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# Application of Colloidal Chemistry and Polymer Chemistry in Papermaking Industry

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**Abstract:** Colloidal chemistry is a science to study the physicochemical properties of generalized colloidal dispersion systems. Polymer chemistry is a new comprehensive subject that studies the synthesis, chemical reaction, physical chemistry, physics, processing and application of polymer compounds. The development of polymer chemistry mainly experienced four periods: the utilization and processing of natural polymers, the modification of natural polymers, the production of synthetic polymers and the establishment of polymer science. Since the 1930s, with the development of synthetic polymers, polymer related sub disciplines such as reaction kinetics, chemical thermodynamics, structural chemistry, polymer physics and biopolymers have been gradually established, forming a systematic polymer science. Papermaking industry is an industrial sector that manufactures all kinds of paper and paperboard. It includes the pulp manufacturing industry that uses wood, reed, bagasse, straw, wheat straw, cotton straw, hemp stalk, cotton and other raw materials to manufacture pulp, the paper and paperboard industry, and the processing paper manufacturing industry that produces coated, polished, glued, laminated and other processing paper and font paper plate. Paper industry is an important industry closely related to the development of national economy and the construction of social civilization. This paper focuses on the relationship between colloidal chemistry, polymer chemistry and papermaking industry, especially its application in cooking, washing, bleaching, papermaking and water treatment, and introduces in detail the current situation and development trend of flocculation method for papermaking wastewater according to colloidal chemistry theory.

**Keywords:** Colloidal Chemistry, Polymer Chemistry, Theory, Application, Flocculation

## 1. Introduction

Colloidal chemistry is a science to study the physicochemical properties of generalized colloidal dispersion systems. In 1861, Thomas Graham put forward the term "colloid", which marked the emergence of colloidal chemistry. In 1864, British scientist Graham carried out a large number of experiments on colloids and made pioneering research in many aspects, leading to the establishment of a systematic discipline - colloidal chemistry. But it was not until 1907 that the Russian scientist fayman gave a precise definition to the concept of colloid. He proposed that colloid is a dispersed state in which the particle size is between 1 and 100 nm. Nowadays, the application of colloidal chemistry has penetrated into many fields, such as papermaking, food processing, fine chemical industry and so on [1-3].

As a branch of chemistry, polymer chemistry is a relatively young discipline established in the 1930s. However, the use of natural polymers has a long history. As early as ancient times, people's life had been closely related to natural polymers. Polymers support all aspects of people's food, clothing and shelter. Protein and starch as human food, as well as cotton, wool and silk woven into clothes are natural polymer materials. In ancient China, people learned to use silk to spin silk; In the Han Dynasty, people used natural polymer hemp fiber and bamboo fiber to invent papermaking, which had a great impact on world civilization. At that time, the Chinese had learned to use paint, which was later spread to neighboring countries and even the world. It can be said that ancient China was a world leader in the processing technology of natural polymers, such as silk weaving, papermaking and paint manufacturing. The development of polymer chemistry mainly experienced four periods: the utilization and processing of natural polymers, the modification of natural polymers, the production of synthetic polymers and the establishment of polymer science. Since the 1930s, with the development of synthetic polymers, polymer related sub disciplines such as reaction kinetics, chemical thermodynamics, structural chemistry, polymer physics and biopolymers have been gradually established, forming a systematic polymer science [4-6].

This paper focuses on the relationship between colloidal chemistry, polymer chemistry and papermaking industry, especially its application in cooking, washing, bleaching, papermaking and water treatment.

## 2. Application of Colloidal Chemistry Theory in Paper Cooking Process

From the point of view of colloidal chemistry, pulping process is the process of dispersing large pieces of plant raw materials into cellulose dispersion. In the cooking process, the effective components of the cooking liquid should fully enter the interior of the raw materials. In the process of infiltration, there are two functions: one is capillary action, which mainly depends on the pressure difference through the catheter or tracheid (or fiber) cavity. Capillary permeability is directly proportional to the fourth power of capillary radius, directly proportional to pressure difference and inversely proportional to the viscosity of cooking solution. When the moisture content of fiber raw material is low, the infiltration is accelerated after removing the air in the raw material capillary. The test shows that the capillary permeability along the longitudinal direction is much greater than that in the transverse direction. The second is diffusion, which makes the ions in the cooking liquid diffuse and immerse into the raw material by concentration difference. When the moisture content of fiber raw material reaches the fiber saturation point (i.e. the capillary is completely filled with water), the process of ion infiltration into the center of raw material mainly depends on diffusion. The diffusion depends on the effective capillary cross-sectional area. The test shows that in alkali cooking, the internal swelling of wood occurs, and the diffusion of alkali liquor in the longitudinal and transverse directions is almost the same, so the penetration rate is similar [7].

## 3. Application of Colloidal Chemistry Theory in Washing Process

From the point of view of colloidal chemistry, the composition of pulp and waste liquid is a liquid heterogeneous system. Because the density difference between aqueous pulp and black liquor is small, filtration is often used for separation. Filtration uses the slurry layer with many capillary channels as the medium to separate the washing liquid from the suspended solid fiber under the promotion of the pressure difference on both sides of the slurry layer. The diffusion process is the transfer process of matter. Diffusion washing of pulp is to use the difference that the concentration of residual waste liquid in pulp is greater than that of washing liquid to make the solute molecules in waste liquid inside and outside the fiber wall automatically move to water, and the water molecules also move to the fiber for replacement, which is molecular diffusion [8].

## 4. Application of Colloidal Chemistry Theory in Bleaching Process

From the point of view of colloidal chemistry, bleaching process is a process in which bleach ions remove lignin or destroy the chromophore through chemical action. Modern bleaching is multi-stage bleaching, each stage uses different chemicals and technical conditions, and there is generally inter stage washing between each stage. Chlorination (c): react with elemental chlorine in acidic medium. Alkali treatment (E): dissolve the products that react with caustic soda (NaOH). Chlorine dioxide (d): react with chlorine dioxide ($ClO_2$) in acidic medium. Oxidation (o): reacts with molecular oxygen in alkaline medium under high pressure. Hypochlorite (H): reacts with hypochlorite in alkaline medium. Hydrogen peroxide: reacts with hydrogen peroxide in alkaline medium. Ozone (z): reacts with ozone in acidic medium. In the early stage of bleaching process, the lignin of pulp is mainly removed. This bleaching process can be used as the continuation of cooking delignification process. Generally speaking, the obvious whitening effect only occurs in the removal of residues.

## 5. Application of Colloidal Chemistry Theory in Papermaking Process

It is easy to understand papermaking chemistry from the perspective of colloidal systems. For example, most colloidal systems can be divided into hydrophobic and lipophilic systems. The following are the main characteristics of these two systems. Characteristics of the liquid drainage system: (1) suspension non solution system of particles; (2) The attraction or affinity between solvent and particles is small; (3) System instability leads to aggregation; (4) There are particles and suspended media that strongly affect the behavior of the system at the interface. Characteristics of lipophilic system: (1) True solution of polymer or aggregation of small molecules; (2) Strong attraction between solvent and ion; (3) there is no real decomposition surface between the particle and the medium. If the dispersion medium is water, it can be called hydrophobic and hydrophilic colloidal system accordingly. Because the dispersion of papermaking system is generally carried out in aqueous medium, the dispersed colloidal system in papermaking system can also be called hydrophobic system and hydrophilic system [9-11].

Some typical colloidal systems in the wet end of papermaking are listed below. Hydrophobic colloidal system: (1) pigment dispersed in water; (2) Fine fibers dispersed in water; (3) Rosin colloidal particles dispersed in water; (4) Dispersed rosin sizing solution. Hydrophilic colloidal system: (1) water-soluble starch; (2) Water soluble colloidal particles; (3) Hemicellulose soluble in water; (4) Water soluble surfactant, dispersant and wetting agent; (5) Water soluble retention aids, filter aids and forming AIDS. Two kinds of hydrophilic colloids are very important. The first one is retention aid, filter aid, dry strength agent and wet strength agent, which will affect the behavior of hydrophilic substances. The second is associated compounds, such as wetting agent, surfactant, defoamer and dispersant.

In general paper-making systems, pigments and fines and water are humid and functional substances, but in fact, the surface of fines is usually covered with a layer of cellulose and hemicellulose gel. Even if the rosin particles react with water to a certain extent after dispersion, it is impossible to form a very stable colloidal dispersion system. Another view on this problem is that a single particle can also be wet and adsorb a certain amount of water on its surface, but it is still a dispersion system with hydrophobic characteristics [12].

The study of hydrophobic dispersion systems mainly discusses the speed when they return to the equilibrium aggregation state. All hydrophobic colloidal systems listed above will return to the aggregation state in the papermaking process. In actual production, paper workers hope to control the aggregation process of this colloid, so that various substances can be evenly distributed in the paper and retained in the paper to the greatest extent. If the aggregation process of this colloid system cannot be well controlled, the paper quality will be reduced and precipitation will occur. The stability of hydrophobic colloidal dispersion system is usually expressed by the ability to maintain dispersion and measured by the time it takes for colloidal particles to precipitate from the liquid. This phase separation may be due to the fact that the original dispersed particles become larger aggregates due to gravitational sedimentation. The main types of aggregation mechanisms of hydrophobic colloids include coagulation and flocculation. Coagulation: instability of colloidal suspension under the action of salt and polyelectrolyte with low molecular weight and high charge density; Flocculation: colloidal suspension is unstable through the combination of particles and long-chain polymers.

When solid particles are dispersed in water, electrostatic charges will accumulate at the solid-water interface. In the wet end system of papermaking, this charge may be generated by the adsorption of ionized carboxyl and sulfonate on the fiber surface and material molecules such as hemicellulose, dissolved lignin, retention aid and cationic starch on the surface. Mineral fillers such as porcelain clay and titanium dioxide will also generate charge through the ionization of water at the interface and the adsorption of other charged substances.

The electrokinetic phenomenon in papermaking process is a stable factor in wet end chemistry. Because cellulose is usually negatively charged, it is necessary to reduce their mutual repulsion in order to adsorb rosin gum and filler with the same negative charge on paper fibers. When the bauxite electrolyte is added, the pH value of the suspension decreases. When the zeta potential is close to zero by controlling the addition amount, the mutual repulsion force of particles becomes smaller, and the fine solid particles will gather on the fiber surface. From the point of view of charge, the suspended colloidal particles have the same sign charge, and the existence of interface charge will affect the distribution of ions in papermaking fiber suspension. There are ions with the same sign on the surface of colloidal particles, and counter ions are distributed around it. On the one hand, counter ions are attracted by the electricity of colloidal particles and tend to be close to colloidal particles, on the other hand, they tend to be far away from colloidal particles due to their own electric repulsion.

The stability of a hydrophobic suspension system can be measured by the time of maintaining the dispersion. The stability of the system depends on the relative size of repulsive force and attraction between suspended particles, as well as the possible collision between particles. There are many sources of attraction and repulsion, and there is always van der Waals attraction between particles with the same chemical composition; If the colloid has the same charge, electrostatic repulsion force will be generated due to the action of electric double layer. On the contrary, the charged electric double layer will produce attraction, so the stabilizing and unstable forces can be changed by the influence of adsorbed polyelectrolyte. Carboxyl groups (uronic acid) of cellulose and hemicellulose, acid groups contained in lignin and sulfonic acid groups from pulping process in paper are ionized in water to send some ions to water (called counter ions), and the batching component particles have charges opposite to the symbols of the sent ions. It can be seen that the surface of the particle has charges with the same symbol, and the counter ions are distributed around it. On the one hand, the counter ions tend to be close to the component particles due to the electrical attraction of the colloidal particles, on the other hand, they tend to be far away from the component particles due to their own electrical repulsion [13].

DLVO theory holds that the electrical repulsion force between colloidal particles is due to the change of potential distribution caused by the overlap of electric double layers when two colloidal particles are close to each other to a certain extent. The attraction between colloidal particle surface and counter ion belongs to van der Waals force, which is also rooted in electrical action, including electrostatic attraction between polar molecules with permanent dipole moment. There are three types of electrostatic attraction between polar molecules with permanent dipole moment and the attraction between non-polar molecules (also known as dispersion force). Their common feature is that the attraction potential energy is inversely proportional to the sixth power of distance. It can be seen from the above that the best particle charge value during papermaking can be found in the paper batching system, and then controlled from the additives.

The aggregation of colloidal particles is the main cause of colloidal instability. The aggregation of colloidal particles can be divided into two types: one is aggregation and the other is flocculation. Coagulation refers to that many fine solid particles in the wet end of papermaking form cluster and string aggregates. In this aggregation, the fine solid particles still maintain their individual identity, but lose their independence in dynamic properties. The whole condensate is used as a moving unit. Because they are not fused into new fine solid large particles, their specific surface area does not decrease. Although the surfaces of fine solid particles will be connected together at the contact, the binding between fine particles in the condensate is weak, so the coagulation process is reversible, and it can be redispersified by adding glue solvent. The other is flocculation, which means that two or more fine solid particles are aggregated and fused into a new large fine particle, accompanied by the reduction of specific surface area. At this time, the specific surface free energy of the system is significantly reduced, For example, when the polyelectrolyte with long chain molecule is adsorbed on the surface of fiber or fine solid particles, the flocculent polymerization between fine solid particles and fiber is realized through bridging and inlaying mechanisms. The resulting floc polymer can withstand high water shear force, that is, the binding is strong, and the floc polymerization process is irreversible.

# 6. Application of Polymer Chemistry in Wastewater Treatment

Waste liquid is mainly composed of organic matter and inorganic matter, in which organic matter is the main energy to produce calorific value. According to different pulping raw materials and production process conditions, the proportion of organic matter and inorganic matter in the solid matter of waste liquid is also different. Generally, the organic matter of black liquor accounts for about 65% ~ 70%, the inorganic matter accounts for 30% ~ 35%, the organic matter of red liquor accounts for about 85% ~ 90%, and the inorganic matter accounts for 10% ~ 15% (all mass fractions). Due to the existence of various colloidal substances in black liquor, it has colloidal properties under certain conditions. When the effective alkali content in black liquor accounts for 1.5% of the solid Over 14%, alkali lignin was completely dissolved in black liquor and existed as hydrocolloid without precipitation; But when the effective alkali content is lower than 0.5% At 71%, the stability of alkali lignin colloid is greatly reduced and it is easy to precipitate from black liquor. In the evaporation process, with the increase of black liquor concentration, some alkali lignin colloids are damaged and local precipitation will occur due to water loss and salting out. Therefore, more saponification can be separated from semi concentrated black liquor.

Due to the variety of papermaking raw materials, high content of impurities, and some paper is recycled for many times, the composition of papermaking wastewater is very complex and difficult to purify. In the process of waste paper treatment, through unit operations such as deinking, screening and washing, a large number of fine fibers and other fine solid particles are produced. These suspended solids cause high turbidity and chroma in the wastewater. At the same time, because the wastewater contains a large number of fine fibers, resins, pigments and other chemical and physical impurities, it has a large pollution load of COD, BOD and chromaticity, which is difficult to be directly biodegradable. Using chemical coagulation sedimentation method, that is, using appropriate flocculant to treat wastewater, the fine fibers and other fine solid particles can be precipitated. After proper treatment, the precipitated mud can be used as box board pulp, and the water can be recycled as industrial water. Therefore, the key to papermaking wastewater treatment is to select efficient, economic and reasonable flocculant [14].

Because polymer flocculant has the advantages of good flocculation effect, decolorization ability and simple operation, people generally give priority to the use of polymer flocculant. Polymer flocculants can be divided into synthetic inorganic polymer flocculants, organic polymer flocculants and natural organic polymer flocculants.

The application of inorganic flocculant has a long history, but inorganic polymer flocculant was developed in the late 1960s. The varieties of inorganic polymer flocculants have gradually formed a series in China. Cationic types include polyaluminium chloride (PAC), polyaluminium sulfate (PAS), polyferric phosphate (PFP), polyferric sulfate (PFS), polyferric chloride (PFC), etc. Anionic types include activated silicic acid (as) and polymeric silicic acid (PS). Inorganic composite types include poly aluminum ferric chloride (PAFC), poly ferric silicate sulfate (PFSS), poly ferric silicate chloride (PFSC), poly aluminum ferric silicate (pf2si), poly aluminum phosphate (ppafp), silicon calcium composite poly ferric chloride (scpafc), etc. Because the pulp is negatively charged, cationic polymer flocculant is generally selected, which plays the dual role of neutralizing charge and flocculation bridging, and the precipitation effect is good. At present, polyaluminium chloride (PAC) is commonly used as flocculant to remove suspended solids and colloidal particles from pulp. Its advantage is that it can remove turbidity and color at the same time, and the dosage is only 1p4-1p2 of aluminum sulfate. The flocculation effect changes little when the water temperature decreases. Its disadvantage is that it is easy to generate fine alum, difficult to separate solid and liquid, and low pulp recovery efficiency. According to the research report, aluminum salt flocculant has certain toxicity. If the aluminum content in water is higher than 015mgpl, salmon will die, it will also have toxic and side effects on plants and microorganisms, and it is easy to cause Alzheimer's disease to people. Researchers are studying a new high-efficiency inorganic polymer flocculant to replace polyaluminium chloride (PAC).

Compared with inorganic polymer flocculant, organic polymer has the advantages of less dosage, fast flocculation speed, less influence by coexisting salt, pH value and temperature, less amount of sludge and easy treatment, so it has broad application prospects. Polyacrylamide (PAM) is the most widely used organic polymer flocculant. It has three types: non-ionic, cationic and anionic. Polyacrylamide (PAM) with high molecular weight (above 106) is an anionic flocculant with strong flocculation and non-toxic. It produces non-ionic adsorption on fine particles suspended in water, resulting in cross-linking between particles. Polydimethylpropylene ammonium chloride (pdadma) and dimethylpropylene ammonium chloride acrylamide copolymer (dmdaac-am) are cationic polymer compounds. When used in water treatment, they can obtain better results than the commonly used inorganic polymer flocculants and organic polymer flocculants. They can be used alone or together with inorganic flocculants. The copolymer of dimethyl diallyl ammonium chloride (DMDAAC) and vinyl trimethoxysilane can be used to flocculate the lignin of paper mill pulp, remove the ink in the wastewater, remove turbidity and decolorize the papermaking wastewater. According to the U.S. patent report, polydimethylpropylene ammonium chloride (DMDAAC) with molecular weight greater than 2000 (preferably close to 100000) is mixed with inorganic coagulant such as $AlCl_3$ in the ratio of 95:5 ~ 50:50 to treat low turbidity water, which can overcome the treatment of 20% by organic flocculant × 10 - 6 (or lower) low turbidity water has the disadvantage of poor effect, and can solve the problems of large dosage of inorganic flocculant, large and fine sludge and difficult to treat. Polydimethylpropylene ammonium chloride (DMDAAC) is widely used in papermaking industry abroad. Through the adsorption between polydimethylpropylene ammonium chloride (DMDAAC) and negatively charged pulp, the purpose of purifying water quality for recycling and reuse, retaining filler and improving the strength of paper can be achieved, and the antistatic performance of paper can also be improved. Inorganic polymer flocculant polyaluminium chloride (PAC) and organic polymer flocculant cationic polyacrylamide (CPAM) were used to treat waste paper regeneration wastewater. The COD removal rate was more than 75% and the light transmittance was 92% - 99% [15].

Natural polymer flocculants can be divided into carbohydrates, xanthate lipids, chitosan and chitin. Among many modified polymer flocculants, the research and development of starch modified flocculant is particularly attractive. The research, development and application of graft copolymerization of various starch with acrylamide, acrylate and acrylonitrile have been widely carried out in China. The cost price of cationic flocculant prepared with starch acrylamide copolymer is lower than cationic polyacrylamide (CPAM), the dosage is also lower than cationic polyacrylamide (CPAM) and polyacrylamide (PAM), and the biodegradability is improved. Its efficiency in sewage treatment and sludge dewatering is obviously better than that of domestic cationic polyacrylamide (CPAM) and non-ionic polyacrylamide (PAM). Microbial flocculant is a kind of macromolecular organic matter produced by microorganisms with flocculation ability, mainly including glycoprotein, mucopolysaccharide, cellulose and nucleic acid. It is a natural high molecular flocculant made of biotechnology, microbial fermentation, extraction and refining. It can be widely used in the purification of pulp wastewater, brick factory wastewater and dye wastewater. At present, the commonly used flocculants are difficult to remove the colored substances in the wastewater. As long as 2ml of 2% alcaligenues - latus culture and 115ml of polyglucosamine are added to 80ml papermaking wastewater, the visible flocs can be formed and float on the water surface, the decolorization rate can reach 9416%, and the light transmittance of the lower clean water is almost the same as that of tap water. The flocculation activity of microbial flocculant is affected by many factors such as molecular structure, molecular weight and active group. At present, the main problem of microbial flocculant research is to find out the appropriate flocculating microorganisms and their culture medium, so as to shorten the culture cycle and improve the flocculation activity as much as possible. The advantages of microbial flocculant are very prominent, mainly as follows: less precipitation and easy solid-liquid separation; Easy to be decomposed by microorganisms, non-toxic and harmless; No secondary pollution; Wide application range; It has turbidity removal and decolorization properties. Therefore, microbial flocculant is the development direction in the future, and will eventually replace most or all of the common flocculants.

# 7. Conclusion

Colloidal chemistry is a frontier subject which is widely used. Its application in paper industry has attracted more and more attention of paper workers. Using colloidal chemistry theory to understand and analyze the cooking, washing, bleaching, papermaking and waste liquid treatment process in pulping and papermaking is a new subject. Some existing problems in pulping and papermaking can be well solved from the perspective of colloidal chemistry. Taking the treatment of papermaking wastewater by flocculation as an example, there has been industrial production of microbial flocculant in Japan. At present, China is still limited to experimental research, and its application in papermaking wastewater treatment is almost blank. In order to find efficient, non-toxic, economic and safe flocculants for papermaking wastewater treatment, we should develop, cultivate and utilize microbial flocculants as soon as possible.

# 8. Future Development of Papermaking Industry

While developing output, China's paper industry pays more attention to the improvement of quality. Now we are constantly adjusting the industrial structure, eliminating small equipment with small scale, high pollution and high energy consumption, and actively investing in new paper machines with high speed and wide width. With rapid technological progress, circular, low-carbon and green economy has become a new development theme. The development of the industry is increasingly globalized, the logistics and transportation capacity is increasingly improved, and the transportation cost is greatly reduced. The transportation cost of trans ocean transportation from coastal factories to overseas customers can even be lower than that of inland freight transportation to domestic customers, and globalization is strengthened. Overseas investment is becoming more and more common. With the increasing globalization of the paper industry and the lack of waste paper resources in China's forestry, the establishment of overseas factories is conducive to enterprises to improve the layout of the industrial chain and enhance the competitiveness of the global market.

# Conflicts of Interest

The author declares that he has no competing interest.

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