

Review of the Application of Attapulgite and Their Colloids

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Abstract: This paper provides a systematic summary and organization of the relevant knowledge on the colloids of attapulgite. It aims to comprehensively understand the characteristics, preparation methods, and application areas of conjugated block copolymer colloids. Additionally, it conducts a comprehensive analysis and evaluation of the research achievements in the field of conjugated block copolymer colloids. By reviewing a large number of literature sources, the application status, advantages, disadvantages, challenges, and problems of conjugated block copolymer colloids in different fields are explored. This facilitates in-depth thinking and analysis of the potential and development directions of conjugated block copolymer colloids, thereby promoting further research and application in both academia and industry. It also encourages communication and collaboration in related fields, providing guidance and inspiration for future studies. Moreover, this review proposes potential research directions and innovative points to drive further advancements in this field.

Keywords: Attapulgite, Performance enhancement, Development trends.

1. Introduction

Attapulgite colloids are a unique type of colloidal system composed of colloidal particles formed by attapulgite(ATP) nanocrystals in solution. Attapulgite is a layered silicate mineral with abundant layered structures, primarily found in a sedimentary form with a high content of hydroxyl groups on its surface, providing negatively charged sites capable of adsorbing a large number of metal ions [1]. When attapulgite comes into contact with water, water molecules can enter the interlayer spaces of attapulgite, causing it to swell and disperse, forming colloidal particles. These colloidal particles possess high surface activity and adsorption capacity [2], thus holding significant application value in various fields.

Attapulgite colloids find extensive applications in the field of nuclear engineering and nuclear technology. Firstly, attapulgite colloids play a crucial role in nuclear waste management. Due to their high adsorption and ion exchange capacities, attapulgite colloids can be employed to adsorb and immobilize radioactive substances in radioactive waste, thereby reducing their environmental contamination [3]. Additionally, attapulgite colloids can be utilized for the encapsulation and isolation of nuclear waste, effectively preventing its release into the surrounding environment.

Furthermore, attapulgite colloids have wide-ranging applications in soil remediation and environmental pollution control. With their excellent adsorption performance and ion exchange capabilities [4], attapulgite colloids can adsorb and remove harmful substances and heavy metal ions from soil, thus restoring the ecological environment of the soil [5]. As an important colloidal system, attapulgite colloids have broad applications in nuclear engineering and nuclear technology. They can be utilized not only for nuclear waste treatment and radiation shielding but also for soil remediation and environmental pollution control. Therefore, in-depth research and understanding of the characteristics and applications of attapulgite colloids hold significant scientific and practical significance.

2. Characteristics, Preparation, and Applications of Attapulgite Colloids

2.1. Characteristics

Attapulgite colloids are colloidal systems composed of attapulgite minerals. They consist of tiny particles formed by attapulgite minerals and the surrounding solution, exhibiting high specific surface area and adsorption capacity [6]. These particles form a colloidal system in the solution, which can be water or other liquid media. Ions, molecules, and other particles in the solution also interact with attapulgite particles, influencing the properties and behavior of the colloids.

One of the characteristics of attapulgite colloids is that their particle size typically ranges from nanometers to micrometers, providing a large specific surface area and surface activity. This endows attapulgite colloids with significant potential in adsorption, catalysis, dispersion, stabilization, and other applications [7-9]. Additionally, the properties and behavior of attapulgite colloids are influenced by factors such as ion concentration, pH value, and temperature in the solution.

Attapulgite colloids typically exist as particles in the nanometer to micrometer range, and these particles can have irregular shapes such as flakes, rods, or spheres. Their sizes usually range from a few nanometers to several tens of micrometers, providing a large specific surface area [10]. This characteristic imparts strong adsorption capacity to attapulgite colloids, enabling them to adsorb organic compounds, heavy metal ions, and other pollutants from solutions, thereby purifying and removing contaminants [11]. The layered structure of attapulgite colloids also contributes to their excellent ion exchange capacity. They can undergo exchange reactions with ions in the solution, affecting the ion concentration and chemical equilibrium of the solution. Due to their large specific surface area and surface activity, attapulgite colloids exhibit good dispersion stability in solutions. This allows them to form stable colloidal systems that are resistant to sedimentation or aggregation. Attapulgite colloids also possess catalytic activity and can serve as

catalyst supports [12]. When used as catalysts, they facilitate chemical reactions, enhancing reaction rates and efficiency [13]. These properties make attapulgite colloids have broad potential applications in fields such as environmental science, materials science, and chemical engineering.

2.2. Preparation Methods of Attapulgite Colloids

Common methods for preparing attapulgite colloids include sol-gel method [14] and co-precipitation method [15].

2.2.1. Sol-Gel Method

The sol-gel method is a commonly used approach for preparing attapulgite colloids. In this method, a suitable amount of attapulgite powder is mixed with a solvent to form an attapulgite sol. Then, under appropriate temperature and humidity conditions, the attapulgite particles in the sol undergo a gelation process to form a colloidal gel. Finally, the attapulgite colloids are obtained through drying or heat treatment. The sol-gel method offers advantages in preparing high-purity and uniformly dispersed colloidal particles, controlling the morphology and size of the colloidal particles, and fabricating colloidal materials with special structures and properties [16-19]. However, the method has some drawbacks, including its complexity, the need for strict control of temperature, humidity, and reaction time, as well as the relatively long preparation period and waiting time. Therefore, it is suitable for preparing high-purity and uniformly dispersed colloidal particles and fabricating colloidal materials with special structures and properties.

2.2.2. Co-precipitation Method

The co-precipitation method is a technique for precipitating attapulgite colloids from a solution. This method typically involves using two or more solutions containing attapulgite ions. By adjusting the pH, temperature, and concentration of the solutions, attapulgite ions undergo co-precipitation reactions. During the co-precipitation process, attapulgite ions gradually form colloidal particles and precipitate from the solution. Finally, the attapulgite colloids are separated from the solution through centrifugation, filtration, or sedimentation methods. The co-precipitation method offers advantages such as relative simplicity and convenience in the preparation process. The morphology and size of the colloidal particles can be controlled by adjusting the pH, temperature, and concentration of the solution [20-23]. Additionally, it allows for the preparation of large quantities of colloidal particles. However, the co-precipitation method may result in impurities in the product and poor dispersion of the colloidal particles, leading to aggregation. It is suitable for situations where large quantities of colloidal particles need to be prepared quickly.

In addition to the sol-gel method and co-precipitation method, there are other methods for preparing attapulgite colloids, such as hydrothermal method [24] and ion exchange method [25]. The choice of method depends on factors such as the research objectives, experimental conditions, and desired colloidal properties.

2.3. Effects of Preparation Conditions on Attapulgite Colloid Properties

1) pH Value

Li et al. [26] investigated the influence of pH and the addition of electrolytes on the stability of attapulgite clay colloids. The study revealed that attapulgite colloids were

stable without interference, but changing the pH or adding electrolytes would reduce their stability. Qiaohui Fan et al. [27] found that the adsorption of attapulgite clay was mainly controlled by ion exchange or outer-sphere complexation under low-pH conditions, while it was mainly controlled by inner-sphere surface complexation under high-pH conditions. The charge state of the attapulgite clay surface changes at different pH values, thereby affecting the stability and dispersion of the colloidal particles. Higher pH values typically result in colloidal particles carrying a negative charge, making them more easily stable and dispersed.

2) Temperature

Li Wang et al. [28] discovered that increasing temperature could induce an expansion effect in the internal structure of attapulgite adsorbents. Lei Chen et al. [29] demonstrated that with rising temperature, the adsorption capacity of attapulgite as an adsorbent increased. Therefore, the temperature during the preparation process can influence the size and morphology of attapulgite colloidal particles. Higher temperatures contribute to an increased reaction rate and particle growth rate, resulting in larger-sized colloidal particles. Additionally, temperature can affect the thermodynamic stability of colloidal particles, with higher temperatures making colloidal particles more prone to aggregation.

3) Concentration and Reaction Time

Shi et al. [30] conducted a study on improving the specific surface area of attapulgite clay using different chemical reagents and varying heating times. The results showed that under the conditions of 5% sulfuric-phosphoric mixed acid and a certain heating time, the specific surface area of attapulgite clay increased from the original 140 m²/g to 400 m²/g. Therefore, the concentration of attapulgite clay in the solution can affect the size and morphology of colloidal particles. Higher concentrations usually result in larger-sized colloidal particles, while lower concentrations may lead to smaller colloidal particles. Additionally, concentration can also influence the dispersion and stability of colloidal particles. Longer reaction times generally lead to an increase in the size and morphological changes of colloidal particles, as a sufficiently long reaction time allows for more reactions to occur and colloidal particle growth to take place.

2.4. Improvement of Attapulgite Colloid Properties

2.4.1. Enhancement of Adsorption Performance

Modifying the structure, chemical composition, and surface properties of attapulgite colloids can significantly impact their adsorption performance. For example, increasing the colloid's pore structure and pore size distribution can enhance the adsorption surface area and pore volume, thereby increasing the adsorption capacity. Zou et al. [31] modified natural attapulgite clay through acid activation, heat treatment, and organic modification, determining the optimal modification methods and conditions. The modified attapulgite clay exhibited excellent performance in water treatment processes. Qu et al. [32] achieved the efficient adsorption of phosphates by co-modifying attapulgite clay with lanthanum and iron through electrostatic interaction, surface precipitation, and ligand exchange. This modified material, known as MT-LHMT, exhibited outstanding adsorption performance over a wide pH range. Wang et al. [33] improved the adsorption and removal performance of attapulgite clay (ATP) for phenol by synthesizing a cationic

surfactant with dual cationic active centers (Gemini) and composite modification with cetyltrimethylammonium bromide (CTAB).

2.4.2. Stability Improvement

The stability of attapulgite colloids is a crucial factor in their practical applications. By controlling the colloid's structure and surface properties, their stability under different environmental conditions can be enhanced. Du et al. [34] demonstrated that attapulgite clay colloids exhibit good stability and can adsorb uranium (VI), thus slowing down its migration. Ma et al. [35] successfully synthesized well-dispersed Ag_3PO_4 nanoparticles (with a particle size of 5 nm) on the surface of attapulgite clay (ATP) and applied them in the photocatalytic removal of Orange II pollutants from water, improving the photocatalytic activity and stability. Zhang et al. [36] prepared nanoparticles through surface modification of attapulgite clay minerals and applied them in the preparation of stable Pickering emulsions. The research findings showed that increasing the mass fraction of nanoparticles can enhance the stability of the emulsion, while increasing the pH value and volume fraction of the oil phase can lead to an increase in the droplet size of the emulsion.

Modifying the interlayer ion exchange capacity and interlayer structure of colloids can improve their stability under extreme conditions such as high temperature and pH. Additionally, synthesizing nanoscale attapulgite colloid and controlling its particle size and morphology can enhance its dispersibility and stability. These improvement methods can enhance the stability of attapulgite colloids, prolonging their lifespan and effectiveness in practical applications.

2.4.3. Functionalization Improvement

Composite or modified attapulgite colloids with other functional materials can impart additional functionalities and application characteristics. Aiping Hui et al. [37] stabilized emulsions using modified attapulgite particles with *Fructus mume* extract, achieving enhanced antibacterial activity and storage stability. The functional Pickering emulsion demonstrated significant inhibition effects against multiple drug-resistant bacteria, showcasing its potential in the field of antibacterial applications. Liu et al. [38] successfully prepared attapulgite nanoparticles (ATP NPs) coatings on silk fabrics using hyperbranched polymers as additives via an impregnation method. The treated silk fabric exhibited excellent antibacterial and UV resistance properties, meeting the requirements of multifunctional products. Ma et al. [39] grafted magnetic Fe_3O_4 nanoparticles onto attapulgite nanomaterials and modified them with polyethyleneimine (PEI), resulting in functionalized magnetic attapulgite composite (ATP- Fe_3O_4 -PEI). This composite efficiently removed Congo Red (CR) dye molecules from dye wastewater and demonstrated good recyclability, maintaining a removal rate and capacity of over 82% and 799 $\text{mg}\cdot\text{g}^{-1}$, respectively, even after four cycles. Antosik et al. [40] functionalized attapulgite by grafting 3-mercaptopropyltrimethoxysilane (MPTMS) onto its surface, successfully applying it for the modification of heat-resistant organosilicone pressure-sensitive adhesives. The functional filler improved the compatibility between attapulgite and specific resins, resulting in a novel self-adhesive material that exhibited both excellent self-adhesive properties and higher heat resistance.

2.5. Future Research Directions and Development Trends

Future research directions and development trends in the field of attapulgite colloids can be explored in the following aspects:

2.5.1. Nanoscale Attapulgite Colloids

With the rapid development of nanotechnology, the synthesis of nanoscale attapulgite colloids has become a research hotspot. As a natural nanomaterial, attapulgite clay possesses unique structures and properties, thus offering a wide range of potential applications [41]. Controlling the particle size, morphology, and structure of nanoscale attapulgite colloids can allow for the modulation of their performance and applications [42]. Duan et al. [43] demonstrated the advantages of nanoscale attapulgite clay in enhancing the electrochemiluminescence (ECL) sensitivity of immobilized $[\text{Ru}(\text{bpy})_3]^{2+}$, providing a better approach for practical ECL determination. Liu et al. [44] fabricated castor silk using attapulgite colloid nanoparticles with rod-shaped ATP particles and a particle size of 100 nm. The silk exhibited excellent antibacterial properties, with inhibition rates of 88.9% and 84.3% against *Staphylococcus aureus* and *Escherichia coli*, respectively. Chae et al. [45] used nanofiber-like clay mineral attapulgite as an additive to improve the sedimentation issue caused by density mismatch in soft magnetic carbonyl iron-based magnetorheological fluids and enhance their dispersion stability. Although the magnetorheological properties slightly decreased, the materials still exhibited typical magnetorheological behavior under applied magnetic fields. Liao et al. [46] prepared magnetic attapulgite composite nanoparticles (ATP- Fe_3O_4 -APTES) with excellent adsorption performance for heavy metal ion wastewater treatment by grafting Fe_3O_4 nanoparticles and 3-aminopropyltriethoxysilane (APTES).

2.5.2. Surface Modification and Functionalization

Surface modification and functionalization can alter the surface properties and intermolecular forces of attapulgite colloids, thereby enhancing their adsorption performance, stability, and functionality. Future research can focus on new surface modification and functionalization methods to achieve more efficient, controllable, and sustainable improvements. Shi et al. [47] found that different calcination temperatures significantly affected the appearance, mineral composition, and active SiO_2 content of attapulgite, which further influenced the chemical water content, cement slurry reactivity, and mechanical properties of attapulgite-cement mortar. Liu et al. [48] successfully developed a surface modification technique using nanoscale attapulgite colloid particles to functionalize cotton fabrics, resulting in multifunctional cotton textiles. The treated fabrics exhibited improved morphology, microstructure, thermal stability, UV resistance, antibacterial properties, and breathability. This treatment method not only enhanced the performance of cotton textiles but also met the market demand for natural products. Attapulgite's surface was changed by Shi et al. [49] using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KH792), and three phase change materials (PCMs) were combined with the modified attapulgite to create shape-stable composite phase change materials (FSCPCM). The findings demonstrated that surface modification increased by 31.5% and 27.8%, respectively, the crystallinity and latent heat of paraffin/attapulgite and polyethylene glycol/attapulgite FSCPCM. After 800 cycles, the improved FSCPCM

maintained constant thermal performance. Shi et al. [50] synthesized a novel fast-swelling porous guar gum-g-poly(acrylic acid sodium-styrene copolymer)/attapulgite superabsorbent hydrogel through a free radical graft copolymerization reaction in an aqueous solution. The surfactant was successfully removed by methanol/water washing, and a porous structure was formed. Castor oil-based quaternary ammonium salt surfactants (COQA) were created by Yan et al. [51] by employing refined castor oil (CO) in ester exchange and quaternization reactions. The surface of the attapulgite was then mixed with COQA to alter ATP. Although the crystal structure of the silicate remained constant, the presence of COQA, which was bound to the surface of rod-shaped crystals, was primarily blamed for the morphological changes of the modified ATP (M-ATP). The microstructure of M-ATP was looser than that of pure ATP.

2.5.3. Environmental Remediation and Water Treatment Applications

Attapulgite colloids have significant potential for applications in environmental remediation and water treatment. Future research can focus on the application of attapulgite colloids in the adsorption and removal of pollutants such as heavy metals, organic contaminants, and microplastics [52]. Additionally, exploring the composite and modification of attapulgite colloids with other materials can enhance their application effectiveness and economic feasibility in water treatment [53]. Abdulkareem et al. [54] demonstrated that brown attapulgite-silver nanoparticle composites containing silver nanoparticles with sizes ranging from 27–44 nm and attapulgite effectively inhibited bacterial growth when applied in feldspar latex paint. Zhang et al. [55] found that the presence of attapulgite provided an effective strategy for long-term corrosion protection of magnesium alloys. By combining attapulgite with shape memory polymers (SMP) to form a bilayer self-healing superamphiphobic coating, the coating exhibited excellent superamphiphobicity, initial corrosion resistance, self-healing capability, and superhydrophobicity. Yan et al. [56] synthesized castor oil-based quaternary ammonium salts and used them as modifiers for attapulgite. They investigated the effects of modifier dosage, temperature, pH, and other factors on the removal efficiency of acetone and phenol in wastewater through batch experiments. Under suitable conditions, the modified attapulgite achieved maximum removal rates of 65.71% for acetone and 78.72% for phenol. Chen et al. [57] successfully synthesized a novel attapulgite clay@carbon (ATP@C) nanocomposite adsorbent through a one-pot hydrothermal carbonization process using attapulgite clay (ATP) and magnesium aluminum silicate as inexpensive and environmentally friendly materials. The nanocomposite exhibited high adsorption capacity for Cr(VI) and Pb(II) ions in water, with maximum adsorption capacities of 177.74 and 263.83 mg·g⁻¹, respectively. The study demonstrated that the ATP@C nanocomposite can serve as a low-cost, sustainable, and efficient adsorbent for the removal of toxic ions from water. This research provides a promising approach to address water pollution and promotes the development and utilization of green chemicals.

2.5.4. Sustainable Development and Resource Utilization

Attapulgite is an abundant natural mineral resource, and its sustainable development and utilization are of great significance. Future research can focus on resource assessment, development and utilization, and environmental impact of attapulgite. Wang et al. [58] prepared a floatable

porous foam adsorbent using attapulgite and sodium alginate (SA) through freeze-drying and post-crosslinking methods. The adsorbent exhibited significant adsorption performance, strong chemical stability, and easy recyclability due to its floatability in aqueous solutions. Wang et al. [59] synthesized Ag nanoparticle/attapulgite (Ag-NPs/APT) nanocomposites through solvent-free reaction in situ, which efficiently catalyzed the reduction and decolorization of Congo Red (CR) dye. Ag nanoparticles with different sizes and loading amounts were generated in situ through thermal decomposition of silver acetate and uniformly immobilized on attapulgite. In the presence of NaBH₄, the nanocomposite showed excellent catalytic activity and rapidly decolorized CR solution at low dosages. The efficient reduction of CR dye was achieved through Ag nanoparticle-mediated electron transfer. After multiple cycles, the nanocomposite retained good catalytic activity, making it suitable for repeated use in catalytic reactions. Wang et al. [60] designed recyclable attapulgite composite materials by incorporating magnetic adsorbents, millimeter-scale adsorbents, and filtration membranes/nets. They demonstrated the synthesis, application, and mechanism of the recyclable ATP nanocomposites, improving the separation and recovery capabilities of ATP to achieve maximal resource utilization and minimal environmental impact.

In summary, future research directions and trends mainly include the synthesis and application of nanoscale attapulgite colloids, surface modification and functionalization, environmental remediation and water treatment applications, and sustainable development and resource utilization. Through research in these areas, the application scope and performance optimization of attapulgite colloids can be further expanded, contributing to environmental protection and sustainable development.

3. Conclusion

Attapulgite colloids possess characteristics such as high specific surface area, excellent adsorption performance, high temperature stability, and tunable morphology and structure. These properties make them highly valuable in various fields, including environmental remediation and water treatment, catalysis, functional materials, and sustainable development. As an adsorbent, attapulgite can effectively remove pollutants such as heavy metal ions, organic contaminants, and microplastics from water. As a catalyst support or catalyst itself, it can be applied in catalytic reactions such as organic synthesis and energy conversion. Through surface modification and functionalization, attapulgite can also possess specific functionalities such as photocatalysis, drug delivery, and biomedical applications. Furthermore, attapulgite, as an abundant natural mineral resource, holds significant importance for sustainable development through resource assessment, development and utilization, and consideration of environmental impacts. Thus, attapulgite colloids provide new solutions for addressing environmental issues and promoting sustainable development. Future research can focus on the following aspects:

- 1) While attapulgite colloids have achieved certain results in pollutant adsorption, there are still challenges to be addressed, such as improving adsorption capacity and selectivity. Future research can explore methods like surface modification, composite material design, and structure control to further enhance the adsorption performance of attapulgite colloids.

2) The application of attapulgite colloids is currently concentrated in the fields of environmental remediation and water treatment, catalysis, and functional materials. Future research can expand the application scope of attapulgite colloids to areas such as energy storage and conversion, pharmaceuticals, and soil remediation to meet the needs of different fields.

3) The adsorption and catalytic mechanisms of attapulgite colloids are not yet fully understood. Future research can employ a combination of experimental and theoretical simulation methods to explore the adsorption and catalytic mechanisms of attapulgite colloids, revealing their modes of action and influencing factors, and providing theoretical guidance for further optimization and design of attapulgite colloids.

4) Attapulgite is an abundant natural mineral resource, and its sustainable development and utilization are of great significance. Future research can explore sustainable attapulgite resource utilization methods, such as green synthesis approaches, waste reuse, and recycling, to reduce environmental impacts and achieve effective resource utilization.

In conclusion, future research can focus on improving adsorption performance, expanding application fields, exploring mechanisms, and developing sustainable resource utilization of attapulgite colloids. These studies will contribute to the further development and application of attapulgite colloids and provide new solutions for addressing environmental issues and promoting sustainable development.

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