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Rapid humification of biomass *via* hydrothermal conversion: a comprehensive review

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Humic acid (HA), a crucial substance for maintaining soil fertility and health, plays a vital role in sustainable agricultural development and environmental remediation. Hydrothermal humification (HTH) offers the advantage of producing HA analogues from biomass in a significantly shorter timeframe compared with natural processes, thereby enhancing carbon efficiency. This approach aligns with green chemistry principles by promoting the sustainable utilization of resources while minimizing environmental impacts. However, research on the hydrothermal production of HA is still in its early stages, with the underlying conditions, influencing factors, and conversion mechanisms remaining unclear. Furthermore, the potential applications of hydrothermal HA are not yet fully understood. Drawing from nearly a decade of research, this article addresses the mechanism of hydrothermal conversion of biomass into HA and discusses the impacts of diverse HTH operating parameters such as reaction time, biomass composition, reaction solvent, and reaction temperature on the humification process. Given the current lack of research on the applications of hydrothermal HA, we demonstrated the potential applications and challenges of hydrothermal HA by exploring the use of HA from various other sources in diverse scenarios, including agriculture, environmental protection, functional material preparation and animal husbandry. Furthermore, the challenges and research directions for the commercial application of hydrothermal HA are discussed, aiming to provide a reference for studies on HA derived from biomass *via* hydrothermal conversion.

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1. Hydrothermal humification (HTH) offers the advantage of generating humic acid (HA) analogues from biomass in *a much shorter timeframe* than the natural process. This enhances carbon efficiency and aligns with green chemistry principles by promoting sustainable biomass utilization while minimizing environmental impact. However, the mechanisms underlying the hydrothermal conversion process remain unclear, and the potential applications of hydrothermal HA are not yet well understood.
2. We explore the potential applications and challenges of hydrothermal HA by exploring the use of HA derived from various sources in different scenarios, including agriculture, environmental protection, functional material preparation and animal husbandry.
3. The challenges and research directions for the commercial application of hydrothermal HA are discussed, aiming to provide a reference for the study of HA production from biomass *via* hydrothermal conversion.

1. Introduction

Humic substances in soil play a crucial role in soil fertility and sustainable agricultural development. These substances are predominantly derived from the decomposition and transformation of animal and plant residues through microbial processes and a series of chemical reactions.[1] Humic substances comprise complex organic polymers, including humic acid (HA), fulvic acid and humins, which are primarily composed

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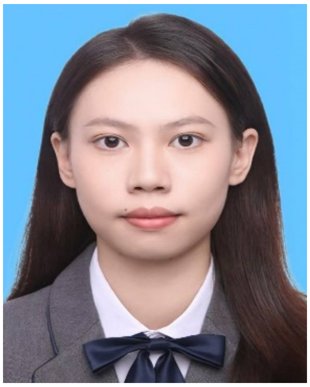
of aromatic and aliphatic rings as well as functional groups, such as phenolic hydroxyls, ether bonds, and carboxylic acid groups.[2] Humic substances in soil and water influence soil structural stability, promote complexation of heavy metals and facilitate transformation of pollutants in terrestrial and aquatic environments.[3–5] HA is the most abundant substance in humic substances. Research has demonstrated that natural HA can alter soil properties in agriculture, reduce soil heavy metal content, enhance fertilizer efficiency, protect plant growth and development, improve crop quality, and optimize pesticide efficacy.[6] In addition to its agricultural uses, HA has been found to have significant applications in environmental protection, electrochemistry, medicine, and animal husbandry.[7,8]

The wide availability of HA from renewable natural sources has led to increased attention on HA. Consequently, investigating the source and transformation processes of HA is of utmost importance to achieve maximum humification. Currently, there are four widely accepted molecular models of HA: the fulvic acid model, classical HA model, two-dimensional model of HA, and three-dimensional model of the HA structure.[9] There are three conversion pathways for HA formation: natural sedimentation, microbial methods, chemical oxidation and thermochemical methods.[10] These methods require varying conversion times. Natural sedimentation takes decades to centuries, while microbial methods involve weeks or months of composting and microbial metabolism. Thermochemical methods, such as pyrolysis and hydrothermal treatment, require hours or days for the reaction and extraction of HA from materials such as corn stover, sludge, and animal manure.[11]

Compared to natural sedimentation and biological conversion, thermochemical conversion demonstrates the key advantage of rapid conversion.[12,13] The hydrothermal humification (HTH) process stands out due to its ability to shorten the reaction period and increase the yield of HA.[14,15] However, HTH reactions are complex and variable, depending on numerous reaction parameters, such as reaction time, and reaction temperature. The selection and control of the reaction conditions, as well as the dynamic changes during the reaction process, can significantly impact the humification results, such as HA yield and characteristics. There are lots of emerging studies about HTHs from biomass, including reports covering the operational process,[10] transformation pathway,[16] and the characteristics of hydrothermal HA, key influencing factors of the HTH process, and the potential applications of HA.[6]

In recent years, a few reviews on the HTH of biomass have emerged. The synthesis technology and application of artificial humic substances (A-HSs) were emphasized along with the application of A-HSs synthesized by these technologies in agriculture and environmental remediation.[17] Many reviews have summarized the pathways of preparing HA by biological and abiotic methods and the influence of key factors within those processes, and introduced the differences between compost and hydrothermal treatment in the production of humic acid, including the main mechanism of the humification process and the influence of the reaction factors.[9] Other reviews have described the mechanism of hydrothermal humic acid production, the influence of hydrothermal conditions on humic acidification, the properties of hydrothermal humic acid, and its applications in agriculture and the environment field.[11] Current reviews have focused on the effects of the reaction temperature and time on HTH, but lack comprehensive discussions on other factors, particularly the conversion mechanisms and pathways of the various components in the feedstock. Researchers have shown that artificial HA possesses a richer array of functional groups, offering promising prospects for agricultural and environmental applications. It can improve soil properties, promote plant growth, and mitigate the toxicity of pollutants such as heavy metals. However, research on artificial HA is still in its early stages, and the potential applications of hydrothermal HA remain largely unexplored, leading to an incomplete understanding of its full application potential.[17–19]

Based on the articles mainly published from 2010 to 2024, this review provides a comprehensive introduction of HA from biomass, which evaluates the impact of diverse HTH operating parameters and process schemes on the mechanism, yield, and characteristics of HA production. Furthermore, it delves into the practical applications of HA across multiple domains, including agriculture, environmental protection, electro-



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chemistry, healthcare, industry, and animal husbandry. This work can serve as a valuable reference for the research and application prospects of HA from HTH and aid in better regulating the formation of HA during biomass waste conversion.

2. Conversion mechanism and influencing factors of hydrothermal humification

Hydrothermal treatment, a thermochemical conversion process conducted under subcritical or supercritical water conditions (180–360 °C, 2–20 MPa),[20] can rapidly valorize biowaste within hours or minutes, transforming it into valuable materials such as bio-oil, HA, hydrochar, and chemicals.[21,22] This promising technology shortens reaction cycles, enhances catalytic efficiency, reduces energy input (compared to pyrolysis), and minimizes secondary pollution.[23] Recent advancements have demonstrated its feasibility for converting biowaste into hydrothermal humic substances,[24,25] simulating natural humification through a mild chemical process under both acidic and alkaline conditions.[26] In the hydrothermal process for producing HAs, solvent environment facilitates the dissolution of humic substances and humic acid extraction. Notably, hydrothermal treatment stands out with its various beneficial features, like a wide adaptability to biomass feedstocks, short reaction cycles, and reduced greenhouse gas emissions, allowing turning waste management into a source of economic benefits.[27] A study indicated that the yield of HAs in the hydrothermal process is twice that of composting.[28] Although hydrothermal treatment offers many advantages, it also faces several challenges. First, the hydrothermal process for HA production involves complex chemical reactions and various chemical substances, which pose difficulties in the purification, identification, and quantification of HAs.[29] Second, the hydrothermal process requires a significant amount of energy input, with the process often operating at temperatures above 160 °C. Third, catalysts are commonly used to minimize the generation of undesired solid byproducts, shorten reaction times, and reduce reaction risks.[27,30] However, the effect and mechanism of catalysts in hydrothermal conversion are not straightforward and require further understanding. Additionally, the scale of hydrothermal processing for biomass waste is still limited to laboratory settings. Before large-scale application, the unstable HA yields in hydrothermal treatment still need to be addressed as current research in this area is still insufficient.[9]

2.1. Conversion mechanism of humic acid

Currently, there are several theories regarding the generation of HAs in the natural environment, including the Maillard reaction (also known as the sugar–amine condensation theory), the lignin theory, and the polyphenol theory.[31] Additionally, there are several other theoretical hypotheses, such as the microbial synthesis hypothesis, the cell autolysis hypothesis, and the polyphenol hypothesis originating from lignin.[32] The process of hydrothermal conversion to produce HAs is complex and involves a series of chemical reactions and continuous component transformations (Fig. 1). Generally, during the humification process, the feedstocks undergo

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Dr Zhidan Liu is a professor at the Laboratory of Environment-Enhancing Energy, College of Water Resources and Civil Engineering, China Agricultural University. His research group has long been engaged in research on biomass waste treatment and energy resource utilization as well as interdisciplinary research on energy-water-environment-materials and has carried out systematic research on hydrothermal technology. He has been continuously selected as one of the Elsevier China Highly Cited Scholars since 2020 and is ranked among the top 2% of the world's top scientists. He has received the Yangtze River *Young Scholar from the Talent Program of the Ministry of Education of China and the Second Prize of Natural Science (1st) from the Ministry of Education. He serves as a Guest Editor/Editorial Board Member for journals such as IJHE and IJABE. He has published more than 150 academic papers and has been granted over 30 invention patents.*

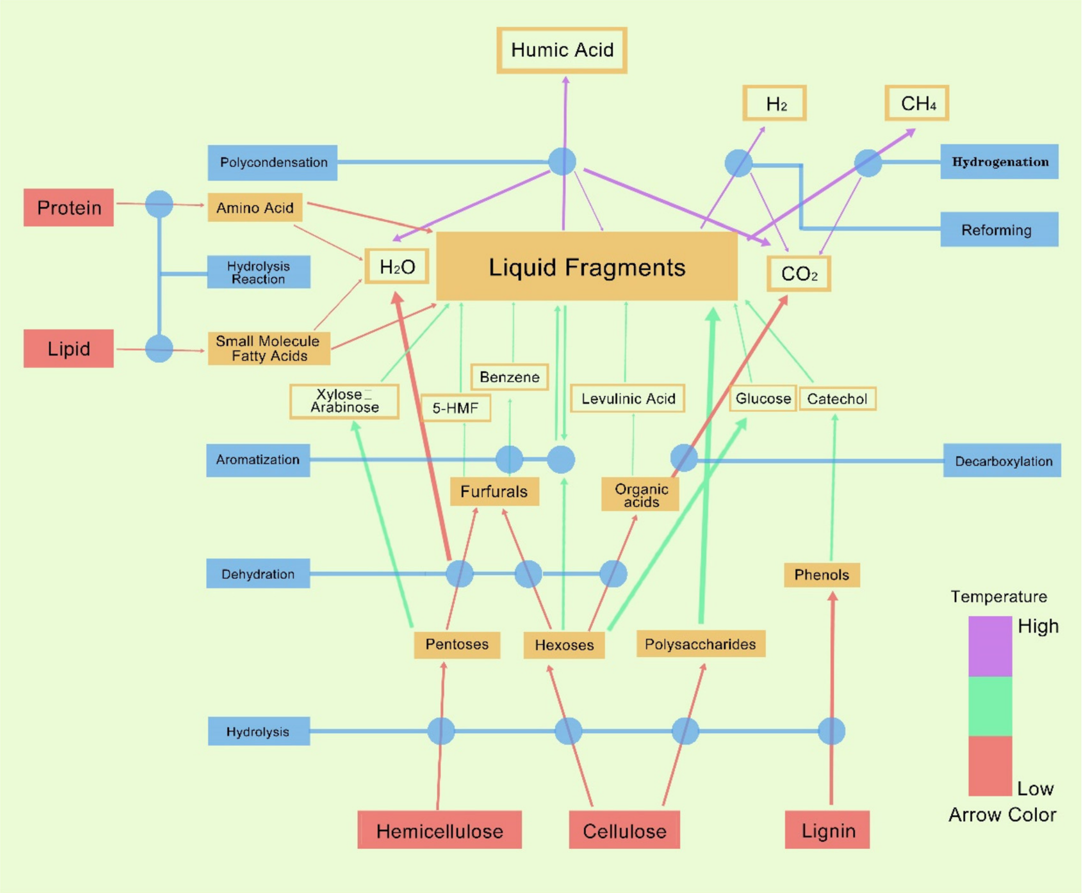

Fig. 1 Formation principles of humic acid from various resources.

hydrolysis and condensation reactions. In biochemical processes for HA production, these reactions are mostly driven by microorganisms. In abiotic oxidation processes, such as catalytic oxidation polymerization, alkali–oxygen reactions, and HTH, these reactions are mostly induced by heating, oxidation, and pressure. Under low-temperature conditions, biomass undergoes hydrolysis reactions, primarily involving components such as cellulose, hemicellulose, lignin, lipids, and proteins. These components rapidly hydrolyze into monosaccharides, such as xylose, arabinose, and glucose, as well as small molecules, such as furans, phenols, and organic acids. These are the key precursors for the formation of HAs.[16,33] As the temperature increases, the precursors of HAs gradually decompose or degrade. For example, arabinose and xylose decompose into furfural, while glucose degrades into 5-hydroxymethylfurfural, acetic acid, or γ-valerolactone, which catalyzes the later generation of hydrothermal HA.[34] With further temperature increases, the Maillard reaction or aldehyde–alcohol reaction becomes dominant, leading to complex reactions, such as molecular rearrangement in HA.[35,36] This results in changes in the structure and molecular weight of HA, leading to the formation of high-molecular-weight HA (Fig. 1). However, when the temperature exceeds a certain threshold, the Maillard reaction is inhibited, resulting in a decrease in the content of HA, ultimately forming humic aggregates in the thermal environment.[9,18,37] There are three conversion pathways for HA: (1) one-step HTH. Here, the pretreated biomass raw materials are heated in an alkaline solution and cooled to room temperature to obtain liquid products; then HA is obtained by acidification treatment; (2) acid–base two-step HTH. Here, the acidic solution is selected as the dissolved solution (first step), and then an alkaline solution is selected for the humification using degradation products as the feedstock (second step); and finally the liquid product is acidified after the two stages to obtain HA; (3) hydrochar-based two-step HTH. Here, the raw materials go through a high-temperature hydrothermal carbonization process to generate hydrocarbons (first step), and then an alkaline solution is selected for the humification using the hydrocarbons as the feedstock (second step); and finally acid precipitation is used to extract HA[38] (Fig. 2). Additionally, research suggests that reactions involving free radicals and photosensitization under frozen conditions may contribute to the formation of humic-like substances by promoting the oxidation and polymerization of aromatic compounds. By simulating natural low-temperature processes, it has been observed that aromatic and phenolic compounds can transform into polymers with humic-like structures under freezing conditions.[39]

2.2. Influencing factors in humic acid conversion

The production of HA *via* the hydrothermal process is influenced by various operational parameters. These parameters include the raw materials' characteristics, reaction temperature, reaction time, reaction rate, pressure, gas atmosphere, solution environment, catalyst, and extraction methods used for product separation (Fig. 3). Each of these factors can affect the composition of the substances and the yield of HAs.[10] Among these, the reaction raw materials, temperature, and reaction time have been found to have the most significant influences on the production process.[40] Therefore, this chapter will particularly focus on the impact of these three variables, as well as covering the solution acidity/alkalinity and the choice of catalysts, on the production of HAs.

2.2.1. Reaction temperature. The reaction temperature is an important parameter in the conversion process of HA. The physicochemical properties of water change to promote the hydrolysis of raw materials, followed by a series of reactions to generate humic substances with increasing temperature (Fig. 3).[9] Generally, the yield of HA increases with temperature in a certain range, but further increasing the temperature past this range leads to a gradual decrease in HA yield.[29,41] There are four reasons for the decrease in humification rate and HA yield with further increasing the temperature: (1) the further temperature increase leads to the continuous degradation and transformation of HA compounds owing to their unstable characteristic; (2) higher temperature leads to the decomposition of hemicellulose and cellulose into monophenols, leading to less HA polymerization; (3) higher temperature leads to the carbonization of HA and the formation of hydrochar, which can also undergo condensation and repolymerization reactions; (4) the occurrence of the caramelization reaction produces humins at higher temperatures, resulting in a decrease in HA yield.[42,43] This indicates that increasing the reaction temperature up to a certain point appropriately benefits the production of HA in HTH processes, and an optimal temperature can be found within a certain temperature range. However, the optimal temperature varies with the feedstocks and other operational parameters. The highest yield of HA from broccoli waste was reported to be 0.61% at 195 °C, while the yield decreased with further increasing the temperature.[27] Corn cob residues were used as raw materials and the yield of HA was increased from 0.2% to 1.5% as the temperature was increased from 180 °C to 210 °C, but then decreased to 0.9% when further increasing the temperature to 220 °C.[44] The HA yield of food waste was increased from 22.5% to 32.6% when the reaction temperature was increased from 200 °C to 215 °C, but decreased with the further increase in temperature, using food waste as raw materials.[42]

2.2.2. Reaction time. Besides the reaction temperature, the reaction time is another important parameter in HTH reactions. In general, a long reaction time leads to a strong HTH process and high reaction efficiency.[45] However, similar to the reaction temperature, with further increasing the reaction time, the yield decreases because HA undergoes self-degradation, cleavage, and transformation, and small molecules generated from HA cleavage tend to undergo condensation reactions, such as coking and aggregation.[24,46] Therefore, there is also an optimal time in the HTH reaction process. Utilizing the control variable method, some studies have observed the effect of the reaction time on the yield of HA (Fig. 3e). One study reported that within the range from 30 min to 60 min, the yield of HA increased from 32.5% to 38.5%, and then as the reaction time was further increased, the yield began to decrease, whereby from 60 min to 180 min,

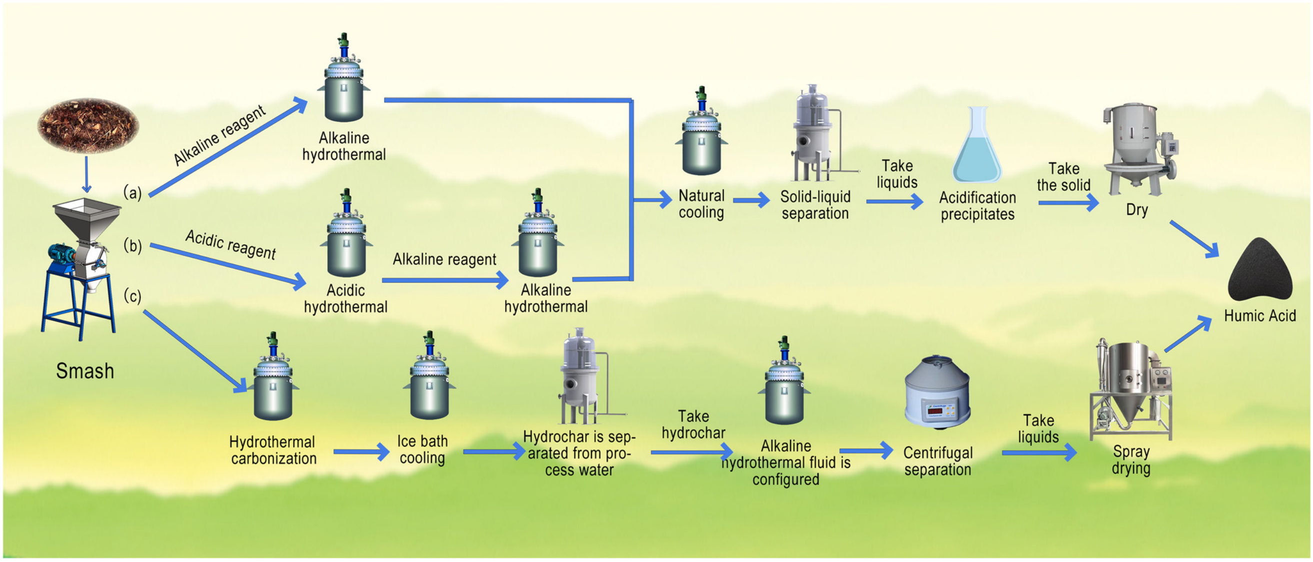

Fig. 2 HA production pathways: (a) one-step alkaline solution method, (b) two-step hydrothermal acid–base solution method, and (c) hydrothermal carbonization method (revised from ref. 10 with permission from Elsevier, Copyright 2023).

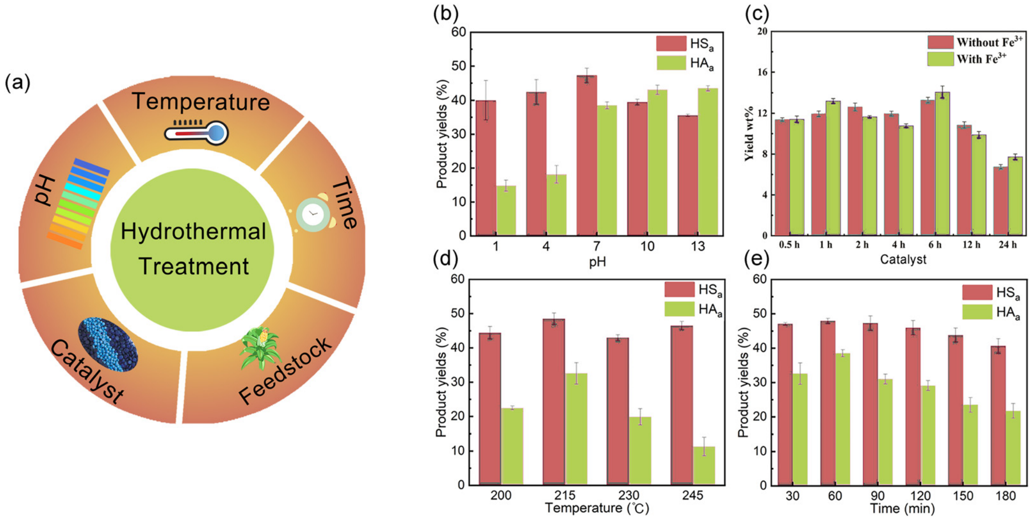

Fig. 3 (a) Factors influencing hydrothermal humification, including time, temperature, catalyst, feedstock and pH. (b) Effect of pH on humic acid yield (reproduced and revised from ref. 42 with permission from Elsevier, Copyright 2022). (c) Effect of the catalyst on humic acid yield (reproduced and revised from ref. 42 with permission from Elsevier, Copyright 2022). (d) Effect of time on humic acid yield (reproduced and revised from ref. 42 with permission from Elsevier, Copyright 2022). (e) Effect of temperature on humic acid yield (reproduced and revised from ref. 42 with permission from Elsevier, Copyright 2022).

the yield decreased from 38.5% to 22.5%.[42] In another study on waste, it was found that after the reaction time exceeded 10 min, the yield of HA gradually decreased.[27]

2.2.3. Reaction solution pH. Different pH values of the reaction solution can result in different yields of HA. Generally, the alkalinity in the solution environment is positively correlated with the yield of HA. Taking the conversion of lignocellulose as an example, during the hydrothermal process, lignocellulose undergoes depolymerization, dehydration, and condensation reactions to form HA. The conversion rate of HA in lignin varies under different acid–base conditions. Compared with other pH conditions, alkaline hydrothermal processes show significantly higher conversion rates of HA. This could be attributed to the diminished solubility of lignin under acidic conditions, leading to a decrease in the formation of lignin fragments and a subsequent reduction in the conversion of HA. On the other hand, under alkaline hydrothermal conditions, lignin decomposition provides more aromatic compounds to react with fulvic acid, resulting in the formation of HA.[11,16] However, this does not directly mean that a higher amount of alkaline reagents would lead to a higher yield of HA. Using food waste as a raw material to produce humic acid, Chen *et al.* found that when the pH value was changed from 10 to 13, the yield of humic acid did not increase significantly.[42] Furthermore, continuously adding alkaline reagents will increase the reaction costs and cause acid–base neutralization issues in subsequent reactions. Moreover, the separation of HA is generally achieved through acidification precipitation, so highly alkaline solutions hinder the extraction of HA and affect the final conversion rate.[40] Furthermore, although the amount of HA generated under acidic hydrothermal conditions is small, acidic solutions are beneficial for the dissolution of biomass, and so that the key precursors for the formation of HA can be quickly generated. Some studies have shown that treating biomass raw materials in acid–base two-step processes during the reaction can deepen the humification process, increase the humification products, and improve the yield of HA.[47]

2.2.4. Reaction catalysts. During the reaction process, different catalysts are usually added based on the characteristics of the raw materials, solution environment, and reaction time to improve the reaction rate. The catalysts include acids, bases, and metal salts.[48] In HTH production, alkaline catalysts are commonly chosen since the high-pressure reactor is generally made of non-corrosive steel and other metal materials. Also, strong alkaline catalysts show better HA production effects than weak alkaline ones.[49] The application and choice of catalysts can significantly improve the extraction efficiency of HA in HTH. For example, one study reported that Fe-based catalysts increased the yield of HA when corn stalks were used as raw materials, which was attributed to the accelerated decomposition rate of the corn stalks promoted by the Fe-based catalysts.[50] Fe^{3+} as a catalyst can change the generation of HA, but the effect is not always positive.[51]

2.2.5. Reaction feedstocks. HTH can occur with a wide range of raw material sources, including agricultural residues, forest waste, and bioenergy crops, such as corn straw, wood chips, and food waste. The HTH process involves the decomposition, reorganization, and self-condensation of raw materials, including carbohydrates, proteins, and lipids.[49] However, the composition and physicochemical properties of substances involved can vary significantly across different raw materials, leading to notable differences in the yield of humic acid (HA), the physicochemical properties of the resulting HA, and the required reaction parameters.[16,52] Typically, carbohydrates in biomass undergo retro-aldol addition reactions during the hydrothermal process, breaking down into hydroxyl- and keto-acid-containing organic acids with high water solubility. Proteins can significantly promote HA formation through reactions between amino acids and glucose.[49] Lignin, on the other hand, hydrolyzes into phenolic compounds under neutral or alkaline conditions, while simultaneously promoting the carbon skeleton reorganization and condensation. During this process, it has been found that the pH of the solution gradually decreases, demonstrating a self-neutralization effect.[49] A previous study performed hydrothermal reaction studies using various biomass sources, such as glucose, wood chips, and tulip tree fruit stands, and found there were significant differences in the yield and properties of the obtained humic acids depending on the raw material. Specifically, glucose was almost completely converted into liquid products, resulting in a very high liquid yield and a negligible solid yield. In contrast, tulip tree fruit stands had a solid yield of 73.0% and a liquid yield of 45.8%, while beechwood sawdust showed a solid yield of 78.4% and a liquid yield of 54.1%. Using glucose as the raw material produced artificial fulvic acid, which was lighter in color, had a lower molecular weight, and contained more carboxylic acid groups. In comparison, tulip tree fruit stands and beechwood sawdust generated artificial HA, which exhibited higher aromaticity due to the presence of lignin. Additionally, the tulip tree fruit stands contained lipids and waxes, which contributed to the hydrophobic nature and longer aliphatic chain structures of the resulting humic acid.[49]

3. Application potential of humic acid

HAs offer a wide range of possible applications in various fields (Fig. 4). The applications of HA are extensive, ranging from pollution control and soil fertility enhancement to environmental bioremediation and renewable energy production. These versatile compounds hold great promise for addressing carbon efficiency, environmental challenges, and promoting sustainable practices in various industries.[53] However, there are still few studies that have paid attention to the application of HA from HTH because most of the current studies have tended to focus on the formation mechanism. Compared with HAs obtained from natural microbial transformation, artificially synthesized HAs from HTH contain high-water-solubility compounds, such as carbohydrates and amino acids, suggesting that HAs from HTH can be easily used in soil by plants.[54] HA synthesized by hydrothermal reactions between sludge and biomass can recover the phosphorus elements from sludge into liquid products while heavy metals are enriched in solid products, which indicates that it may exhibit less environmental toxicity.[55,56] In this chapter, the role and function of HA in various fields are summarized, which can reflect the strong application prospects of hydrothermal HA.

3.1. Application potential in agriculture

HA can improve the soil property, enhance nutrient utilization efficiency, and promote plant physiological activity (Fig. 5). HAs play an effective role in improving soil structure and porosity, water retention, and nutrient content owing to their rich active groups, such as phenolic hydroxyl, carboxyl, carbonyl, and alcoholic hydroxyl groups.[57] The colloidal properties of HA enable soil particles to form stable aggregates, improving the soil porosity and hence its nutrient retention capacity.[58,59] The presence of active hydrophilic groups allows forming hydrogen bonds with water, which imparts HA with strong water-absorption and -retention capabilities, enhancing the soil water-holding capacity.[60] A highly water-absorbent resin was prepared using HA that demonstrated excellent water-absorption and -retention capabilities.[61] Drought-resistant products based on HAs can effectively promote photosynthesis in plants.[18] Based on the multifunctional role of HA in soil, its combined application with other fertilizers, such as nitrogen fertilizers, can significantly improve the soil's physicochemical properties.[62] Additionally, it has been shown that HAs can promote microbial activity, achieving stable soil organic carbon sequestration and reducing the soil bulk density.[63,64] HAs also play a significant role in optimizing the soil environment, whereby the active groups in Has, such as hydroxyl and carboxyl groups, can undergo adsorption, redox, and ion-exchange reactions with soluble salts and heavy metal ions, improving the physical state of soils (Fig. 5).[65,66]

HAs can also enhance the nutrient utilization efficiency and promote the growth of plants. On the one hand, HA can directly serve as a nutrient source for C, N, and S for supporting the growth of horticultural plants.[67] On the other hand, HA can enhance the utilization efficiency of nutrients in soil. It was found that HA increased the uptake of Na, Ba, P, N, and K ions from soil.[68] HA also stimulates the activity of H-ATPase in plants and promotes the formation of root hairs and lateral roots.[69] The expansion of the plant root system increases the surface area for nutrient uptake, thus strengthening the absorption, assimilation, and cycling of nutrients and ensuring the availability of nutrients.[17,70] Additionally, research indicated that HA chelates various nutritional elements, which can improve some plant growth parameters, including the plant height, panicle length, and seed number.[71,72] Moreover, it can regulate soil microbial populations and activity,[73] and enhance the transformation of nitrogen and carbon to stimulate plant growth and accelerate nutrient uptake.[74] HA can directly participate in the intracellular biochemical and biophysical metabolic processes of plants, such as cell development, photosynthesis, and hormone synthesis, thereby improving plant physiological activity and promoting plant growth and development.[61,75] In another study, it was found that the addition of HA in soil increased the absorption of N, P, K, Ca, and Mg elements (in pineapple leaves) by 52%, 71%, 50%, 58%, and 59%, respectively.[76]

HAs from both HTH and natural microbial transformation are amorphous colloids that contain various functional

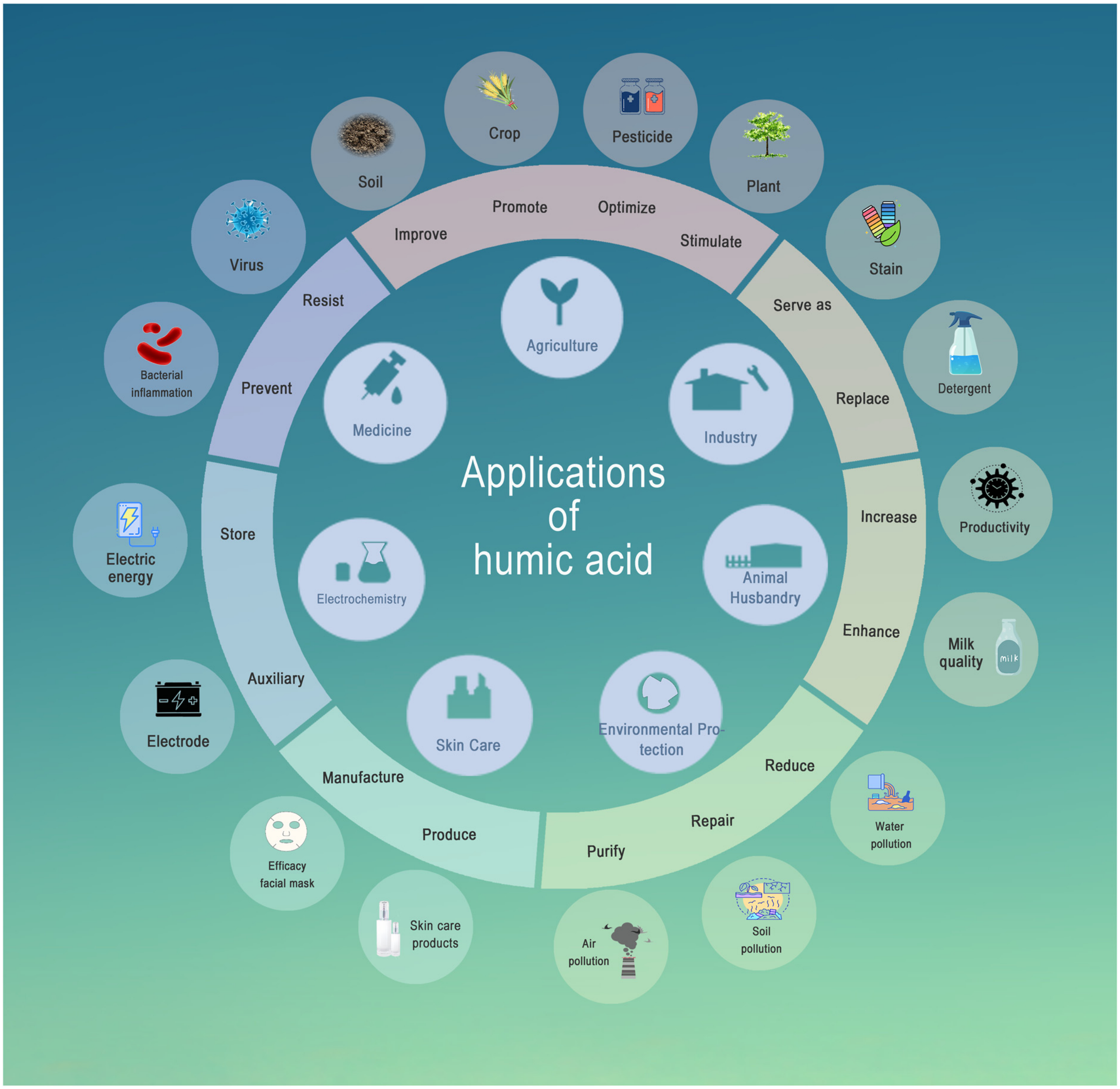

Fig. 4 Application potential of HA in various fields.

groups, such as carboxyl, hydroxyl, quinone, aliphatic groups, aromatic hydrocarbon groups, and nitrogenous groups.[77–80] It can be seen that HA from HTH can also exhibit the function of improving the soil property because of its rich and similar functional group structure to natural HA. More importantly, the richer functional groups in hydrothermal humic acid may have even more pronounced effects.[11,81] Some reports have indicated that the hydrothermal humification of sludge has good potential for nitrogen and phosphorus fixation.[82,83] The nitrogen content of HA prepared by the hydrothermal humification of sludge was high as 15%, and about 90% of the phosphorus could be recovered from the sludge through a hydrothermal oxidation precipitation method. The phosphorus content of the solid product obtained was 9.47%. Therefore, the HTH of sludge can promote the recovery of nitrogen and phosphorus elements. A previous study produced HA from corn straw using HTH, which demonstrated that HA from HTH improved soil quality, water retention, nutrient slow-release, and plant growth in pot experiments, suggesting its potential use in sustainable agriculture and soil remediation.[84] Another study showed that preparation of HA (from hydrothermal conversion)–urea fertilizers with high aromaticity or a low molecular weight is an effective way to improve nitrogen use efficiency in the early stage of soil cultivation and maintain nitrogen fixation in the later stage of soil cultivation.[1] In another article, the effect of hydrothermal HA on lettuce was studied, and experiments showed that adding HA to soil could significantly increase the wet and dry weights of lettuce.[81]

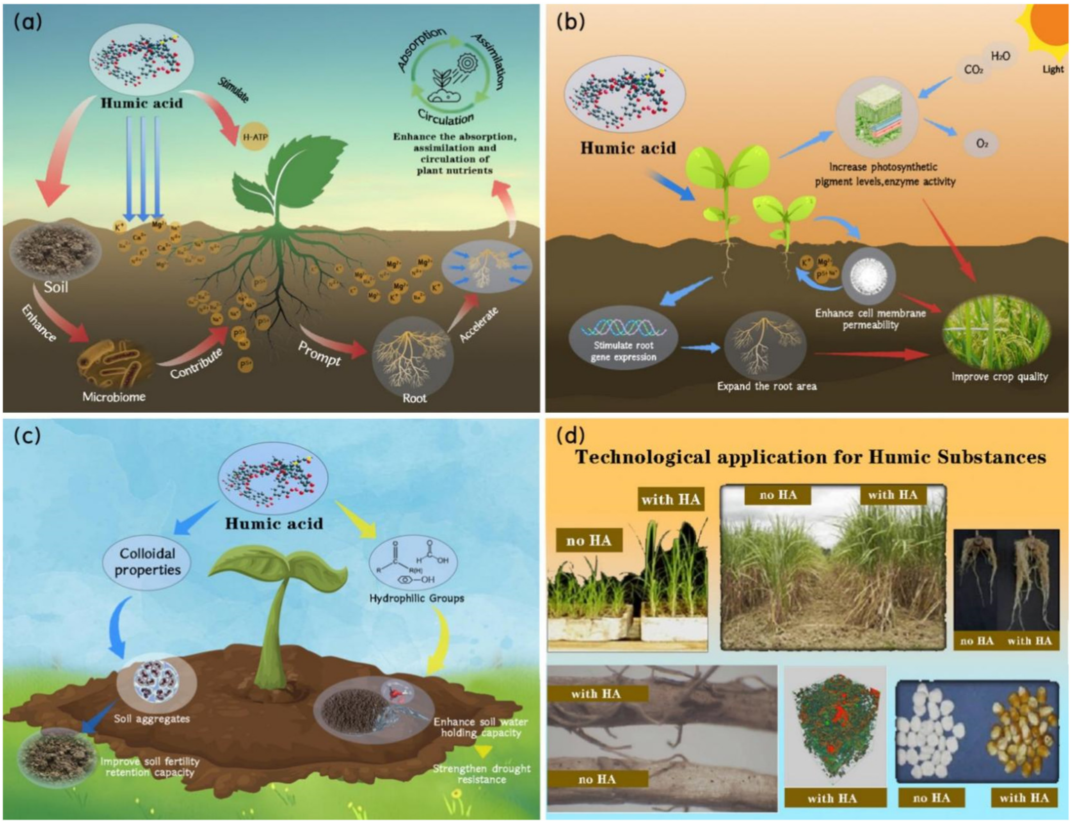

Fig. 5 (a) Principle of HA to improve plant nutrient utilization. (b) Principle of HA to enhance the physiological activity of plants. (c) Principle of HA to improve soil properties. (d) Behavior of plants and soil with and without humic acid (reproduced from ref. 59, published under Creative Commons licence; reproduced from ref. 58 with permission from Elsevier, Copyright 2020; reproduced from ref. 75, published under Creative Commons licence).

3.2. Application potential in environment protection

The functional groups in HA, such as phenols, carboxyl, hydroxyl, quinone, aliphatic groups, aromatic hydrocarbon groups, and nitrogenous and sulfur-containing groups, have various effects in environment protection and remediation, including combining with heavy metals, organic pollutants, radionuclides, and other pollutants, and participating in the photolysis of pollutants (Fig. 6).[80,85–88]

HA can serve as an electron medium for chemical reactions and microbial metabolic processes, undergoing degradation or reduction reactions with pollutants in water. The amphiphilic structure and redox capabilities of HAs contribute to their interactions with heavy metals.[53] HAs are considered environmentally friendly alternatives for water pollution control and have been proven to be effective for water environmental remediation.[18,89]

As previously mentioned, HAs have colloidal properties and are rich in various functional groups, such as carboxyl, hydroxyl, and amino groups. They can interact with sulfur oxides, nitrogen oxides, ammonia, *etc.*, to reduce environmental pollution. Research has confirmed that HA has anti-smog effects by acting on secondary particles of PM2.5, such as ammonium nitrate and ammonium sulfate.[90] In a previous study, HA inhibited the conversion of acetyl coenzyme A in methanogenic bacteria by electron competition, thus affecting methane generation.[91] It was found in sludge test experiments that when adding HA : VSS (volatile suspended solids) at 15%, the methane-generation-inhibition efficiency was 35.1%; when HA : VSS was 20%, the inhibition efficiency of methane generation was 74.3%.[92] Given the binding ability of functional groups and heavy metals in HAs, HA can be used for the soil remediation of heavy metal pollution. For example, HAs have been reported to reduce the toxicity of metal elements in soil by altering valence states through redox processes, while the functional groups, such as carboxyl groups, on HA molecules interact with ionic metals to form spherical HA–metal chelates, leading to precipitation adsorption and hence a reduction in toxicity.[3,93] Previous studies found that modified HA–ATP composites not only showed enhanced adsorption effects on polycyclic aromatic hydrocarbons (PAHs) but could also avoid secondary pollution of the soil by harmful chemicals.[94]

The rich oxygen-containing functional groups in HA from hydrothermal conversion can increase the adsorption sites and affinity of HA and regulate the surface charge of HA, and their adsorption has been proven to have great potential in environmental protection applications. For example, HA pre-

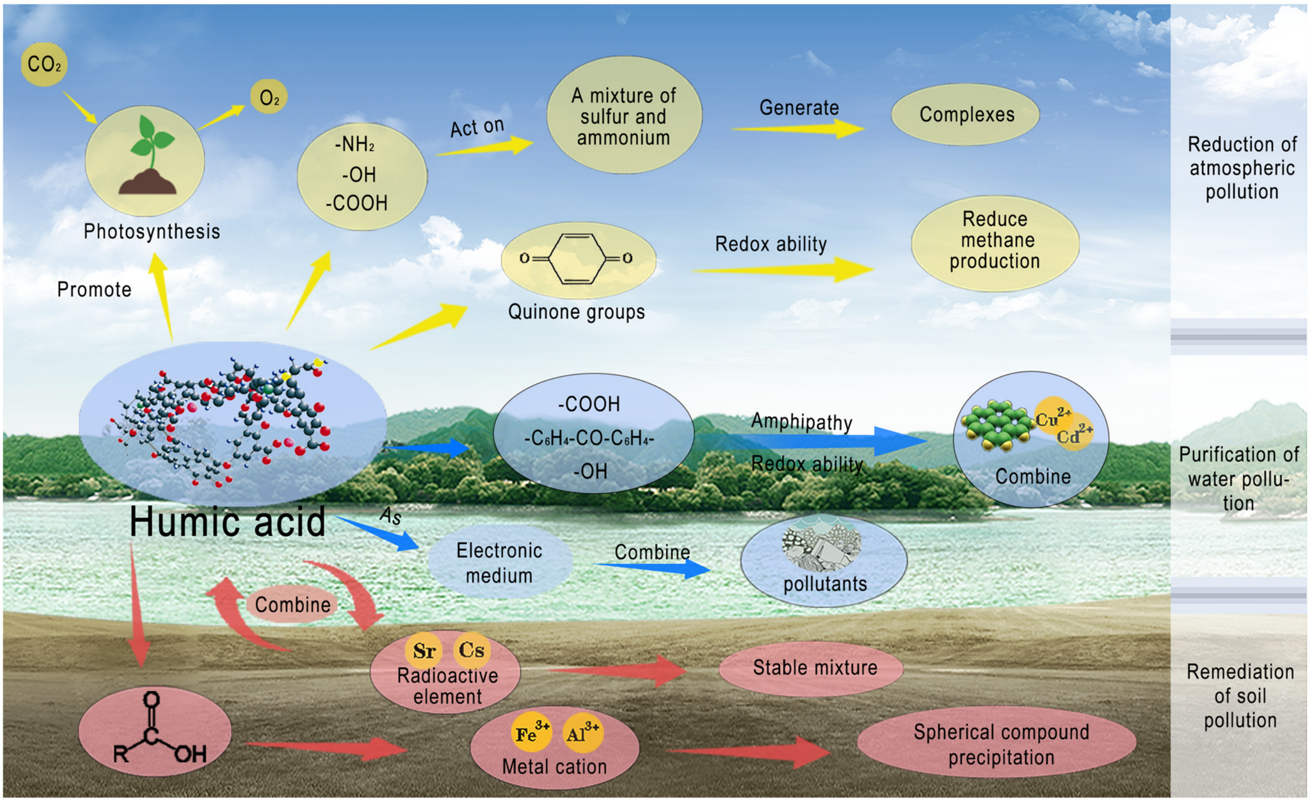

Fig. 6 Role of HA in reducing soil, water, and air pollution.

pared by the alkaline hydrothermal conversion of biomass using oxygen had an adsorption capacity of 24.4% for divalent cadmium.[81] In addition, HA from hydrothermal conversion can be used in combination with other materials to enhance the overall adsorption performance.[95] For example, it was reported that composite materials synthesized from HHA and iron could adsorb various heavy metals,[96] whereby the maximum adsorption capacities for Cd^{2+}, Pb^{2+}, and Ni^{2+} from water were 290.81, 374.99, and 296.85 mg g^{-1}, respectively. These results highlight the advantages of hydrothermal HAs in environmental applications. In summary, HA from HTH as an adsorbent has broad application prospects.

3.3. Application potential in electrochemistry

The rich functional groups in HA give it high application value in the electrochemical field. For instance, HA can be used to prepare porous carbon materials for energy storage and humidity sensors (Fig. 7), indicating the high potential of HA from HTH in electrochemical applications.[97–100] HA has also been used to modify electrodes, whereby it was found that HA-modified electrodes can interact with water and metal ions, thus amplifying electrical signals through electron transfer.[101] In addition, HA-modified electrodes can interact with pollutants to detect their electrical activities.[7] Due to the hydrophilic functional groups of HA, HA-modified electrodes can also be used as humidity sensors, exhibiting a decrease in impedance with increasing relative humidity.[102] Moreover, HA also has applications in microbial fuel cells. It was reported that an HA-modified bioanode could reduce the activation energy of ion oxidation, thereby improving the electron-transfer efficiency between microorganisms and electrodes and enhancing the electrochemical performance.[103] Research has shown that HA-based energy-storage materials have excellent rate capabilities and capacitance performance.[100] A hybrid capacitor prepared using a combination of HA and activated carbon[104] and an asymmetric capacitor prepared using HA and nickel sulfide[105] both showed high power density and energy density. In another study, a concentrated battery was constructed based on reduced graphene oxide membranes and HA, which demonstrated high stability, durability, maximum open circuit voltage maximum power values, and a longer duration than general batteries.[106] In another study, graphene–SnO_2 HA nanocomposites were synthesized, and exhibited an ultra-high reversible specific capacity.[107] In another study, reduced graphene oxide and HA composite materials were used to prepare supercapacitor electrodes.[108] However, there is currently no research on the application performance evaluation of HA prepared by a hydrothermal method for storing electrical energy and preparing capacitors.

3.4. Application potential in healthcare and animal husbandry

HAs have a wide range of functions in healthcare. Many researchers have studied the pharmacological properties of HA

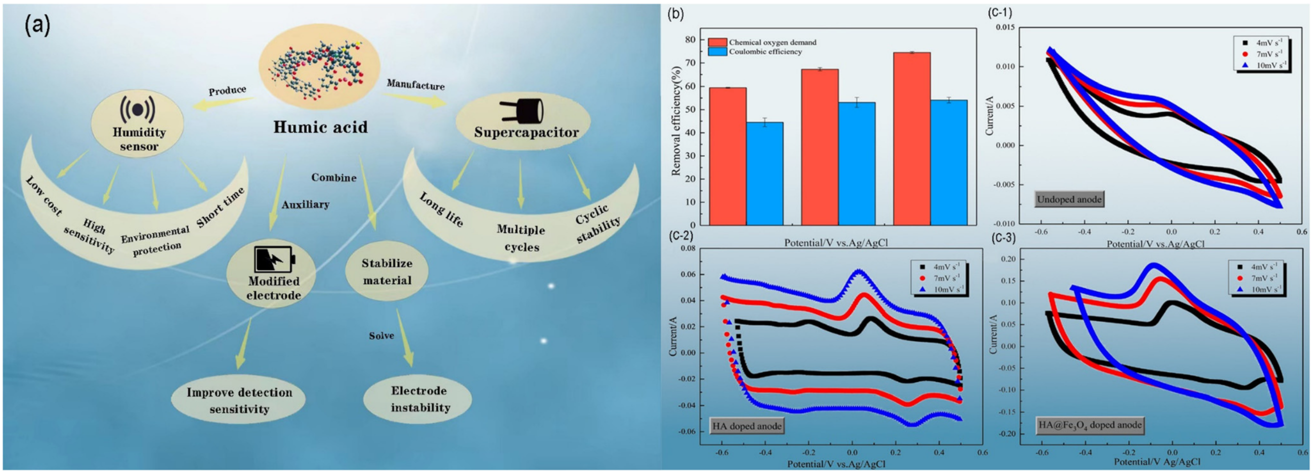

Fig. 7 (a) Applications of HA in the electrochemical field. (b) Coulombic efficiency and oxygen demand removal efficiency of microbial fuel cells in the absence of HA, HA, and HA@Fe_3O_4. (c-1) Undoped anode. (c-2) Anode containing HA. (c-3) Anode containing HA@Fe_3O_4 (reproduced from ref. 130 with permission from Elsevier, Copyright 2019).

and found that it has antibacterial, anti-inflammatory, antiviral, and analgesic properties, with the additional advantages of having no side effects on the body and causing no irritation to the skin.[109] HA molecules have a negative charge in neutral and alkaline solution environments and can inhibit the replication of viruses (including COVID-19, vaccine viruses, and cytomegalovirus) by binding to the cationic domain of viruses, exerting antioxidant effects, and enhancing the permeability of cell membranes (Fig. 8).[110–113] Besides, it has been found that the addition of HA can inhibit the infection of human lymphocytes *in vitro* and its anti-HIV activity was also confirmed.[114] The anti-mutagenicity activity of HA has also been observed,[115,116] suggesting that HA can be used as a mutagenesis inhibitor. HA also provides new ideas for its use in drug development. Sodium humate, a product of the combination of HA and sodium hydroxide, was investigated as an effective clinical medicine for use in veterinary practices for the treatment of various animal diseases.[117] In other experiments, HA was found to be able to alleviate neuronal damage and reduce brain tissue death in rats, indicating its potential application in hypoxic-ischemic brain injury.[5] HA was also used investigated as an active ingredient in efficacy masks to prevent the secondary activation of viruses after chemical facial treatments.[118] Additionally, HA has the potential to be used as a component in lipsticks and lip balms.[119,120] Therefore, HA has extensive application value in healthcare. Furthermore, in an animal husbandry study, it was found that HA could reduce the levels of mycotoxins and improve the gastrointestinal health of animals, aiding maintaining normal metabolism, thereby enhancing animal production.[121] As a feed additive, HA can accelerate the efficiency of animals' absorption of feed, thus expediting the metabolism of livestock, thereby enabling increasing the production speed, and improving product quality.[122] It was found that the nitrogen element in HA molecules can stimulate feed protein into muscle protein, thereby improving the growth capacity of lean meat.[123] Meanwhile, studies have shown that when HA is used as a dispersant in ceramic suspensions, it can effectively reduce viscosity.[124] The excellent dispersing effect of HA can play a key role in the preparation of composite materials. For instance, a novel HA-g-PSSNa dispersant based on HA not only demonstrated good dispersibility but also exhibited excellent slurry manufacturability.[125]

4. Challenges and perspectives for the application of hydrothermal humic acid

Previous studies have shown that hydrothermal humic acids (HTHAs) possess significant agricultural, soil, environmental, and material functions.[18,19,52] However, the development of HTHAs remains in its early stages. The complexity of the raw materials' properties and reaction conditions has so far limited the ability to obtain stable and uniform products. While current research has attributed the application potential of HTHAs primarily to their abundance of functional groups, their specific mechanisms of action remain unclear. Presently, the production of HTHAs is still confined to laboratory-scale studies, with limited yields and a lack of large-scale production facilities and practical applications. Furthermore, the hydrothermal conversion process often requires highly alkaline solutions and substantial energy input, raising concerns about operational safety and environmental impacts, which require further assessment.

4.1. Obtaining high-quality and stable humic acid *via* hydrothermal humification

To achieve the production of HA from biomass for application in various fields, the first step should be obtaining high-

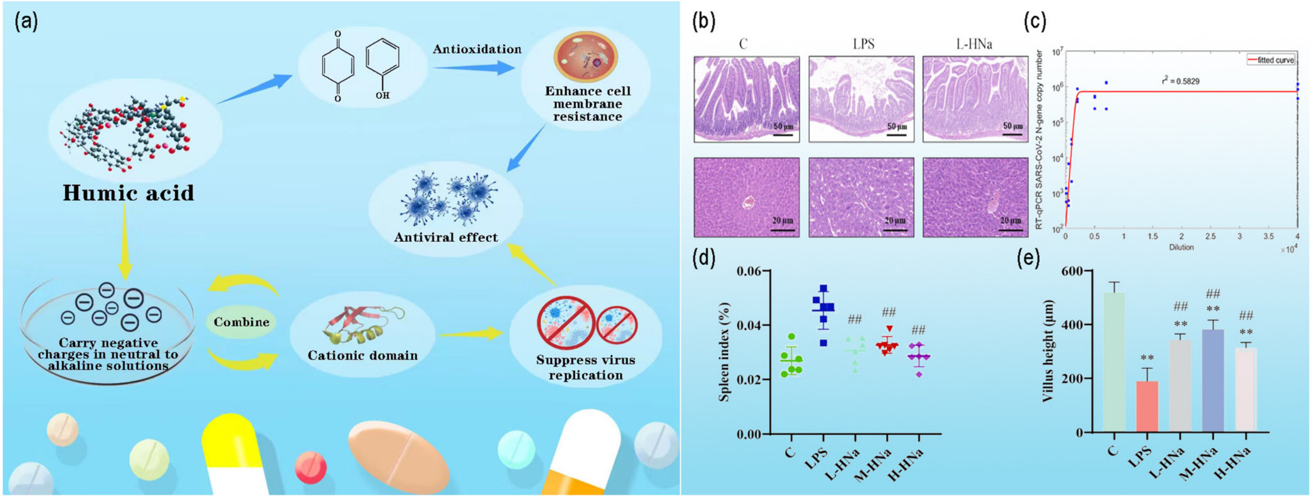

Fig. 8 (a) Antiviral pathway of HA. (b) Images of the jejunum and liver of mice (reproduced from ref. 117, with permission from Elsevier, Copyright 2023). (c) Inhibition curves of humic substances against SARS-CoV-2 virus B1.1.7 variants (reproduced from ref. 131, published under Creative Commons licence). (d) Spleen index of mice (reproduced from ref. 117, with permission from Elsevier, Copyright 2023). (e) Mouse jejunal villi length (reproduced from ref. 117, with permission from Elsevier, Copyright 2023). (C is the control group; LPS is the structural damage group induced by lipopolysaccharide; L-HNa, M-HNa, H-HNa are the experimental groups receiving 0.1%, 0.3%, 0.5% sodium humate, respectively).

quality and stable HA *via* hydrothermal humification. Producing HAs through hydrothermal conversion represents a sustainable and effective method for obtaining these compounds from various organic materials. The feasibility of the hydrothermal conversion of HA has been confirmed, but the current production of HA through hydrothermal conversion is still in the early stage.[126] It is still necessary to further deepen the research on the generation mechanism of HA, and to optimize the reaction conditions and reactors used with the original biological waste to obtain high HA yields. The reaction mechanism of HA production through hydrothermal conversion has not yet been completely elucidated. Further detailed studies of the reaction mechanism could help better understand the reaction process and regulation of the reaction conditions. This includes studying the reaction kinetics, reaction thermodynamics, and reaction pathways to explore how to improve the production efficiency and purity of HA. It is already known that the reaction conditions for hydrothermal conversion, such as reaction temperature, additives, pH value, reaction medium, and reaction time, have significant effects on the production efficiency and purity of HA.[29] In addition, considering the different functions of hydrothermal HA, it is also important to explore the targeted preparation of functional HA materials by regulating the preparation process of hydrothermal HA. Therefore, it is particularly important to study how to optimize the reaction conditions to further improve the production efficiency and purity of HA.

4.2. Understanding the application effects and mechanisms of hydrothermal humic acid

To achieve the production of HA from biomass for applications in various fields, the second step should be to comprehensively understand the application effects and mechanisms of hydrothermal HA. The application potential of HA has been gradually tapped in the past decade, but research on the application of hydrothermal HA remains limited. Although hydrothermal HA appears to have greater application potential based on a comparison of its functional groups, there is still a lack of case studies with hydrothermal HA. In the field of agriculture, HA is usually used in the form of a compound agent, which has been shown to improve the physical and chemical properties of the soil and improve the ability of plants to resist biological stresses as a regulator, but the overapplication of such agents can cause problems, such as soil acidification, microbial community imbalance, and leaf burns, so the rational use of HA is key.[69] In the field of environmental protection, HA mainly relies on the redox ability of its functional groups to reduce environmental pollution, but the specific contribution of the various functional groups is still unknown. Therefore, in the face of different sources of HA, there will be different environmental remediation effects in environmental treatment, and future research should focus on the specific mechanism of HA redox pollutants.[3,18] Besides, it is necessary to consider the purity and product specifications required for specific applications, and to develop appropriate quality control, certification and labeling procedures.[127,128]

4.3. Developing large-scale equipment for hydrothermal humic acid production

To achieve the production of HA from biomass for application in various fields, the third step should be developing large-scale equipment for hydrothermal HA production. Current research related to HA applications are based on laboratory studies, and lack large-scale application verification. Promoting the commercial application of hydrothermal HA and studying the design and scale-up of reactors for hydrothermal conversion are also important aspects that should receive special focus. The material selection, structural design, and operating parameters of the reactor can affect the production efficiency of HA.[129] Therefore, studying how to design an efficient and stable reactor and achieving scale-up from small-scale laboratory studies to industrial production is crucial. HA has already demonstrated potential for use in multiple areas, such as preparing fertilizers, soil conditioners, coatings, cosmetics, and others. It is further necessary to study how to improve the stability and safety of HA in these areas and how to further utilize the generated HA for resource maximization.

4.4. Evaluating the environmental and economic benefits of hydrothermal humic acid

To achieve the production of HA from biomass for application in various fields, evaluating the environmental and economic benefits of hydrothermal HA is required. During the process of hydrothermal conversion to produce HA, some environmental issues, such as waste gas, wastewater, chemical reagents, and solid waste, may arise.[93] Therefore, it is necessary to evaluate the environmental impacts of the hydrothermal conversion to produce HA and formulate corresponding environmental protection strategies based on the actual impact level. Although artificially synthesized HA has excellent performance, its impact on the structure and function of ecosystems as an exogenous substance still needs in-depth research. For example, the impact of HA on the original biological communities in water bodies, sediments, and soil environments, as well as the secondary pollution and environmental risks generated during the remediation process, are key issues that urgently need to be explored before promoting the application of HAs in the field of environmental remediation. Additionally, the cost of raw materials, energy, and equipment is an important factor that needs to be considered for the commercialization of this process. When compared with existing biological conversion methods for producing HA, it is necessary to evaluate its technical–economic performance and safety to ensure the development of economically feasible conversion technologies, as well as effective methods for dealing with byproducts to make the production of HA competitive with existing methods.

5. Conclusions

The hydrothermal humification of biomass is an effective approach for producing humic acid (HA) to improve the carbon efficiency of biomass utilization. This article explored the conversion mechanisms involved in hydrothermal HA production, compared the potential of various raw materials for HA conversion, and examined how factors such as the reaction time, temperature, pH, and additives influence the conversion efficiency. With significant application potential in agriculture, environmental protection, and functional material production, HA has gained much attention, indicating the high application of hydrothermal HA. Given the currently unclear mechanisms of hydrothermal HA transformation and the few available application studies that have been performed, achieving high-quality and consistent-quality HA through hydrothermal methods, understanding the application effects and mechanisms, and developing large-scale equipment for hydrothermal HA production are critical steps toward commercializing HA. At the same time, evaluating the environmental and economic benefits of hydrothermal HA is required. This review offers a comprehensive reference for ongoing research on hydrothermal HA.

Author contributions

Yangjiuzhou Wang: Conceptualization, data curation, formal analysis, writing – original draft, writing – review & editing. Changbin Yuan: Conceptualization, data curation, formal analysis, writing – original draft, writing – review & editing. Kai Zhang: Writing – original draft. Jinyu Tong: Writing – original draft. Ningjie Ma: Visualization. M. M. Ali: Writing – original draft. Yongdong Xu: Conceptualization, data curation, formal analysis, writing – original draft, investigation, supervision, writing – review & editing. Zhidan Liu: Conceptualization, data curation, formal analysis, funding acquisition, project administration, supervision, writing – review & editing.

Data availability

No primary research results, software or code has been included and no new data were generated or analyzed as part of this review.

Conflicts of interest

The authors declare no Competing Financial or Non-Financial Interests.

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