






NANO- AND PHOTO- CATALYSIS IN CURRENT CHEMISTRY: POSSIBILITIES AND CHALLENGES

Article

Received: 2 July 2024 | Revised: 31 August 2024 |
Accepted: 13 September 2024 | Published online: 23 September 2024

UDC 544.42+519.242.7

<https://doi.org/10.31489/2959-0663/3-24-12>

Qianqian Li¹ , Jinlin Li¹ , Yinqiao Zhao¹, Yingjie Zhu¹,
Murzabek I. Baikenov² , Xiaofei Liu³ , Xintai Su^{1*} 

¹*School of Environment and Energy, Guangdong Provincial Key Laboratory of Solid Wastes Pollution Control and Recycling, South China University of Technology, Guangzhou, Guangdong, China;*

²*Karaganda Buketov University, Karaganda, Kazakhstan;*

³*College of Chemistry and Chemical Engineering, Xinjiang Agricultural University, Urumqi, China*

(*Corresponding author's e-mail: suxintai@scut.edu.cn)

Thermal Catalytic Production of Potassium Humate Fertilizer from Tobacco Straw and Its Performance in Wheat Hydroponics

Production of artificial humic acid (AHA) from waste biomass will contribute to environmental protection and agricultural productivity. However, there is still a lack of a faster, more efficient and eco-friendly way for sustainable production. In this study, potassium humate was prepared from agricultural waste tobacco straw by thermal catalysis using environmentally friendly Fe₂O₃ as a catalyst. The yield of potassium humate was successfully increased to 68.77 %. In the present study, using characterization methods such as TG-DTG and UV, it was found that the potassium humate prepared from tobacco straw had lower aromaticity, smaller molecular weight, as well as better solubility and better quality. In addition, the effect of potassium humate fertilizer on wheat biomass was also investigated in this experiment by wheat hydroponics. The results showed that the germination rate of wheat increased by 17 % and the fresh and dry weights increased by 6.94 % and 19.31 %, respectively, with the addition of potassium humate prepared with iron catalyst. This study provides a green and simple technology for the resourceful utilization of tobacco straw to produce high value-added potassium humate, and enriches the source of raw materials for potassium humate, expanding its application in the field of crop growth.

Keywords: Tobacco straw, potassium humate, wheat growth, wheat hydroponics, artificial humic acid (AHA), biomass, tobacco straw, thermal catalysis, fertilizer.

Introduction

Agricultural production is the second largest contributor of greenhouse gases (19.9 percent), after the energy sector (68.1 percent). A large amount of solid waste is generated annually from agricultural production [1]. Common agricultural wastes include rice straw, tobacco straw, wheat straw, corn stover and bagasse, etc. In total, about 998 million tons of agricultural waste is generated globally each year, of which about 110 million tons of agricultural waste are generated annually in Europe, China, Japan, and India, and 240 million tons of agricultural waste are generated annually in the United States [2–3]. These agricultural wastes mainly contain cellulose, hemicellulose, lignin and starch, and are rich in high value components and bioactive compounds such as dietary fibre, polysaccharides, proteins and fatty acids [4]. It also contains other polar organic functional groups such as ethers, phenols, carboxyl groups, ketones, aldehydes and alcohols [5]. Humus is produced by microbial degradation of dead biomass (e.g. lignin), which is difficult to break down further. The properties and structure of humic substances depend on the specific conditions un-

der which they are extracted from water or soil. Although humic substances come from different sources, their properties are very similar [6]. In soils and sediments, humic substances can be divided into three main fractions: humic acid (HA), fulvic acid (FA) and humin (HM). The main elements are carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S), and it also contains many reactive groups and a large variety of reactive functional groups, such as hydroxyl, alcohol hydroxyl, phenol hydroxyl, quinone group, carbonyl group, and a small amount of methoxyl, amino group, alkenyl group and so on. These functional groups are capable of forming coordination compounds or other biochemical reactions with a variety of substances such as metal ions, and are used in many fields such as industry and environmental protection.

In addition, Fe-based catalysts applied to the synthesis of AHS have gained increasing attention due to the excellent biocompatibility and environmental friendliness. The addition of Fe catalysts to establish the Fenton reaction promoted the lignin macromolecular structure formation for the artificial synthesis of humic-like substances and an increase in the yield of AHA. Additionally, Fe can be used in biomass pyrolysis to catalyze lignin depolymerization. This indicates the great potential of Fe catalysts in supporting biomass structural transformation. As one of the typical Fe catalysts, iron oxyhydroxide (FeOOH) has a high density of hydroxyl radicals on its surface and exhibits acid-base bifunctional catalytic activity with excellent catalytic performance, which makes it a reliable choice for promoting the artificial humification process. FeOOH, similar to other metal hydroxides, can be used in many aspects, such as photocatalysis, electrocatalysis and coal liquefaction, and has a very high application value. However, FeOOH's role in abiotic humification has not been explored, and its effect on each part of AHS has not been investigated.

Although HA from mineral sources is easy to obtain, the humus content of mineral sources such as lignite and weathered coal is low, and the preparation of HA with higher molecular weights and lower yields is still a problem that needs to be solved urgently. The preparation of biochemical HA from biomass waste has become an efficient way to utilize agricultural resources, and it is also one of the main sources of HA preparation. After a series of physical treatments, the straw is hydrolyzed, catalyzed and oxidized into HA by chemical reagents, and then biochemical HA is obtained by filtration, washing, drying, crushing and grinding. The biochemical HA obtained by this method has a low molecular weight, is rich in oxygen-containing functional groups, and is highly active. Therefore, due to the non-renewable nature of coal, the raw material for HA, as well as its high price and transport costs, a new and efficient HA production technology has been developed from existing, renewable and inexpensive materials. Some researchers have proposed methods to convert biomass solid waste into HA-like substances by modeling the humus formation process in nature. For example, some chemicals obtained modified humic acid-based cross-linked composite pre-tuned to the sorbed copper ion. Such tuning forms adsorption centers in the polymer network of the composite, which can repeatedly and highly specifically interact with the template, and highly selectively extract target molecules from solution, leading to significant increase in sorbent capacity [7]. Some chemicals accelerated the humification process and synthesized HA with a structure similar to that of natural HA by using black soil and leaves as precursors and hydrothermal treatment at 200 °C for 24 h [8]. Some chemicals converted food waste into artificial HA under hydrothermal conditions, which resulted in a HA yield of 43.5 % after only 1 h of treatment, and also produced mineral-like HA with similar structure and composition [9]. Therefore, it is feasible to prepare HA-like substances from biomass. However, since the disadvantages of hydrothermal conversion are its duration and low yield, as well as the high equipment requirement, there is an urgent need to find a simple and efficient HA extraction method. In this study, potassium humate was prepared by thermal catalysis using tobacco straw as a waste biomass feedstock and environmentally friendly Fe₂O₃ as a catalyst. Fe₂O₃ can also modulate the properties of AHS by changing the content and nature of AHA (Artificial Humic Acid) and AFA (Artificial Fulvic Acid). The main results of this work were: 1) The yield of potassium humate was successfully increased to 68.77 % at a roasting temperature of 225 °C, a roasting time of 2 h, and an iron catalyst dosage of 1 % (relative to the mass fraction of tobacco straw); 2) Using characterization methods such as TG-DTG and UV, it was found that the potassium humate prepared from tobacco straw has a lower aromaticity, a smaller molecular weight and better solubility and better quality; 3) It can be proved by comparing the results of TG-DTG, UV and other characterization methods that the addition of Fe₂O₃ catalyst contributed to the increase of xanthic acid content and oxygen-containing functional group content in potassium humate. In addition, the effect of potassium humate fertilizer on wheat biomass was also investigated in this experiment by wheat hydroponics. The results showed that the germination rate of wheat increased by 17 % and the fresh and dry weights increased by 6.94 % and 19.31 %, respectively, with the addition of potassium humate prepared with iron catalyst. This study provides a green and simple technology for the resourceful utilization of tobacco straw to produce high value-added potassium humate, and enriches the

source of raw materials for potassium humate, expanding its application in the field of crop growth. Overall, the main objective of this study is to provide a new and sustainable pathway for the accelerated production of AHS from waste biomass, thus effectively utilizing a large amount of waste biomass.

Experimental

Tobacco straw is a lignocellulosic raw material that is abundant, inexpensive and easily available. Tobacco straw was used as a typical waste biomass in this study. Potassium humate was prepared by weighing a certain amount of tobacco straw and crushing it through a 200 mesh sieve. The experiment was divided into two groups, the first group mixed 10g of tobacco straw powder and catalyst Fe_2O_3 in the ratio of 1:0.01 by mass and added to 30 % KOH solution; the second group added 10g of tobacco straw powder only to 30 % KOH solution. Equal amount of 30 ml of deionized water was added to the two groups of mixtures and fully dissolved after sonication. The two groups of mixtures were transferred into an oven and then dried at 70 °C. Then the two mixtures were completely ground, transferred into a crucible, wrapped with tin paper, transferred to a high-temperature blast drying oven, and roasted for 120 min at 225 °C. After roasting, the product obtained was quenched by adding deionized water. After standing for some time, the product was transferred to a beaker and dissolved in water, the soluble organic substances were completely dissolved by ultrasonication, and the solid-liquid separation was achieved by filtration. The solid and liquid were transferred to an oven and dried at 70 °C to obtain potassium humate samples, which were weighed. The sample obtained without catalyst addition was named S-HLS-K and the sample prepared with catalyst addition was named CS-HLS-K.

The test crop was wheat, potassium humate was extracted with KOH as leaching agent to obtain potassium humate and then adjusted the pH to pH 6.5–7.5 (the pH range suitable for wheat growth), the experiment was conducted in April 2024 in the laboratory of the School of Environment and Energy, South China University of Technology, Guangzhou, China. Wheat seeds were provided by Guangdong Academy of Agricultural Sciences. The prepared S-HLS-K and CS-HLS-K potassium humate fertilizers were added to the experimental groups, and clean water was used as the control group, which was uniformly placed in the laboratory for cultivation. Seedlings were raised in a hydroponic potting apparatus (the potting apparatus is divided into two parts, with a planting basket on the upper part and a transparent bottle on the lower part, and the planting basket has a uniform gap on the side to facilitate the absorption of nutrients by the growing down root system) on 11 April 2024. The experiment was carried out in an environment with an average day and night temperature of 23–25 °C, relative humidity of 50–65 % and natural light conditions. The water was replenished regularly every morning and evening, and 50 wheat seeds were born in each planting basket, evenly and randomly arranged. After one week of wheat growth, wheat seedlings were harvested on 18 April 2024 and the growth of wheat seedlings was determined. Each treatment was repeated three times to ensure the accuracy of the experiment.

Analytical Methods

In this experiment, based on the specific steps of the titration method of ammonium ferrous sulphate in the national standard GB/T 34765-2017, the xanthate content of the prepared potassium humate was determined and compared with that of the commercial mineral source potassium humate.

In order to investigate in depth, the detailed chemical composition of the produced potassium humate versus that of the commercial mineral source potassium humate, a series of elemental analytical characterization techniques were employed in this study to determine the content of five key elements, namely carbon, hydrogen, oxygen, nitrogen and sulphur, in the samples. These detailed elemental analytical data provided a revealing characterization of the elemental composition of the samples. In addition, based on the measured H/C and O/C atomic ratios, the degree of aromatization and the number of oxygen-containing functional groups of the samples can be further deduced. In this experiment, a high-precision Vario EL cube type elemental analyzer (Elementar, Germany) was used to ensure the accuracy and reliability of the data.

UV-1800PC model UV-visible spectrophotometer manufactured by Shanghai Meppan Instruments Co was used for the UV-Vis absorption spectroscopy analysis and detection of substances. First, a 0.05 mol/L sodium bicarbonate solution was configured using a 250 mL volumetric flask. Subsequently, 5 mg of S-HLS-K and CS-HLS-K samples were weighed and each dissolved in the previously configured sodium bicarbonate solution, and the solution was fixed using a 50 mL volumetric flask to ensure homogeneity and then allowed to stand. During the detection stage, the scanning wavelength range was set to 200–900 nm and the samples were detected sequentially. Special attention was paid to the absorbance ratio at wavelengths 465 nm and 665 nm, i.e., E_4/E_6 .

Fourier infrared spectroscopy plays an important role in the study of compositional and structural characteristics of HA, which can accurately detect the relative content of functional groups in the sample and their existence patterns, providing reference data for the analysis of HA. Nicolet iN 10 Fourier infrared spectrometer (Thermo Fisher Scientific) was used for this experiment. To ensure the accuracy of the experimental results, the instrumental resolution of 0.06 cm^{-1} was set and 32 scans were performed. Also, the scanning range was set between 600 and 4000 cm^{-1} for this experiment to fully analyze the infrared spectral properties of the powder samples.

Scanning electron microscope SEM SU8010 model (Hitachi, Japan) was used to observe the main microstructural morphology of the sample and the size of the material from different angles. It was adjusted by magnification to observe the surface microstructural characteristics of the material.

Results and Discussion

Figure 1 shows the scanning electron microscope (SEM) photographs of commercial iron oxide, from which it can be seen that the commercial iron oxide consists of irregular particles of different sizes, and the particle size is mainly distributed in the 500 nanometres or so.

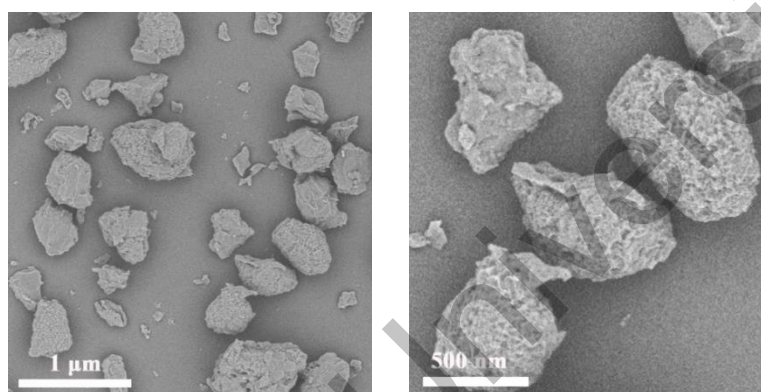


Figure 1. SEM images of commercial Fe_2O_3 catalysts

The effect of addition of iron catalyst on the yield of potassium humate and the content of xanthate and humic acid in the catalytic roasting process was investigated. The results have shown that under the conditions of roasting temperature of $225\text{ }^\circ\text{C}$, roasting time of 2 h, and the amount of iron catalyst of 1 % as a percentage of the mass of the raw material, tobacco straw), the yield of potassium humate can be effectively increased to 68.77 %. It was 3.87 % higher than the yield of potassium humate 64.90 % obtained without adding iron catalyst under the same conditions. The effect of FeOOH on the composition of AHS was investigated by separating and quantifying the residues (RS), AHA and AFA in both AHS. Figure 2(a) and 2(b) present the amount of each component in the AHS before and after addition of iron catalyst, respectively. As it can be seen from the comparison of the content of each component (Fig. 2), Fe catalyst increased significantly the AFA content in AHS from 11.5 wt% to 26.4 wt% and decreased the RS from 56.9 wt% to 52.8 wt%. These changes indicate that the Fe catalyst improved the composition and properties of AHS by increasing AFA with smaller molecular weight and water solubility, which imply that the activity and plant uptake of AHS would be enhanced.

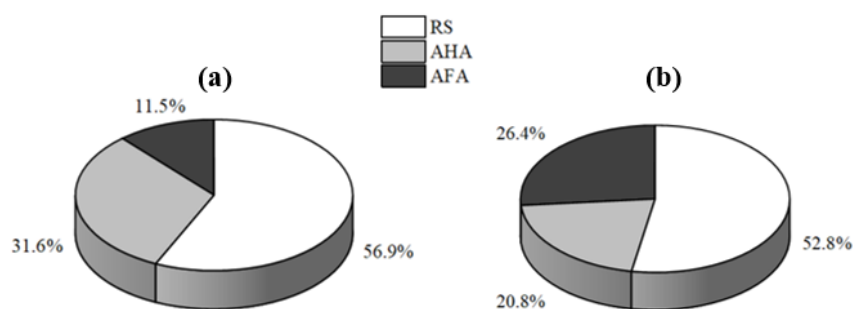


Figure 2. Changes in AHS composition with the addition of iron catalysts

The elemental content and elemental ratios of biomass during the conversion process were determined and calculated by elemental analysis techniques. As shown in Table 1, both HAK and specific samples exhibited high carbon content, this suggests that HA preparation promotes carbon sequestration. The elemental ratios implied that some chemical reactions took place: both H/C and O/C ratios of HAK were lower than those of tobacco straw, indicating that dehydration and decarboxylation reactions occurred during pyrolysis. Low H/C and O/C ratios are often associated with high aromaticity of the material, suggesting that the pyrolysis process promotes the production of more aromatic substrates, which in turn enhances the potential for HA synthesis in this way, allowing the biomass to be transformed into forms such as peat and lignite.

The O/C ratio usually reflects the contribution of carbohydrates and carboxylic acids to artificial HA (AHA) formation. Therefore, a higher O/C ratio implies that AHA contains a higher proportion of compounds such as carboxylic acids and furans. The increase in O/C ratio with the use of Fe catalyst further indicates the positive role of Fe catalyst in promoting the formation of carboxylic acids, furans and other carbohydrates. A higher N/C ratio, on the other hand, is often regarded as one of the characteristics of natural HA in peat or soil, and the high N/C value exhibited by AHA in this experiment not only indicates that its properties are similar to those of natural HA, but also reflects its high degree of humification and plant origin.

Table 1

Organic Elemental Content and Elemental Ratio of Samples

Specimens	Elemental composition (wt.%)					Atomic ratio		
	N	C	H	S	O	N/C	H/C	O/C
Tobacco straw	0.94	43.49	6.92	0.00	49.55	0.02	1.90	0.85
HAK	2.62	57.16	4.12	0.35	35.75	0.05	0.86	0.47
HAK-Fe	2.83	57.07	4.14	0.29	35.67	0.05	0.87	0.47
AHA	3.04	61.17	5.03	0.51	30.25	0.05	0.98	0.37
AHA-Fe	3.22	55.96	4.85	0.00	35.97	0.06	1.04	0.48

Table 2 shows the E_4 , E_6 and E_4/E_6 ratios measured using UV-Vis spectrophotometer. In order to investigate the effect of catalyst on the degree of humification and functional groups of AHA and AFA, the ratio of absorption values of AHA and AFA at 465 nm and 665 nm was further analyzed. The results showed that AHA displayed a higher E_{465}/E_{665} ratio compared to C-HA. This ratio is usually used as an indicator to assess the degree of aromaticity and aromatic carbon condensation, with higher ratios being associated with lower aromaticity. Thus, the AHAs and AFAs prepared in this experiment have lower aromaticity compared to C-HA. Meanwhile, the E_{465}/E_{665} ratio of AHA-2 was higher than that of AHA-1, which indicates that the addition of Fe catalyst had an effect on the aromaticity of HA, i.e., more aromatic rings were broken during the catalysis. Low aromaticity represents high hydrophilicity, which also coincides with the fact that FA exhibits stronger hydrophilicity. Thus, the catalysts altered the properties of AHA and AFA to have lower aromaticity, smaller molecular weight and higher hydrophilicity, which is consistent with the results of the above analyses.

Table 2

 E_4/E_6 ratio for S-HLS-K, CS-HLS-K and M-HA-K

	AHA-1	AHA-2	C-HA
E_{465}	0.406	0.416	0.370
E_{665}	0.164	0.123	0.153
E_4/E_6	2.476	3.382	2.418

The results of the IR spectral characterization of the three potassium humates are shown in Figure 3. The positions of the characteristic peaks in the IR spectra of different potassium humates are almost the same, indicating that they contain very similar functional groups. 3281.2 cm^{-1} represents the stretching and bending vibrations of -OH and N-H. The characteristic peaks at 1558.9 cm^{-1} are due to the stretching of C=C in the aromatic ring [10], and the peaks at 1393.1 and 1052.8 cm^{-1} represent C-O vibrations in the aromatic ring and ether, respectively. The lower characteristic peaks of CS-HLS-K near 1558.9 cm^{-1} , 1393.1 cm^{-1} and

1052.8 cm^{-1} indicate that CS-HLS-K has lower aromaticity, which is consistent with the analysis of the results of the UV-determined E_4/E_6 ratio.

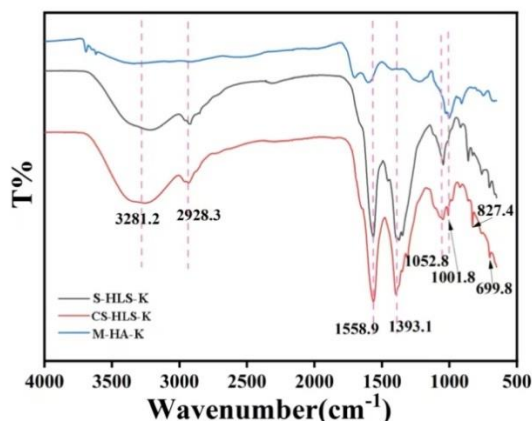


Figure 3. Infrared spectra of S-HLS-K, CS-HLS-K and M-HA-K

Figure 4 shows the TG-DTG analysis performed in N_2 atmosphere, which was used to monitor the changes in tobacco straw during heat treatment. The weight loss of tobacco straw was gradual, with the fastest rate of weight loss occurring at 283 °C. The weight loss of the tobacco straw was also observed in the heat treatment process. From room temperature to 150 °C, the weight loss of tobacco straw was attributed to the evaporation of adsorbed and crystalline water or the partial release of some light volatiles. At temperatures above 150 °C, the fibers begin to degrade rapidly. The first important stage of thermal decomposition occurs between 150 and 350 °C, during which the glucosyl and glycosidic bonds break, releasing small amounts of gases such as carbon dioxide and methane. At this stage, the mass loss of tobacco straw reaches 38.3 %, indicating that the biomass structure undergoes a large transformation in this temperature range. A second stage of mass loss of tobacco straw was observed in the range of 350–550 °C, which was caused by a richer structure of aromatic compounds. Typically, cellulose and hemicellulose undergo significant transformation at temperatures below 300 °C, whereas lignin is relatively stable with only minor changes. Initial interaction and pyrolysis of hemicellulose, cellulose and lignin occurs during a mild pyrolysis process at 200–300 °C. At this stage, some hemicellulose and a small amount of lignin were degraded. The mild pyrolysis process promotes the onset of lignocellulose depolymerization and further destroys the structure of lignocellulose.

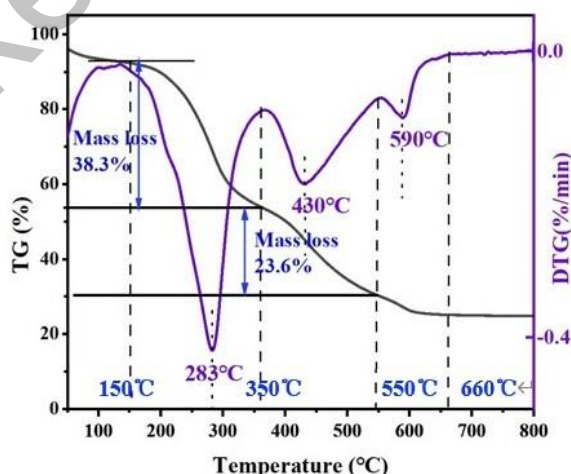


Figure 4. TG-DTG curves of pyrolysis of tobacco straw under N_2 atmosphere

The growth conditions of the three groups of wheat seeds in water and after spraying with different kinds of potassium humate solutions for 1 week are shown in Figure 5. As can be seen from the figure, the

growth difference of wheat plants above ground and the growth difference of roots were both large. Compared with the control group (Fig. 5B(a)), the addition of CS-HLS-K solution (Fig. 5B(c)) promoted the growth of wheat more obviously.

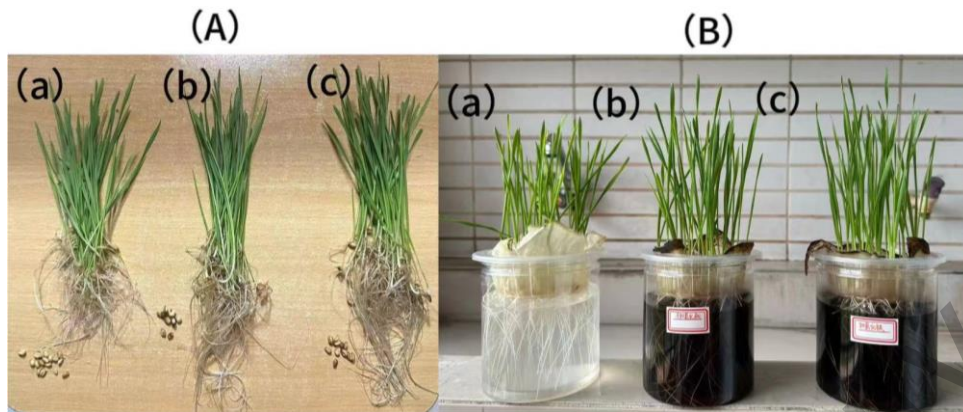


Figure 5. (A) Wheat plant laying after one week of hydroponics (B) Wheat plant growth after one week of hydroponics (a) Clear water group; (b) 10 mg/L S-HLS-K solution; (c) 10 mg/L CS-HLS-K solution

Each biomass of wheat plants (germination rate, total fresh and dry weight of wheat plants) was determined and after three replications, the effect of different potassium humates on germination rate of wheat seeds is shown in Figure 6, and the effect on the average aboveground and root length of wheat plants, fresh and dry weight of wheat plants is shown in Figure 7. It can be seen from Figure 6 that the germination rate of treatment group 3 increased by 17 % compared to that of the fresh water control group, and that the germination rate of treatment group 3 increased by 6 % compared to that of treatment group 2, indicating that the promotion of wheat germination was more pronounced in treatment group 3 compared to that of treatment group 2. As can be seen from Figure 7, the fresh and dry weight of wheat plants increased by 6.94 % and 19.31 %, respectively, in comparison with fresh water control group. Compared with the fresh water control group, all parameter of 2 and 3 treatments increased, which proves that the addition of potassium humate can have a certain promoting effect on the growth of wheat. Based on the data of the indexes, it was estimated that the growth promotion effect of different potassium humate solutions was CS-HLS-K > S-HLS-K. The wheat with CS-HLS-K solution had the highest germination rate, the best root growth and the greatest increase in the fresh and dry weights, and the growth promotion effect of CS-HLS-K was the most significant, which might be due to the addition of catalysts to increase the oxygen-containing functional groups of the material $C=O$, $O-C-O$, as well as the content of nitrogen, potassium and other elements required for the plant growth, thus effectively promoting the growth of all parts of wheat. In addition, CS-HLS-K's lower aromaticity, less molecular weight, and better solubility and quality are also conducive to the promotion of crop growth.

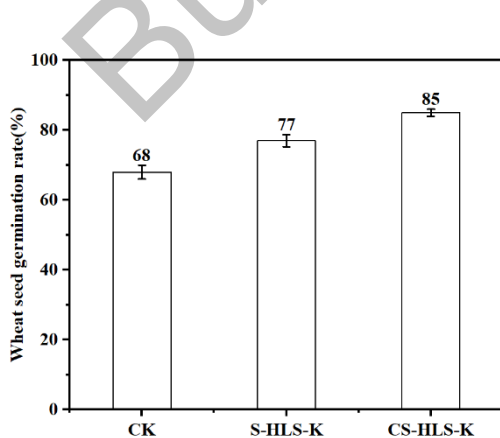


Figure 6. Germination rate of wheat seeds

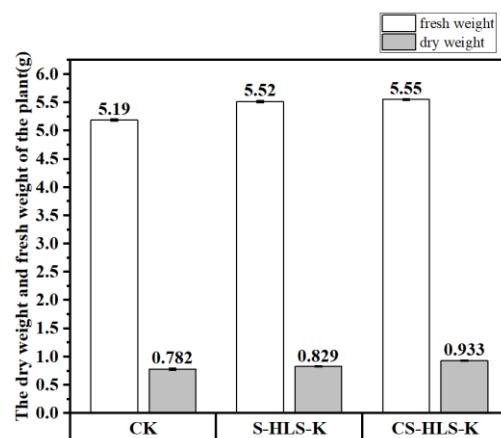


Figure 7. Fresh and dry weight of wheat plants

Conclusions

The green and clean Fe_2O_3 was used as a catalyst for the catalytic preparation of potassium humate analogues. Under the thermal catalysis condition of 225 °C, time of 2 h and catalyst amount of 1 % (mass percentage of raw tobacco straw), the quality measurement results have shown that the catalytically prepared CS-HLS-K had lower aromaticity, smaller molecular weight, better solubility and superior quality as compared to M-HA-K. The addition of catalyst promoted the macromolecular humification process and the carbonation and oxygenation process of tobacco straw. It also increased the number of oxygen-containing functional groups in potassium humate. The results of plant growth experiments have shown that CS-HLS-K increased the germination rate of wheat by 17 % and the fresh and dry weights by 6.94 % and 19.31 %, respectively, compared to that of the clear water control group, indicating that CS-HLS-K had a more significant growth promotion effect on wheat compared to M-HA-K. The study in this article not only provides a direction for the resourceful utilization of agricultural waste to prepare potassium humate with better performance, but also offers a certain recommendations for the green production of potassium humate materials and its application in promoting plant growth.

Funding

This work is supported by the project of the Xinjiang Science and Technology Department (2022B01042, 2022E01051, 2022E02098), the Yili State Science and Technology Bureau Project (YZ2023A7, YZD2024A16, YZ2023A11), and the Project of Changji Science and Technology Bureau (2023Z04)

Author Information*

*The authors' names are presented in the following order: First Name, Middle Name and Last Name

Qianqian Li — Undergraduate of Environmental Engineering, South China University of Technology, 510006, Guangzhou, Guangdong, China; e-mail: lqq12180517@gmail.com; <https://orcid.org/0009-0002-2755-4292>

Jinlin Li — Undergraduate of Environmental Engineering, South China University of Technology, 510006, Guangzhou, Guangdong, China; e-mail: 1347565531@qq.com

Yinqiao Zhao — Undergraduate of Environmental Engineering, South China University of Technology, 510006, Guangzhou, Guangdong, China; e-mail: 2924160897@qq.com

Yingjie Zhu — Undergraduate of Environmental Engineering, South China University of Technology, 510006, Guangzhou, Guangdong, China; e-mail: 205834545@qq.com

Murzabek Ispolovich Baikenov — Doctor of Chemical Sciences, Professor, Karaganda Buketov University, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: murzabek_b@mail.ru; <https://orcid.org/0000-0002-8703-0397>

Xiaofei Liu — Associate Processor, College of Chemistry and Chemical Engineering, Xinjiang Agricultural University, 311 East Nongda Road, 830052, Urumqi, China; e-mail: 1136887541@qq.com; <https://orcid.org/0009-0000-9199-2989>

Xintai Su (corresponding author) — Professor, School of Environment and Energy, Guangdong Provincial Key Laboratory of Solid Wastes Pollution Control and Recycling, South China University of Technology, 510006, Guangzhou, Guangdong, PR China; e-mail: suxintai@scut.edu.cn; <https://orcid.org/0000-0001-6615-5273>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **CRedit**: **Qianqian Li** conceptualization, data curation, investigation, methodology, resources, writing-original draft, writing-review & editing; **Jinlin Li** conceptualization, supervision, writing-review & editing; **Yinqiao Zhao** conceptualization, supervision, writing-review & editing; **Yingjie Zhu** writing-review & editing; **Murzabek Ispolovich Baikenov** writing-review & editing; **Xiaofei Liu** writing-review & editing; **Xintai Su** writing-review & editing.

Acknowledgments

Authors thank *South China University of Technology* for access to library facilities.

Conflicts of Interest

The authors declare no conflict of interest.

References

- 1 Kamusoko, R., Jingura, R. M., Parawira, W., & Chikwambi, Z. (2021). Strategies for valorization of crop residues into biofuels and other value-added products. *Biofuels, Bioproducts and Biorefining*, 15(6), 1950–1964. <https://doi.org/10.1002/bbb.2282>
- 2 Lamers, P., Searcy, E., Hess, J. R., & Stichnothe, H. (2016). *Developing the global bioeconomy: Technical, market, and environmental lessons from Bioenergy*. Academic Press is an imprint of Elsevier.
- 3 Cao, L., Zhang, C., Chen, H., Tsang, D. C. W., Luo, G., Zhang, S., & Chen, J. (2017). Hydrothermal liquefaction of Agricultural and Forestry Wastes: State-of-the-art review and future prospects. *Bioresource Technology*, 245, 1184–1193. <https://doi.org/10.1016/j.biortech.2017.08.196>
- 4 Bhatia, S. K., Joo, H. -S., & Yang, Y. -H. (2017). Biowaste-to-bioenergy using biological methods — a mini-review. *Energy Conversion and Management*, 177, 640–660. <https://doi.org/10.1016/j.enconman.2018.09.090>
- 5 Bhujbal, S. K., Ghosh, P., Vijay, V. K., Rathour, R., Kumar, M., Singh, L., & Kapley, A. (2022). Biotechnological potential of rumen microbiota for sustainable bioconversion of lignocellulosic waste to biofuels and value-added products. *Science of The Total Environment*, 814, 152773. <https://doi.org/10.1016/j.scitotenv.2021.152773>
- 6 Fong, S. S., Seng, L., Chong, W. N., Asing, J., Nor, M. F., & Pauzan, A. S. (2006). Characterization of the coal derived humic acids from Mukah, Sarawak as soil conditioner. *Journal of the Brazilian Chemical Society*, 17(3), 582–587. <https://doi.org/10.1590/s0103-50532006000300023>
- 7 Muldakhmetov, Z.M., Gazaliev, A.M., Zhakina, A.Kh., Vassilets, Ye.P., & Arnt, O.V. (2022). Synthesis of a Composite Based on Humic Acid Tuned to Sorbed Copper Ion. *Bulletin of the University of Karaganda Chemistry*, 108(4), 182–189. <https://doi.org/10.31489/2022Ch4/4-22-14>
- 8 Yang, F., Zhang, S., Cheng, K., & Antonietti, M. (2019). A hydrothermal process to turn waste biomass into artificial fulvic and humic acids for soil remediation. *Science of The Total Environment*, 686, 1140–1151. <https://doi.org/10.1016/j.scitotenv.2019.06.045>
- 9 Chen, P., Yang, R., Pei, Y., Yang, Y., Cheng, J., He, D., Huang, Q., Zhong, H., & Jin, F. (2022). Hydrothermal synthesis of similar mineral-sourced humic acid from food waste and the role of protein. *Science of The Total Environment*, 828, 154440. <https://doi.org/10.1016/j.scitotenv.2022.154440>
- 10 Qi, Y., Zhu, J., Fu, Q., Hu, H., Rong, X., & Huang, Q. (2017). Characterization and CU sorption properties of humic acid from the decomposition of Rice Straw. *Environmental Science and Pollution Research*, 24(30), 23744–23752. <https://doi.org/10.1007/s11356-017-9999-9>