a higher proportion of K, Fe, N contents, which is beneficial for HAs fertilizers prepared from the lignite. The release of the nutrients (K, Fe, N) which are essential for the crops is determined by the KOH dosages.

Keywords Lignite · Humic acids · Extraction · NaOH + KOH mixture · FTIR · SEM–EDS

1 Introduction

Humic acids (HAs) are a key indicator of soil fertility because they could improve the soil characteristics by enhancing the water holding capacity, aeration, and aggregation. Therefore, HAs are widely used in modern agriculture and are now produced at an industrial scale too. HAs are most commonly found all over the world in water, soil, lignite, and peat. However, HAs present in water and soil are not abundant, and the HAs content in lignite is 20–40%, which is about 10–80% of organic matter of lignite. Lignite reserves are 130.3 billion tons in China, and the lignite reserves in the southwest region account for about 20% of the national lignite reserves. These lignite contain numerous HAs and lignite wax and are mainly distributed in Yunnan, Zhaotong, Xiaolongtan, and Xianfeng.

HAs extracted from lignite using conventional methods have been testified to have beneficial effects on seed germination, tissue nutrient balance, and crop yield and quality, because they maintain the biological, chemical, and physical characteristics of the rhizosphere with their diverse functionalities in soil and crop growth [2].

Lignite is a low rank coal containing large amounts volatile components and moisture. It is not suitable as a fuel for power plants even after being subjected to gasification, fuel gas production, and pyrolysis, owing to its low caloric value and high moisture content. Therefore, gasification and pyrolysis lead to loss of valuable contents in lignite, and it might be more ideal to utilize lignite for applications that are not related to energy generation. The use of lignite as a raw material for extracting humic substances,

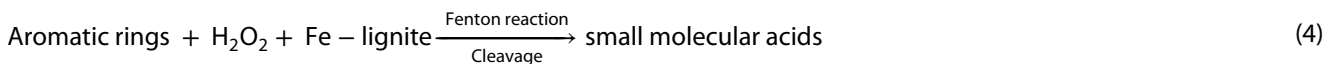
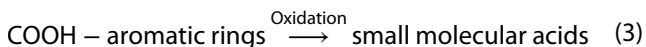
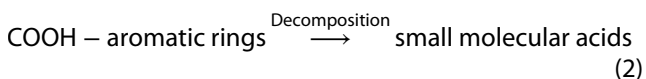
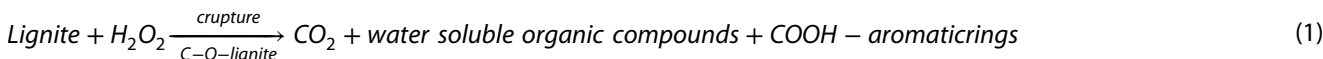
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especially humic acids, is probably the most attractive solution [1].

HAs are extracted from lignite by alkaline extraction [3], acid liquid extraction [4], and microbial conversion [5]. Although acid extraction is operationally simpler, the extracted sample contains impurities. On the other hand, although a desirable purity can be achieved by microbial conversion, the process is lengthy, and the yields are low. In contrast, prior treatment and alkaline extraction are considered more suitable for industrial scale-up as the alkalis are safe and non-toxic. The solvents for alkaline extraction include sodium hydroxide [6]; potassium hydroxide [7]; mixture of sodium hydroxide and sodium pyrophosphate [8]; sodium carbonate; and mixture of sodium carbonate and sodium hydroxide.

Lignite was extracted using NaOH or KOH, and the raw coal was pretreated with oxidizing agents such as oxygen, potassium permanganate, hydrogen peroxide, nitric acid, and hydrochloric acid to produce humic fertilizers [1, 9]. Miura et al. [9, 10] and Dorskocial et al. [1] have shown that hydrogen peroxide could degrade HAs and lignite by oxidizing and cleaving the aromatic moieties to form small molecular acids. The mechanism of oxidation was proposed as follows:



Pretreatments by HNO₃ or HCl to extract HAs from lignite resulted in very low iron contents in HAs [6]. However, further alkaline extraction of the HAs released about 30% of the total iron in lignite. The released Fe ions was solubilized via the formation of large chelates with HAs. As the solubilities of iron hydroxides are poor, formation of large chelates imparted additional stability as compared with inorganic iron compounds of soil alone, thereby enhancing the iron absorption by plants. However, there were 2 disadvantages in this method. The acid pretreatments before the alkali extraction increased the molecular size of HAs such that it was higher than that extracted by alkali alone. This occurred because of the reduction of small molecular compounds by HNO₃ pretreatment. Acid pretreatment before the alkaline

extraction also resulted in a small amounts of nitrogen and carbon and relatively large amounts of oxygen and hydrogen compared with extraction of HAs by KOH alone.

Although dilute NaOH or KOH was used to extract HAs from lignite, high sodium content in HAs was detrimental to soil and retarded plant growth [6]. Thus, many researchers [6–8, 21, 22] focused on studying the effect of different concentrations of KOH on the extraction of HAs, particularly for plants and crops that required potassium as an essential nutrient. However, high concentrations of KOH can oxidize and decompose the aromatic rings in HAs, releasing a large number of small molecular compounds. It was observed that plants could absorb the smaller molecular humic acids more easily compared with the bigger molecular humic acids, and the metabolic activity of plants in the former case was higher than that in the latter case.

The extraction yield of HAs could be increased by increasing the extraction temperature. Cegarra et al. [7] reported that the extraction yield of HAs did not significantly increased by increasing the extraction temperature. And the highest content of nitrogen containing functional groups in HAs were obtained using 0.25 M KOH at room

temperature, while less N-rich compounds and lower functional groups compounds were obtained using hot solvent and concentrated KOH solution. Thus, they concluded that higher temperatures were unsuitable for extraction of HAs from lignite.

Several concentrations and combinations of solvents have been tested in order to obtain HAs in good yield and purity. Cegarra J et al. [8] showed that the highest yield of HAs was obtained with 0.25 M KOH, while the lowest yield was obtained with 0.1 M NaOH. Moderate yields were obtained with NaOH + Na₄P₂O₇ mixture. The use of Na₄P₂O₇ resulted in extraction of compounds with higher functional groups, except phenolic group, thereby indicating its capacity of decomposition [11]. The sizes of the molecular compounds in HAs were larger when Na₄P₂O₇ was used for the extraction. The molecular size distribution of the extracted compounds using NaOH + Na₄P₂O₇ mixture was similar to those extracted using Na₄P₂O₇ alone.

There are very few studies on the effect of NaOH + KOH mixture on the extraction yield of HAs. Our study was

focused on investigating the influence of NaOH + KOH mixture on the extraction yield and characteristics of HAs.

2 Experimental section

2.1 Lignite and extraction of HAs

Lignite was mined from Yunnan Shicaoqing, Guojiashan, and Xianfeng, southeast Chinawas to extract HAs. The detailed characteristics including proximate and ultimate analyses of the lignite were shown in Table 1. The samples were passed through a 80-mesh sieve (<0.178 mm, 98%) and dried in an electric blast drying box at 80 °C.

NaOH, KOH, HCl, and KBr were obtained from Aladdin (Shanghai) company. The extraction reagents included 0.250, 0.375, 0.500, 0.625, 0.750, and 0.875 M NaOH; 0.140, 0.250, 0.290, 0.375, 0.430, 0.500, 0.570, 0.625, 0.710, 0.750, 0.875, and 1.070 M KOH. The alkali mixture was prepared by mixing 25 ml of NaOH and 25 ml of KOH in the desired concentration. Lignite (5 g) was mixed with 50 mL NaOH, KOH or NaOH + KOH solution (1:10 lignite/solution ratio) and constant stirred in sealed bottles by magnetic stirrer for 120 min. Following this, the samples were centrifuged for 10 min at 2200 rpm, and the supernatants were carefully separated from the sediment settled at the bottom. The supernatants were adjusted to pH 1 using concentrated HCl (6.0 M). The precipitants were then centrifuged and filtered and then dried in an electric blast drying box at 60 °C for 3 day until a constant weight was obtained, indicating that the humic acid fractions were completely dried. The insoluble part (sediment) was dried and labeled as “residual,” and the extraction was repeated 3 times with the same extraction reagents. The experimental error was below 1%. All the HAs fractions were stored in polyethylene bags until further characterizations by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray (SEM–EDX) spectroscopy, and X-ray diffraction (XRD).

2.2 Characterization of HAs

The C, H, N, and S contents in humic acids were determined using Vario Micro Cube Elementar (Elementar

Analysensysteme GmbH, Germany); the O content was determined by the difference. All the experiments were performed in duplicates to confirm the accuracy of the data. An IR spectrometer (Varian 640-IR, American) was used to identify the organic functional groups in the HAs at ambient temperature. The humic acids and residual lignite samples (1 mg) were mixed with spectrometry grade dried KBr (100 mg) and then pressed into pellets under 10 MPa for 2 min. Spectra were recorded in the range 4000–400 cm⁻¹.

The phase composition of Na, K, Fe, N, P in humic acids was characterized using an X-ray diffractometer (Rigaku MiniFlex II DESKTOP) equipped with Cu K α radiation ($\lambda = 0.15406$ nm) operating at 40 kV (tube voltage) and 140 mA (current). The samples were scanned in the range 10°–90° at a speed of 7°min⁻¹. The surface morphology of humic acids was visualized by a HITACHI-3500 N scanning electron microscope (SEM) (Hitachi Ltd, Japan). For observations by SEM, HA samples were dried in a desiccator and sputtered with platinum using a HITACHI E-1000 ion sputtering device. Elemental distribution of humic acids was accomplished by EDX spectroscopy. The samples were handled carefully to ensure that the HAs are not destroyed.

3 Results and discussion

3.1 Yields of humic acids

Three coal samples were used as the extraction materials, and NaOH, KOH, and NaOH + KOH solutions were used as the extraction reagents for each type of coal. The results

Table 2 Effect of extraction reagent on the yields of humic acids extracted from different coal sample^a coal sample type on extraction yield of humic acids

Raw materials	NaOH	NaOH + KOH	KOH
Yields extraction of humic acids/%			
GJS	20.18	18.06	15.25
SCX	19.76	18.75	12.70
XF	24.93	23.66	21.81

^aExtraction conditions: concentration, 0.375 M NaOH or KOH; temperature, 80 °C; time, 120 min

Table 1 Proximate and ultimate analyses of the lignite

Coal	Code	Proximate analysis (wt%)				Ultimate analysis (wt%)				
		M	A	VM	FC	C	H	N	S	O ^a
Guojiashan	GJS	32.98	2.90	38.63	25.49	40.29	2.67	0.95	0.76	19.54
Shicaoqing	SCX	21.86	28.26	30.59	19.29	40.71	1.66	0.91	0.77	5.82
xiangfen	XF	32.88	10.97	46.85	9.30	33.57	3.12	1.20	0.78	17.48

M moisture, A ash; VM volatile matter; FC fixed carbon; ^aBy difference

are shown in Table 2. It is evident that the yields of humic acids extracted from three different types of coal samples using the same reagent were different. The extraction yield from lignite (XF) was the highest, and the yields from the same lignite in the presence of various extraction reagents followed the order $\text{NaOH} > \text{NaOH} + \text{KOH} > \text{KOH}$. Hence, we selected lignite (XF) as the optimal raw material for studying the effects of added KOH on the yield and characteristics of HAs extracted using NaOH.

Figure 1a shows that the HAs yields increase rapidly from 17.47% to 24.93% as the dosage of NaOH increases from 0.250 to 0.375 M. The highest yield (28.45%) was obtained with 0.625 M NaOH, and further increase in the NaOH dose decreased the yield of HAs. This observation was in agreement with that reported in the literature [12, 13]. It is reported that the solubility of the extracted HAs in NaOH solution increases with increasing dose of NaOH. The solubility decreases at high ion concentrations as HAs is a type of colloid. High ion concentrations hindered the decomposition of hydrocarbons in the lignite, forming insoluble substances with increasing NaOH dosage. This,

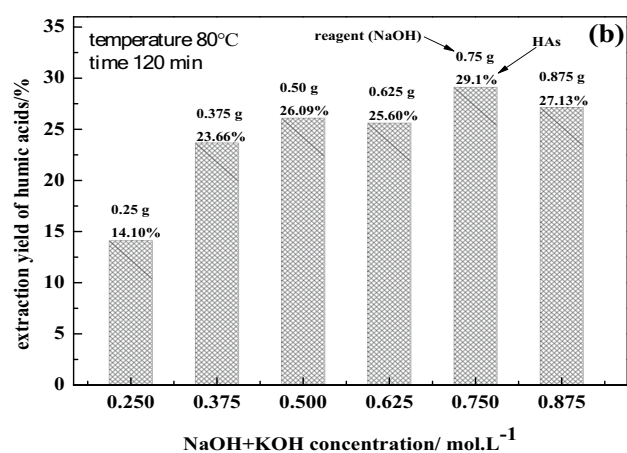
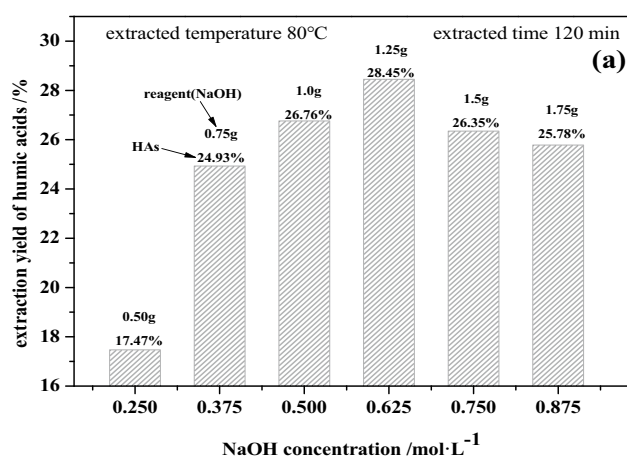


Fig. 1 Effect of addition of alkali on yield of HAs extracted from Chinese lignite with **a** NaOH and **b** NaOH + KOH dosage

in turn, decreased the yields of HAs. Figure 1b indicates that the yield of HAs improved obviously with NaOH + KOH solution as compared with NaOH alone, and the extraction yield reached maximum (29.10%) when the mixture of 0.750 M NaOH + 0.750 M KOH was used. Thus, for obtaining similar yield of HAs, the amount of NaOH required for extraction using NaOH + KOH reduced compared with that required for extracting using NaOH alone.

High concentrations of NaOH is detrimental to soil and plant growth. Besides, potassium is an important nutrient for crops. Considering this, the effect of addition of varying amounts of KOH to the NaOH-extracted HAs was investigated in order to reduce the NaOH dosage to the minimum. Figure 2 shows the influence of KOH on the yield of HAs upon its addition to the HAs extracted using 0.750 M NaOH. The yields of HAs increase as the concentration of KOH increases from 0 to 0.170 M; the maximum yield (31.45%) was obtained using 0.170 M KOH. Beyond this concentration, the extraction yield decreased. The observation can be explained based on the following aspects. First, KOH can prevent the NaOH-induced degradation of soluble hydrocarbons in HAs to some extent. Second, KOH can decomplex the HAs by means of cations. Third, a large number of small molecules could be released at higher KOH concentrations, as high concentrations of KOH could partially decompose higher amounts of HAs as compared with low concentrations of KOH. The highest ionic strength (at the highest concentration of KOH) resulted in relatively lower yield of HAs [6].

Figure 3 shows that the HAs yield with equal weights of NaOH, NaOH + KOH, and KOH solutions were 25.78%, 31.45%, and 26.78%, respectively. NaOH and KOH exhibited synergistic effect in the extraction process, thereby enhancing the yield of HAs. Figure 4a shows that the yields of HAs increased from 23.25% to 31.86% as the extraction

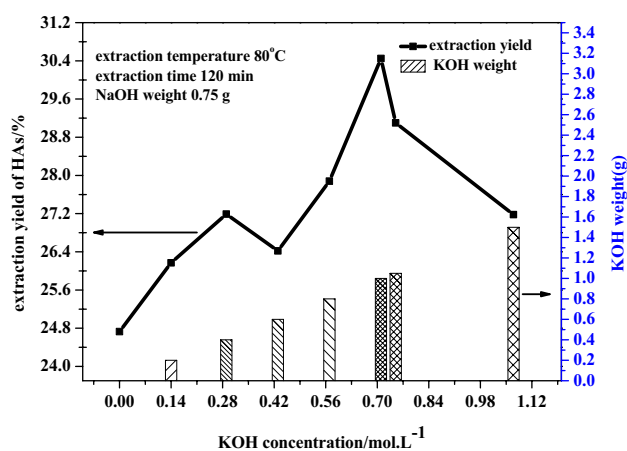


Fig. 2 Effect of the amount of added KOH on the yield of HAs extracted from Chinese lignite

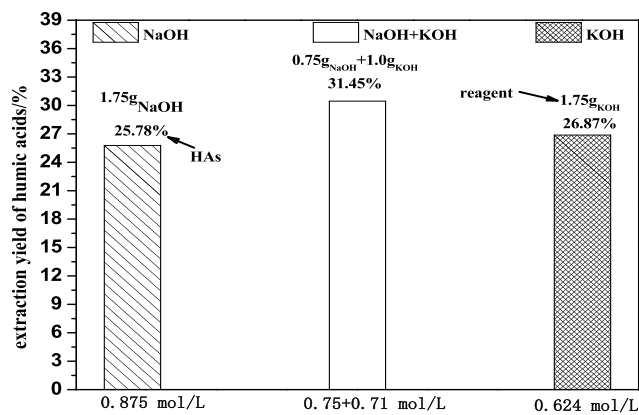


Fig. 3 Effect of alkali on the extraction yield of HAs. Extraction temperature and time were 80 °C, 120 min, respectively

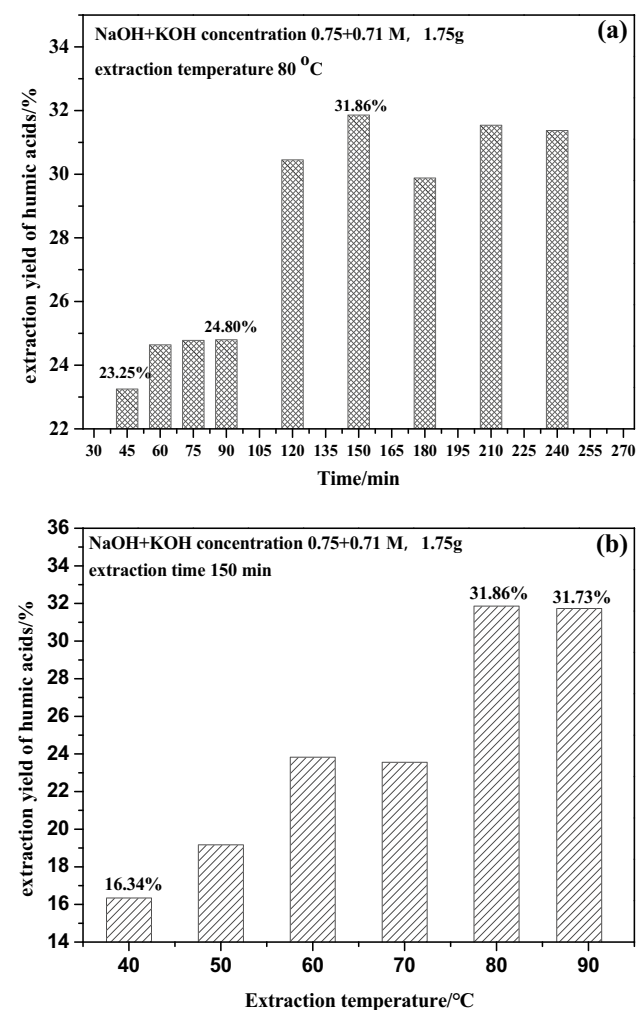


Fig. 4 Effects of **a** extraction time and **b** extraction temperature on the yields of HAs extracted from Chinese lignite

time was increased from 45 to 150 min. The yields were in the range 29.88–31.45% as the extraction time was

increased beyond 150 min, because the HAs could easily decompose at extended extraction times. Figure 4b illustrates that the extraction yield of HAs could be increased by increasing the extraction temperature. The optimum extraction yield was obtained when the extraction temperature was above 80 °C. The yields of HAs were almost the same at 80 and 89 °C. However, the thermal stability of HAs was poor at high temperatures, because of which the extraction yield of HAs decreased. Therefore, extraction of humic fertilizers by hot KOH solutions (higher extraction temperature) was not attempted as it would be ineffective [7].

3.2 Elemental and proximate analysis of HAs and residue

Table 3 shows that HAs extracted with NaOH + KOH had marked differences in the H/C, O/C, N/C ratios compared with those extracted by NaOH alone. The H/C ratio increased gradually with increase of KOH in the NaOH solution, indicating that the HAs contained substantial amounts of aliphatic hydrocarbons. The N/C ratio was highest when 0.710 M KOH was added to the NaOH solution. Cegarra et al. [8] and Butler et al. [14] illustrated that the N content in HAs and the presence of high molecular weight molecules were linearly related. So higher N/C in HAs possibly indicate the presence of high molecular weight compounds as compared with humic acids extracted with other dosages of KOH. The presence of 0.710 M KOH in NaOH resulted in much lower C contents and relatively higher O contents. Consequently, the O content and O/C ratio suggested that NaOH + KOH could oxidize more molecules as compared with NaOH alone. This observation was similar to that reported by Cegarra et al. [6, 8].

The content of inorganic compound (ash) in the KOH-HAs were slightly different (Table 3). As a result, the above results relating to trends in inorganic compounds could infer that potassium did not been added into the humic acids with increase of KOH dosage after extracting from lignite. However, the experiment results obtained were in contrast to this expectation. The XRD patterns of HAs with and without KOH additive are shown in Fig. 5. The diffraction peaks at 28.44°, 40.61°, 50.27°, 58.74°, 66.52°, 73.84°, and 87.76° corresponded to KCl; the diffraction peaks of NaCl and KFeO₂ were observed at 27.43°, 31.78°, 45.60°, 56.63°, 66.33°, and 75.39°, 84.05°, and 16.74°, 19.29°, 33.31°, 36.18°, 57.38°, and 60.06°, respectively. The crystalline structure of KCl is shown in Fig. 6. The elevated dosages of KOH resulted in wider and more intense diffraction peaks, indicating the formation of smaller crystallites of KCl upon the addition of KOH into HAs extracted with NaOH. The diffraction peaks of KFeO₂ became more

Table 3 Proximate and ultimate analyses of the HAs^c

KOH concentration, (M)	Proximate analysis (wt%,d)			Ultimate analysis (wt%,d)					H/C	O/C	N/C
	A	VM	FC	C	H	N	S	O ^{diff}			
0	15.62	47.33	37.05	45.12	4.05	1.11	0.96	33.14	1.08	0.55	0.02
0.14	14.91	47.78	36.07	46.44	3.91	1.25	0.92	32.57	1.01	0.53	0.02
0.29	15.32	48.61	37.31	44.67	3.96	1.29	0.83	33.93	1.06	0.57	0.02
0.43	14.35	49.29	36.36	47.58	4.34	1.32	0.81	31.60	1.09	0.50	0.02
0.57	15.49	49.01	35.50	48.39	4.47	1.53	0.81	29.31	1.11	0.45	0.03
0.71	16.75	53.88	29.37	40.93	4.58	1.84	0.75	35.15	1.34	0.64	0.04
1.07	12.85	50.93	36.22	46.23	4.16	1.69	0.77	34.30	1.08	0.56	0.03

A ash; VM volatile matter; FC fixed carbon; ^b By difference. ^cExtraction temperature and time 80 °C, 120 min, respectively. Concentration, 0.75 M NaOH

intense with increasing potassium contents in HAs, in turn

suggesting that the Fe content in HAs was increased upon

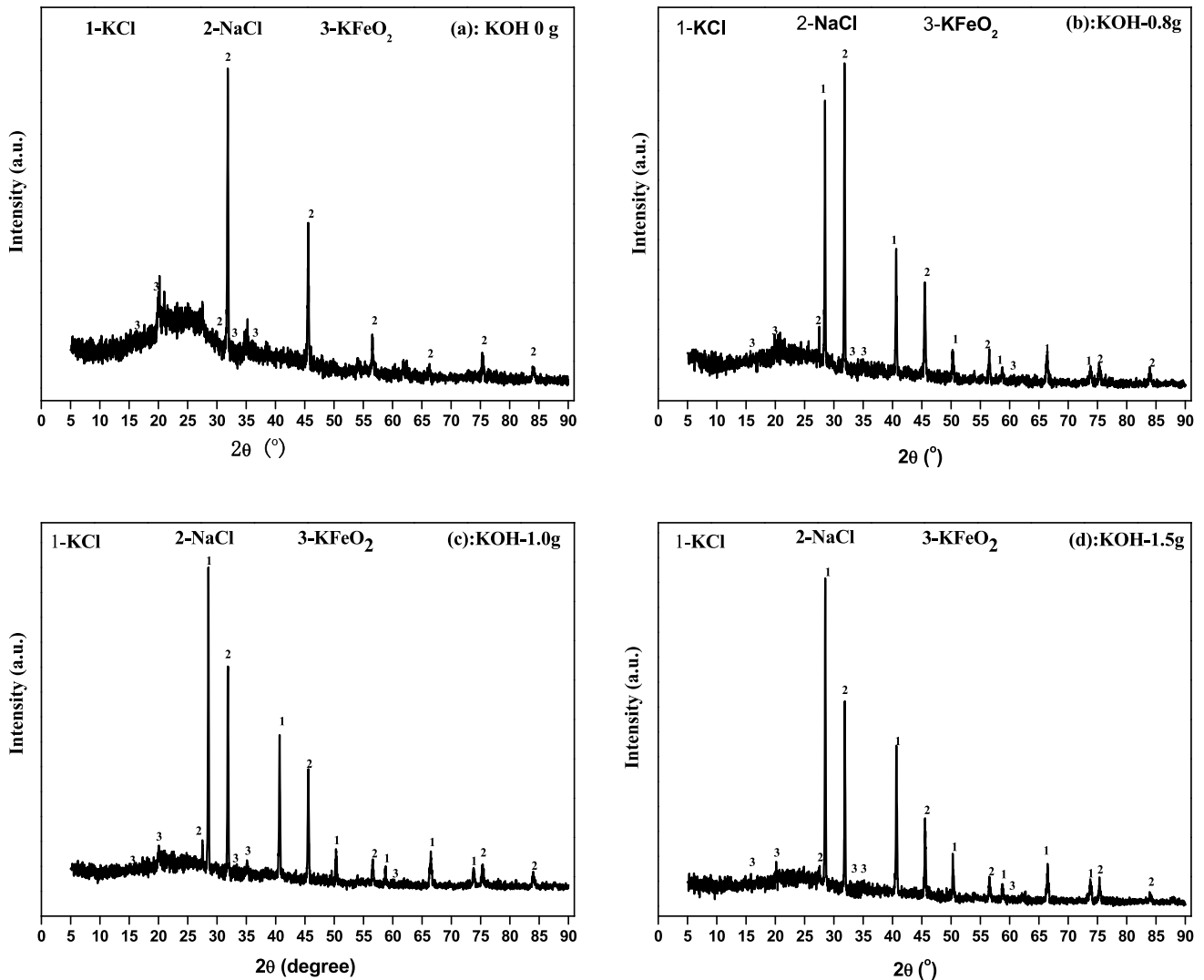


Fig. 5 XRD spectra of HAs extracted from lignite by NaOH + KOH dual extraction systems. Temperature 80 °C, time 120 min, NaOH dosage: 0.75 g

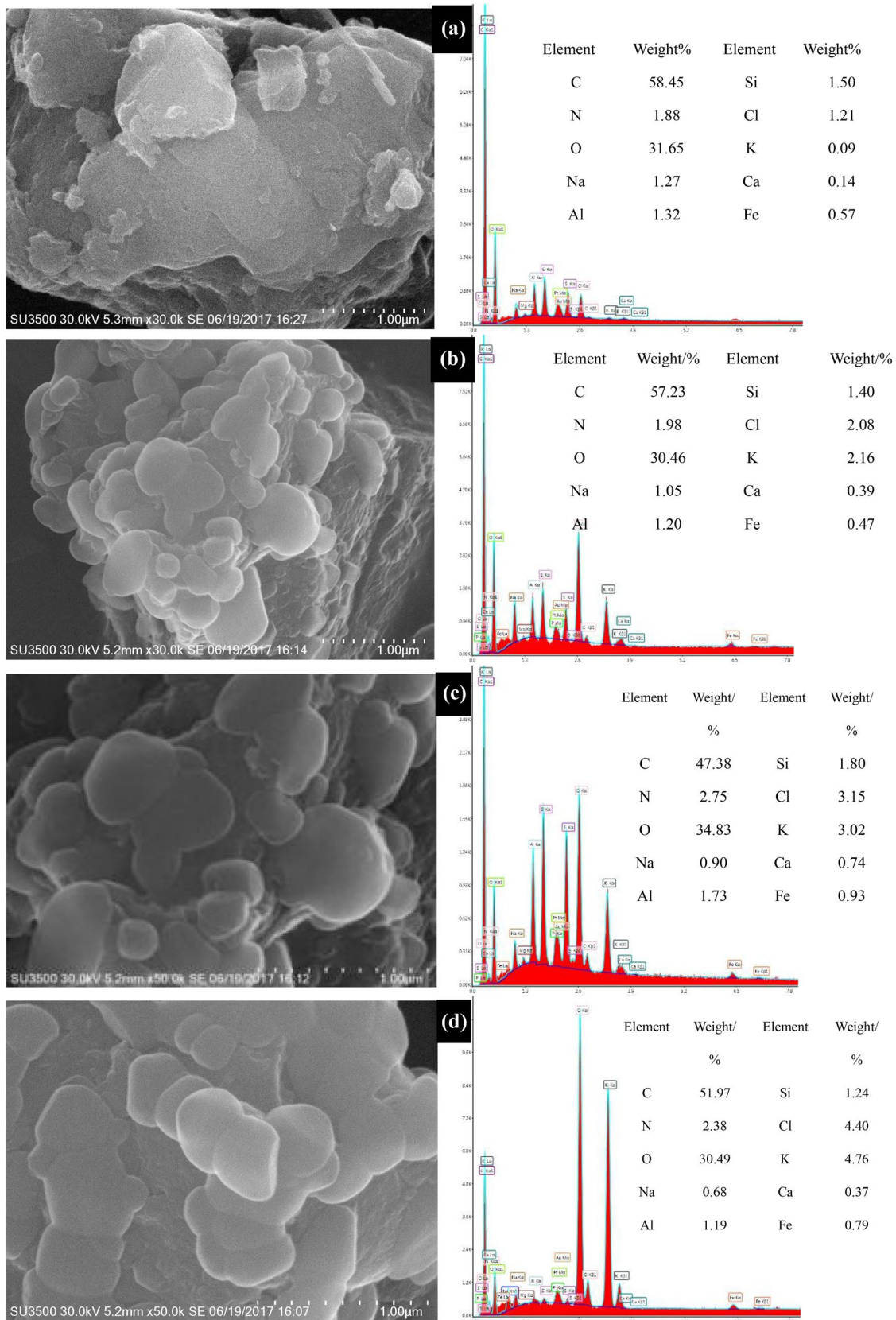


Fig. 6 SEM-EDS images of extracted by NaOH+KOH dual extraction system. Extraction time and temperature were 80 °C and 120 min, respectively. **a** 0 g KOH, **b** 0.8 g KOH, **c** 1.0 g KOH, **d** 1.5 g KOH. NaOH dosage: 0.75 g

the addition of KOH in NaOH solution.

The K, Fe, and N contents in HAs, as determined by SEM-EDS (Fig. 6), were obviously improved with increasing KOH dosage in NaOH solution. While the Na content in humic acids gradually reduced, the K, Fe, N contents increased from 0.09%, 0.47 to 1.98% (0.750 M NaOH + 0 M KOH) to 3.02%, 0.93%, and 2.75% (0.750 M NaOH + 0.710 M KOH), respectively. The Na content corresponded to a decrease from 1.27% to 0.90%. Figure 6 shows the presence of several voids between the layers of HAs, suggesting an irregular, multi layered colloidal structure ((a): KOH 0 M). It was further observed that the surface morphology of HAs changed from multilayer agglomeration to a porous structure, with large number of globular particles and many new pores as compared with that in the absence of KOH. When the concentration of KOH was increased, potassium, iron, and calcium cations (Fig. 6) were octahedrally coordinated to a range of oxygen functional groups such as -OH^- and -COO^- present in HAs [15].

This essentially provided atomic level dispersion and consequently, led to form globular particles and numerous pores. Cegarra et al. [6] reported that a large number of NaOH-soluble Fe species might chelate with HAs [22, 23], imparting higher stability compared with inorganic Fe compounds in soil. This, in turn, results in better Fe uptake by plants.

3.3 FTIR spectroscopy of HAs and residue

The FTIR spectra of HAs and residue with fixed NaOH dosage (25 ml, 0.750 M) and different amounts of added KOH are shown in Fig. 7. The oxygen containing functional group of HAs and residual lignite were determined according to the information in the literature [16–19]. Absorption peaks at $3400\text{--}800\text{ cm}^{-1}$ were attributed to the oxygen containing functional groups in HAs (Fig. 7a). The broad absorption peak corresponded to H bonded O–H groups, O–H stretching in phenols, and N–H stretching vibrations in aromatic rings. It is evident that the intensity of the hydroxyl (O–H) peak did not change, because the moisture absorption during the pellet formation with KBr could not be completely avoided. Absorption peaks at 2972, 2920, and 2850 cm^{-1} were attributed to the aliphatic C–H stretching bonds. Peak of carboxylic or ketone group C=O stretching vibration were observed at 1706 cm^{-1} ; aromatic C=C, H bonded C=O, and dissociated COOH groups showed intense absorption peak at 1617 cm^{-1} with increasing dosage of KOH, indicating an obvious increase in the COOH content of HAs in the presence of added KOH.

The absorption peak at $1399\text{--}1440\text{ cm}^{-1}$ corresponded to O–H deformation. The stretching vibration of phenolic OH slightly increased with increasing KOH, thus confirming that the phenolic OH content in HAs slightly increased.

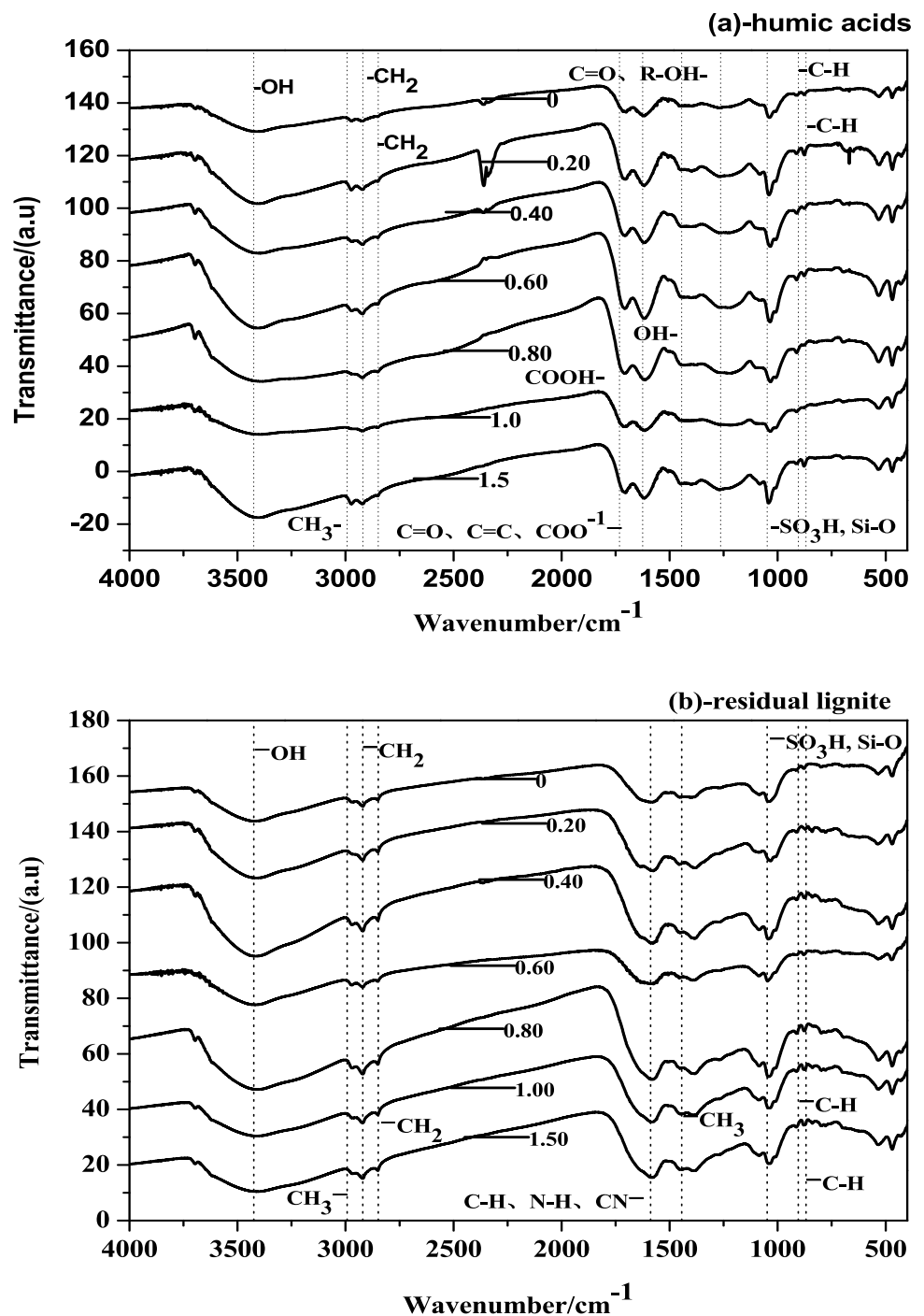
Absorption peak at 1082 cm^{-1} could be attributed to OH deformation or C–O stretching of phenolic OH, considering that the ash content of HAs ranged between 12.85% and 16.75% (Table 3). Meanwhile, the Si and S content in HAs were in the range 1.24–1.80% and 1.01–1.97%, respectively (Fig. 6). This may indicate that the adsorption at 1034 cm^{-1} could be associated with Si–O stretching or stretching vibrations of SO_3H and S=O [17]. Huttinger et al. [20] have reported that alkali (K, Na) and alkali earth oxides (Ca) could act as sulfur scavengers through an exchange reaction to form K_2S , Na_2S , and CaS. Although the (K, Na, Ca) sulfide diffraction peak could not be observed in all the HAs (Fig. 5), the alkali and alkali earth oxides were observed in HAs (Fig. 6). This indicates that they are present in small quantities and are highly dispersed on the surface of HAs.

The spectra of the residual lignite samples (Fig. 7b) had similar patterns with small quantitative differences as compared with HAs. However, no absorption peak corresponding to C=O of COOH and =O were observed at 1706 cm^{-1} and 1617 cm^{-1} , respectively, in the residual lignite when KOH was added into NaOH solution. This demonstrated that hydroxyl (-OH) and carboxyl (-COOH) compounds in HAs extracted from lignite increased gradually with the increase of KOH in NaOH solution.

4 Conclusion

The Yunnan lignite of China was used as an extraction material for extraction by NaOH + KOH solution. For the first time, the yield of HAs was investigated by the addition of KOH to NaOH solution. The analytical procedure was feasible and high yields of HAs from lignite could be obtained. The protocol could be further used for the industrial extraction of HAs. The highest extraction yields were obtained by the reaction XF lignite with mixed alkali (0.75 M NaOH + 0.71 M KOH) at a temperature of $80\text{ }^\circ\text{C}$ and reaction time of 150 min. Meanwhile, the K, Fe, N, and Ca contents in humic acids were the highest when 0.750 M NaOH and 0.710 M KOH were used. It showed the HAs could act as humic fertilizers to stimulate plant growth in agricultural soils as K and N were essential nutrients for plants. Fe in HAs were considered to be chelated, which was more beneficial for plant uptake. Finally, the NaOH + KOH extractants released more oxygen-containing functional groups (-OH , -COOH) compared with those extracted from NaOH alone, showing that KOH in NaOH released more oxidized molecules in XF lignite. As a result, the mixture of NaOH + KOH can be recommended for the preparation of humic fertilizers from Yunnan lignite of China.

Fig. 7 FTIR spectra of HAs and residual lignite in the presence of different KOH dosage. Extraction temperature and time were 80 °C and 120 min, respectively, fixed NaOH dosage: 0.75 g



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Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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