Review article
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A COMPREHENSIVE REVIEW OF HUMIC ACID PRODUCTION TECHNOLOGIES IN CHINA: METHODS, CHALLENGES, AND FUTURE DIRECTIONS

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Abstract. Humic acids (HAs) are vital organic compounds derived from the decomposition of plant and animal matter, playing a crucial role in soil fertility, plant growth, and environmental remediation. This paper provides a detailed review of humic acid production technologies in China, focusing on both natural extraction and artificial synthesis methods. Natural extraction primarily involves the use of low-rank coals such as lignite and weathered coal, while artificial synthesis includes biological composting, chemical oxidation, and hydrothermal humification. Each method is analyzed in terms of raw material selection, reaction mechanisms, process parameters, and environmental impact. The review highlights the advantages and disadvantages of each production method, including efficiency, cost, and environmental considerations. Emerging trends such as the development of low-cost catalysts, bio-hydrothermal coupling, and the integration of different production techniques are also discussed. The paper concludes with recommendations for optimizing humic acid production to enhance sustainability, reduce costs, and improve product quality. This review aims to provide valuable insights for researchers and industry professionals involved in humic acid production and application.

Keywords: humic acid (HA), humic acid production, natural extraction, artificial synthesis, environmental impact

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КОМПЛЕКСНЫЙ ОБЗОР ТЕХНОЛОГИЙ ПРОИЗВОДСТВА ГУМИНОВОЙ КИСЛОТЫ В КИТАЕ: МЕТОДЫ, ПРОБЛЕМЫ И БУДУЩИЕ НАПРАВЛЕНИЯ

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Аннотация. Гуминовые кислоты (ГК) – это жизненно важные органические соединения, получаемые в результате разложения растительного и животного материала, играющие решающую роль в плодородии почвы, росте растений и восстановлении окружающей среды. В статье представлен подробный обзор технологий производства гуминовой кислоты в Китае с упором на методы как естественной экстракции, так и искусственного синтеза. Естественное извлечение в первую очередь предполагает использование низкосортных углей, таких как лигнит и выветренный уголь, в то время как искусственный синтез включает биологическое компостирование, химическое окисление и гидротермальную гумификацию. Каждый метод анализируется с точки зрения выбора сырья, механизмов реакции, параметров процесса и воздействия на окружающую среду. В обзоре подчеркиваются преимущества и недостатки каждого метода производства, включая эффективность, стоимость и экологические соображения. Также обсуждаются новые тенденции, такие как разработка недорогих катализаторов, биогидротермальное сопряжение и интеграция различных методов производства. В заключение приводятся рекомендации по оптимизации производства гуминовой кислоты для повышения устойчивости, снижения затрат и улучшения качества продукции. Целью этого обзора является предоставление ценных сведений исследователям и специалистам отрасли, занимающимся производством и применением гуминовой кислоты.

Ключевые слова: гуминовая кислота (ГК), производство гуминовой кислоты, естественная экстракция, искусственный синтез, воздействие на окружающую среду

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Introduction

Humic acids (HAs) are complex organic molecules resulting from the decomposition of plant and animal matter. They are integral components of soil humus and play a pivotal role in enhancing soil fertility and structure. In agriculture, HAs improve nutrient uptake, stimulate plant growth, and increase crop yields by enhancing soil properties such as texture, water retention, and cation exchange capacity, thereby creating a conducive environment for plant development [1].

Beyond agriculture, humic acids are significant in environmental science. They contribute to carbon sequestration, thus playing a role in mitigating climate change. Additionally, HAs influence the mobility and bioavailability of heavy metals and organic pollutants in soils and water bodies, affecting their transport and potential toxicity. This makes HAs crucial in soil and water remediation efforts, where they aid in immobilizing contaminants and restoring ecological balance [2].

The production of humic acids can be categorized into two primary methods: extraction from natural sources and artificial synthesis.

Natural Extraction: This involves isolating HAs from naturally occurring materials rich in organic content, such as peat, lignite (brown coal), and compost. The extraction process typically employs alkaline solutions to solubilize the humic substances, which are then precipitated and purified [3].

Artificial Synthesis: This method entails the chemical or biological transformation of organic materials into humic-like substances. Techniques include the composting of organic waste, chemical oxidation of biomass, and other innovative processes designed to mimic natural humification.

Evaluating and comparing these production methods is essential for several reasons:

Environmental Impact: Understanding the ecological footprint of each method is crucial. Natural extraction may lead to the depletion of peatlands or other natural reserves, while artificial synthesis could involve energy-intensive processes or the use of chemicals with potential environmental risks.

Economic Considerations: The cost-effectiveness of each method varies. Factors such as raw material availability, processing costs, and scalability influence the economic viability of producing humic acids.

Efficiency and Quality: The yield and quality of humic acids can differ between methods. Assessing parameters like purity, functional group composition, and consistency is vital to ensure the end product meets desired standards for agricultural or environmental applications.

A comprehensive review and comparison of these production methods provide insights into optimizing humic acid production. Such an analysis aids in selecting sustainable practices that balance environmental responsibility with economic feasibility, ultimately supporting the diverse applications of humic acids in enhancing soil health and environmental remediation.

1. Production Processes of Humic Acid (HA)

The production of humic acid is mainly divided into two categories: natural humic acid extraction and artificial humic acid synthesis. This paper elaborates on each method in detail from the perspectives of raw material selection, reaction mechanisms, and process parameters.

1.1. Natural Humic Acid Extraction Process

1.1.1. Raw Material Selection and Pretreatment

Raw Material Type: Low-rank coals (such as lignite and weathered coal) are the primary raw materials due to their high humic acid content (lignite contains 40–70 % total humic acid). For example, lignite from Northeast China has a humic acid content of 67.25 %, while Xinjiang weathered coal contains 46.70 % [4, 7].

Pretreatment: The raw material is crushed and ground to below 40 mesh, followed by drying at 105–110 °C for 2–4 hours to remove moisture [4, 7].

1.1.2. Acid Oxidation Treatment

Oxidant Selection: Nitric acid (HNO_3) is the most commonly used oxidant, typically at a concentration of 1.5–2.0 mol/L, with a coal-to-acid mass ratio of 1:1.5–1:5.0 [7, 8].

Reaction Conditions: The temperature is controlled at 60–90 °C, with a reaction time of 60–180 minutes. For example, when nitric acid oxidizes Yunnan lignite at a coal-to-acid ratio of 1:1.5, the humic acid yield reaches 62.80 % [8].

Reaction Mechanism: Nitric acid oxidizes non-humic acid substances in coal (such as lignin and cellulose), forming nitro-humic acid (NHA) and nitro-fulvic acid (NFA). The reaction equation is as follows:

$$R(COOH)_4 + HNO_3 \rightarrow R(NO_2)_n + H_2O + CO_2.$$

1.1.3. Product Separation and Purification

Extraction: A 2 mol/L NaOH or Na_2CO_3 solution is used for extraction at 60 °C for 60 minutes, with a solid-to-liquid ratio of 1:5 (dry coal powder: extractant).

Centrifugation and Drying: The extract is centrifuged at 3500 r/min for 10 minutes, and the supernatant is acidified to pH 1–2 to precipitate humic acid, followed by drying at 85 °C.

Purity Analysis: The total humic acid content is measured by sodium pyrophosphate titration, while functional group structures are analyzed using Fourier transform infrared spectroscopy (FT-IR) [4, 8].

1.2. Artificial Humic Acid Synthesis Process

1.2.1. Biological Composting Method

Raw Materials: Organic solid waste (such as straw, kitchen waste, and livestock manure), with a carbon-to-nitrogen (C/N) ratio adjusted to 25–30 to optimize microbial activity [9, 10].

Microbial Action: A composite microbial agent (e.g., cellulose-degrading bacteria and actinomycetes) is inoculated, maintaining the compost temperature at 50–65 °C for 30–60 days. For example, adding MnO_2 as a catalyst accelerates humification, increasing humic acid yield by 15–20 %.

Humification Mechanism: Humic acid is formed through sugar-amine condensation (Maillard reaction) and lignin-protein aggregation, with aromatic functional groups accounting for 40–60 % [11].

1.2.2. Chemical Oxidative Polymerization Method

Oxidants and Catalysts: H_2O_2 (5–10 %), O_2, and metal oxides (such as MnO_2 and Fe^{3+}). For example, when H_2O_2 oxidizes corn stalk waste liquid, the electron transfer capacity of humic acid increases twofold [12].

Reaction Conditions: Temperature ranges from 25–70 °C, pH is controlled at 3–7, and the reaction lasts 2–24 hours. In the catechol + glycine system, MnO_2 catalysis increases the carboxyl content of humic acid to 3.325 mmol/g [13].

Reaction Mechanism: Phenolic compounds undergo oxidation to form semiquinone free radicals, which then polymerize with amino acids to generate macromolecular humic acid.

1.2.3. Hydrothermal Humification Method

Raw Materials and Conditions: Biomass (such as glucose and sawdust) undergoes hydrothermal reaction at 200–240 °C and 2–4 MPa for 6–24 hours. For example, fructose reacts at 170 °C for 3 hours, yielding 64.6 % humic substances [14, 15].

Product Characteristics: The synthesized humic acid contains carboxyl groups (1.2–3.4 mmol/g) and phenolic hydroxyl groups (0.8–2.1 mmol/g), with a molecular weight distribution similar to natural humic acid.

Application Optimization: The addition of KOH or H_3PO_4 can regulate product aromaticity. When used for heavy metal adsorption, the adsorption capacity for Pb^{2+} reaches 300 mg/g [16].

1.3. Process Optimization and Challenges

Energy Efficiency and Cost: The nitric acid oxidation method has high energy consumption (reaction temperature > 80 °C), while the hydrothermal method requires significant equipment investment. Future developments should focus on low-temperature catalytic technologies (such as electrochemical oxidation) to reduce costs [12].

Product Standardization: Different processes result in variations in humic acid functional group content (carboxyl content 1.5–4.0 mmol/g), necessitating the establishment of unified quality standards (e.g., ISO 19822).

Environmental Friendliness: Chemical methods generate nitrogen-containing wastewater (NO_3^- concentration > 500 mg/L), requiring membrane separation or biodegradation technologies for wastewater recycling [17].

2. Discussion

2.1. Comparison of advantages and disadvantages

The advantages and disadvantages of different methods are mentioned in Table.

Table

The different Comparison of advantages and disadvantages [5, 6]

Method	Pros	Cons
Natural Extraction	High Efficiency: Utilizes low-rank coals rich in humic acids, achieving yields up to 62.80 %. Established Process: Widely adopted with well-understood protocols	Environmental Concerns: Use of nitric acid poses risks, including the generation of nitrogen-containing wastewater. Safety Risks: Handling strong acids requires stringent safety measures
Biological Composting	Environmentally Friendly: Employs organic waste, enhancing sustainability. Improves Soil Health: Enhances microbial activity and soil structure	Slow Process: Composting periods range from 30 to 60 days. Product Separation Challenges: Isolating pure humic acids from compost is complex
Chemical Oxidation	Controlled Reaction Conditions: Allows for targeted synthesis of humic substances. Rich Functional Groups: Produces humic acids with diverse functionalities	High Oxidant Costs: Utilization of agents like hydrogen peroxide increases expenses. – Environmental Concerns: Chemical residues may pose disposal challenges
Hydrothermal Humification	Rapid Production: Processes biomass quickly under controlled conditions. High Yields: Achieves significant conversion rates of biomass to humic substances	Energy-Intensive: Requires high temperatures (200–240 °C) and pressures (2–4 MPa). Significant Equipment Investment: Necessitates specialized reactors and infrastructure

2.2. Emerging Trends and Advancements

Development of Low-Cost Catalysts

Objective: Reduce production costs associated with chemical oxidants.

Approach: Research focuses on identifying affordable and efficient catalysts to facilitate oxidative polymerization and hydrothermal processes.

Impact: Lowering catalyst costs can make humic acid production more economically viable, especially for large-scale operations.

Bio-Hydrothermal Coupling

Concept: Integrate biological and hydrothermal methods to leverage the benefits of both processes.

Implementation: Utilize microbial pretreatment to decompose biomass, followed by hydrothermal processing to synthesize humic substances.

Benefits: This hybrid approach can enhance overall efficiency, reduce energy consumption, and improve the sustainability of humic acid production.

Integration of Methods

Strategy: Combine different production techniques to optimize outputs.

Examples: Employ chemical oxidation to accelerate biological composting or use hydrothermal treatment to refine products from natural extraction.

Advantages: Such integrations can lead to higher yields, improved product quality, and more sustainable processes by balancing efficiency with environmental considerations.

In summary, while each humic acid production method has its unique set of advantages and limitations, ongoing research and technological innovations are paving the way for more efficient, cost-effective, and environmentally friendly approaches. The future of humic acid production lies in the strategic combination of existing methods and the development of novel catalysts and processes that address current challenges.

Conclusion

In conclusion, both natural extraction and synthetic methods for humic acid production offer distinct advantages and face specific challenges. Natural extraction methods, which often utilize low-rank coals like lignite, are efficient due to the high humic acid content of the raw materials. However, these methods are heavily dependent on the quality of the raw material and involve the use of chemicals such as nitric acid, raising environmental and safety concerns. On the other hand, synthetic methods, including biological composting, chemical oxidation, and hydrothermal humification, provide controlled processes that can produce humic acids with diverse functional groups. Yet, these methods may involve high costs, energy-intensive operations, and complexities in product separation.

Looking ahead, advancements in humic acid production are focusing on optimizing existing methods and exploring innovative approaches. For instance, enhancing hydrothermal processes by integrating acid pretreatment has been shown to increase humic acid yields and reduce heavy metal content, thereby improving the quality of the final product. Additionally, the utilization of biochar as a feedstock in hydrothermal treatments not only aids in waste biomass management but also contributes to the production of high-purity humic acids. These strategies aim to address current limitations by improving efficiency, reducing environmental impact, and promoting sustainability in humic acid production.

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