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Review

Use of flocculants for wastewater treatment

Elena V. Ulrich*, Anna S. Barkova

Kaliningrad State Technical University, Sovetsky pr. 1, Kaliningrad, 236022 Russia

**elen.ulrich@mail.ru*

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Abstract. Polymeric flocculants are used to accelerate the separation of solid and liquid phases in the treatment of drinking water and wastewater. Recently, much attention has been paid to flocculants, both synthetic and biobased, due to their advantages for wastewater treatment processes. Flocculants have many advantages such as biodegradability, non-toxicity, the ability to undergo various chemical modifications, and wide availability from renewable sources. This article provides a review of synthetic and biobased flocculants and lists their potential applications in water treatment. Based on the up-to-date data, a new approach is proposed for searching for modified and grafted flocculants, flocculation mechanisms, test methods, and factors influencing this process. Particular attention is paid to flocculants based on chitosan and its derivatives, since they are cheap and environmentally friendly materials used in industrial practice.

Keywords: polymers, chitosan, flocculation, bridging, neutralization, environment

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Научный обзор

Использование флокулянтов для очистки сточных вод

Е.В. Ульрих*, А.С. Баркова

Калининградский государственный технический университет, 236022, Россия, г. Калининград, Советский пр-т, д. 1

elen.ulrich@mail.ru

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Аннотация. Полимерные флокулянты используются для ускорения процессов разделения твердой и жидкой фаз при очистке питьевой воды и сточных вод. В последнее время большое внимание уделяется флокулянтам как на синтетической, так и на биологической основе. Флокулянты обладают рядом преимуществ: биоразлагаемостью, нетоксичностью, способностью подвергаться различным химическим модификациям и широкой доступностью (в том числе флокулянтов, полученных из возобновляемых источников). В статье представлен обзор флокулянтов на синтетической и биологической основах, а также их потенциального применения при очистке воды. Основываясь на сведениях, отраженных в новейшей литературе, описан новационный подход к поиску модифицированных и привитых флокулянтов, механизмов флокуляции, методов испытаний, установлены факторы, влияющие на протекание этого процесса. Особое внимание уделено флокулянтам на основе хитозана и его производных, поскольку они являются дешевыми и экологичными материалами, используемыми в промышленной практике.

Ключевые слова: полимеры, хитозан, флокуляция, мостикообразование, нейтрализация, окружающая среда

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Introduction

Human activities and global industrialization are increasingly affecting the natural environment, resulting in increasing pollution of natural water sources. Both groundwater and surface water may be contaminated with suspended solids, colloidal particles, and dissolved substances. Wastewater discharged from industrial enterprises is a particular danger to the environment because it contains a wide range of pollutants (sand, clay, silt, sludge, suspended solids, radioactive elements, acids and alkalis, oil and oil products, salts and phenols, dioxides and pesticides, heavy metals, ammonium and nitrite nitrogen, surfactants, various oils, etc.). These substances are toxic to aquatic organisms and wild animals, they affect human health adversely as well. When used indoors, contaminants may cause visual, skin and lung disorders, as well as migraines and nausea. In addition, they may cause breathing problems and malfunction of the kidneys and liver (Qi et al., 2020). Wastewater must go through several stages of treatment before being reused (Shaikh et al., 2018); however, the first step in this process is the removal of suspended and colloidal contaminants.

Wastewater treatment from large particles may be performed through gravity-induced coagulation or flocculation, which does not depend on the surface charge. The most difficult is the purification of water contaminated with fine particles or heavy metal ions; such wastewater pollutants include non-biodegradable pesticides or natural organic and mineral compounds (Blockx et al., 2019). Various methods are used to overcome these problems, ranging from routine and simple procedures (such as precipitation and filtration) to more complex ones, including ultrafiltration, ozonation, and reverse osmosis. The second group of methods makes it possible to remove colloidal particles invisible to the naked eye from water, which are not subject to gravity and thus cannot be effectively filtered. However, these approaches result in higher costs. Therefore, researchers are faced with the challenge of finding cost-effective ways to purify water (Ghimici and Constantine, 2020).

Surface properties and electrokinetic effects are the most important traits of flocculants due to very small size (diameter of typical colloidal particles ranges from 1 nm to 1 μm) and large surface-to-mass ratio in colloidal solutions. Ionization of functional groups, adsorption of ions on the surface of particles, and surface charge usually depend on solution composition and pH (Mohammadi et al., 2019).

Various methods are used to treat industrial and agricultural wastewater: adsorption, biodegradation, coagulation and flocculation, electrochemical adsorption, electrocoagulation, membrane filtration, and Fenton oxidation (Wilts et al., 2018). In particular, flocculants, which accelerate the agglomeration of colloidal particles and the settling of flocculent deposits in the water system (Fujisaki, 2018) and increase the effectiveness of pollution removal, are widely used in water treatment processes, including wastewater (Cruz et al., 2020).

A good clarifying agent is characterized by effective removal of impurities at the lowest possible concentration and in the shortest possible time. Previously, inorganic coagulants (aluminum sulfate and iron chloride) were mainly used for water and wastewater treatment due to their high availability on the market and low price (Qi et al., 2020). Nowadays, polymeric flocculants (both synthetic and natural) are becoming increasingly popular. Non-ionic, anionic, cationic, and amphoteric flocculants are distinguished by the degree of ionization (Table 1).

Table 1. Classification of synthetic and natural flocculants according to the charge of functional groups (with examples).

Natural flocculants			
Nonionic	Ionic		
	Anionic	Cationic	Amphoteric
Starch, guar gum	Carboxymethylcellulose, sodium alginate	Chitosan, cellulose	Protein compounds
Synthetic flocculants			
Nonionic	Ionic		
	Anionic	Cationic	Amphoteric
Polyethylene oxide	Acrylates, methacrylates	Polyamines	Polyacrylamide

Table 2. The maximum permissible content of organic flocculants in the water of fishery reservoirs[1].

Flocculant grade	Chemical base	MPC, mg/dm^3
Flokaton 100-40	Copolymer of acrylamide and N-trimethylammonium	0.006
Flokaton 200-40	Copolymer of acrylamide and 1,2-dimethyl-5-vinylpyridinium methyl sulfate	0.003
Flokaton 109	Poly-N-trimethylammonium ethyl methacrylate benzenesulfonate	0.006
АК-617	Polyacrylamide cationic	0.08
PAA, DR 1-4973	Polyacrylamide non-ionic type	0.01
—	Polyethylene oxide	10.0
VPK 402	Polydimethyldiallylammonium chloride	10^{-3}

Large quantities of all synthetic flocculants known so far affect the environment adversely. Therefore, the content of flocculants in the hydrosphere, especially in water bodies of fishery importance, is strictly controlled (Table 2).

Modern water treatment technologies often use polymeric flocculants. These substances cause the formation of large cohesive aggregates (so-called flakes), which settle in solution. Synthetic polymers are highly effective flocculants at low dosages, but they have low resistance to the limiting dynamic shear stress. Shear stress is a rheological characteristic allowing to predict analytically the flow regimes of suspensions that ensure the preservation of the flocculation structure. The flocculating effect of water-soluble polymers depends on the size of random coils (i.e., on the radius of rotation), which have the most favorable conformation for macromolecules in solution. The lack of biodegradability and, consequently, the burden on the environment, as well as the complexity of processing the sludge after thickening are other significant disadvantages of flocculants based on synthetic polymers. The technological disadvantages of various types of synthetic flocculants are listed in Table 3.

Zetag® and Magnafloc®, flocculants based on water-soluble polyacrylamide (PAA), are mainly used for wastewater treatment (Li et al., 2020). The acrylamide monomer may also be used to graft or crosslink other types of polymers. The advantages of polyacrylamide flocculants include a high flocculation rate, a significant degree of suspension clarification, and low consumption. At the same time, they have a number of disadvantages, for example, ineffectiveness at low temperatures, relatively high cost, and the formation of large volumes of sludge, which affect the pH of the treated water (Walczak, 2020). In addition, most synthetic flocculants are extremely toxic to humans and animals (in particular, hydrobionts). For example, the acrylamide monomer, which may contaminate the polymer in trace amounts, has a dangerous carcinogenic effect. It is possible that small amounts of polymers after water treatment may enter the environment as finely dispersed or as a dilute solution, which causes an additional problem (Grenda et al., 2020).

Natural plant-based flocculants are desirable alternative to the polyacrylamide chemical flocculants. They are environmentally friendly, ease to prepare and use, they biodegrade easily and totally, cause no harmful substances in purified water, and form a small amount of dense sediment (Vajihinejad et al., 2019). Recently, biopolymers (in particular, polysaccharides) have attracted a lot of attention, mainly due to their availability, biodegradability, and high ability to adsorb pollutants from water (Qi et al., 2020). The purified polysaccharide bioflocculant also has thermal stability, when it retains more than 78% of flocculating activity after heating at 100 °C for 25 minutes. The purified bioflocculant is able to reduce chemical and biological oxygen demand (COD and BOD), suspended solids, nitrates, and turbidity of a wastewater with an effectiveness of 65.7%, 63.5%, 55.7%, 71.4%, and 81.3% respectively (Qi et al., 2020). Therefore, the use of bio-based flocculants has now become a common trend.

Biopolymers differ from synthetic polymers by having higher order structures and, sometimes, by an absence of a strict pattern unit (as lignin does).

[1] Order of the Ministry of Agriculture of the Russian Federation dated December 13, 2016 No. 552 “On approval of water quality standards for fishery water bodies, including standards”.

Table 3. Technological disadvantages of various types of synthetic flocculants.

No.	Components	Technological disadvantages
1	Polyacrylamide copolymers, partially hydrolyzed polyacrylamide	• high toxicity (hazard group 3); • energy-intensive preparation of working solutions; • unsuitability for drinking water treatment; • high price (5–7 USD/kg)
2	Low molecular weight cationic polyacrylic products	• high toxicity (hazard group 3); • the application requires high speed centrifuges at the treatment plant; • energy-intensive preparation of working solutions; • unsuitability for drinking water treatment; • high price (5–6 USD/kg)
3	Low molecular weight liquid coagulant based on aluminum oxychloride (17% of basic substance content)	• high toxicity (hazard group 3); • active in a narrow pH range (7.0–8.5); • requires introducing additional reagents (alkalis or acids) to change the pH of the water
4	Anionic coagulants	• special storage conditions are required; • active in a narrow pH range (7.0–8.5); requires introducing additional reagents (alkalis or acids) to change the pH of the water • short shelf life (6 months)
5	Aluminum hydroxide chloride coagulant powder	• high toxicity (hazard group 3); • special storage conditions are required; • requires additional equipment for the preparation of working solutions
6	Technical polyacrylamide with aluminum sulfate	• high toxicity (hazard group 3); • special storage conditions are required; • active in a narrow pH range (7.0–8.5); • requires introducing additional reagents (alkalis or acids) to change the pH of the water

However, as a rule, they are characterized by less polydispersity or even monodispersity. In particular, polysaccharides are macromolecular compounds in which the repeating units are monosaccharides linked in the chain mainly by 1,4-glycosidic bonds. Polysaccharides are naturally synthesized in plants (cellulose, starch, and pectin) or in animals; the latter are chitin and chitosan found in the shells of crustaceans, insects, fish scales, and some fungi (Wei et al., 2018). Their flocculating properties are predetermined by the chemical structure, rich in functional fragments (mainly hydroxyl groups, but also amino groups).

The natural flocculants have been referred as effective for the industrial wastewater treatment. The metabolites, biologically and chemically active substances produced during the vital activity of *Strychnos potatorum, Cactus opuntia, Moringa oleifera, Cassia fistula,* and *Portunus sanguinolentus,* have been tested as flocculants (Diab et al., 2020). Such substances include peptides, lipid-pigment complexes, polysaccharide polymers and their derivatives. They are distinguished by their diversity, high molecular weight, ease of processing, and high absorption ability to remove contaminants. Use of biopolymers, produced by *Strychnos potatorum,* as flocculants began several thousand years ago according to the Sanskrit scriptures (Grenda et al., 2020). In recent years, it has been applied to remove fluoride from drinking water (Xu et al., 2018), dairy wastewater treatment, and textile effluent decolorization. Slime of *Cactus opuntia* may also be used as a flocculant, aided by the presence of cellulose in this natural compound. This plant was used for pre-treatment of water exposed to oil sands to remove heavy metals and chromium from tannery effluents (Sun et al., 2019). In addition, *Strychnos potatorum, Cactus opuntia, Mor-*

inga oleifera, Cassia fistula, and *Portunus sanguinolentus* have been found to be effective in drinking water treatment (Sun et al., 2019).

Flocculants based on natural polymers are most often effective at high doses and are resistant to active mixing. Moreover, they may be easily modified to improve flocculation efficiency. According to the data published so far, the combination of the properties of natural and water-soluble synthetic polymers makes it possible to develop new highly efficient flocculants, such as starch, chitosan, cellulose, and their copolymers with acrylamide for wastewater treatment (Mohammadi et al., 2020).

The study aims to provide the latest data on the use of natural bioflocculants, mainly based on polysaccharides and their derivatives or copolymers, in particular, chitosan, for water treatment. In addition, the mechanisms of flocculation processes, methods for evaluating the effectiveness of new products of this type, and factors affecting the purification process are briefly outlined. Particular attention is paid to new synthetic flocculants and bioflocculants, as well as to future trends in this area.

Materials and methods

The scientific publications and patents of both Russian and international authors on bioflocculation have been considered. In PubMed, the studies published between 1999 and 2022 were searched using the following key words and their combinations: bioflocculant, wastewater, purification, biopolymers, flocculation, bridging, neutralization, environment, polymers, bioflocculation, floccules, precipitation cross-linking agent, chitin, and chitosan. This excluded articles available only in the form of abstracts, as well as bibliographies, editorials, and articles published in languages other than English and Russian. Generalization served as the main method (Moher, 2009). Statistical and research data related to the study of existing methods of flocculation and bioflocculation, the study of the properties of bioflocculants and flocculation conditions were analyzed.

Applicability of bioflocculants for wastewater treatment

A natural reservoir is a balanced ecosystem, configured for self-purification and self-remediation. The natural biological balance may be disturbed (Al-Manhel et al., 2018) as a result of:

– natural aging of the reservoir and the accumulation of natural organic matter (leaves, branches, excrement of fish and waterfowl, dead aquatic plants);

– intensive pollution of the reservoir with technogenic organic substances and nutrients (biogenic) elements (garbage, storm water, sewage, sediment from fields and roads, fertilizers).

Once in a reservoir, organic substances partially dissolve in water and partially sink to the bottom, where they form organic biomass of bottom sediments, which is continuously decomposed by putrefactive bacteria and fungi. At the same time, there is a sharp decrease in dissolved oxygen content in water and an increase in the content of nitrogen and phosphorus. Their excess initially leads (1) to a violation of the biological balance and suppression of the self-purification of the reservoir, (2) to eutrophication of a pond or lake ecosystem, and then (3) to swamping (Al-Manhel et al., 2018).

In order to reduce the negative load on the water areas, including those in Russia, it is necessary to introduce advanced technologies and use deep removal of biogenic elements from wastewater. Therefore, the removal of dissolved organic substances, including those containing nitrogen and phosphorus (for example, protein compounds, nucleic acids, nucleoproteins, etc.), is of particular relevance for the prevention of anthropogenic pollution of the water bodies.

The undoubted advantage of using bioflocculants is the ease of their modification by introducing specific functional groups that may effectively bind impurity molecules. For example, in addition to the existing hydroxyl groups in cellulose and starch, reactive carboxyl or aldehyde groups may easily be inserted into the macromolecular structure.

Flocculation mechanisms

Flocculation and coagulation are the most economical methods for removing solids from water. These processes are often confused with each other; however, these are two different phenomena that may occur independently of each other (Grenda et al., 2020).

During coagulation, the particles aggregate and begin to form flakes, which may be separated from the water. The mechanism of the described phenomenon is associated exclusively with Brownian motion (perikinetic aggregation) or with the movement of a liquid, leading to the association of micelles into larger aggregates (orthokinetic aggregation) (Feng et al., 2020). At the first stage of coagulation, colloidal particles are destabilized under the influence of electrolytes (most often aluminum or iron salts). Hydrolysis of these compounds leads to the formation of colloidal hydroxides, which are adsorbed on the surface of pollutant particles in water. According to the DLVO theory, the addition of an electrolyte reduces the electrical double layer until the dominant influence of the attractive van der Waals forces occurs. This is the reason for the formation of flakes. During collisions and aggregation of particles, ever larger agglomerates form and leave suspension (settle) under the action of gravity. Precipitation occurs after exceeding the critical concentration of coagulation, which depends on the experimental conditions (mixing, measurement time, etc.). The result is pure water without colloids (Tonhato et al., 2019).

The kinetics of flocculation is influenced by several factors: time and speed of solution mixing, surface charge of the flocculant, initial pH of solution, temperature, flocculant dose, initial solution concentration, etc. (Cui et al., 2020). However, the mathematical models, which relate the flocculation rate to the degree of effluent clarification and sludge compaction, have been developed mainly for inorganic flocculants that have a relatively high surface charge density.

Flocculation improves process conditions by combining destabilized particles with each other and increasing their mass, which allows them to be removed by filtration (Cruz et al., 2020). In industrial practice, a combination of coagulation and flocculation is applied using inorganic coagulants (electrolytes) and flocculants (ionic and nonionic polymers). This approach contributes to the formation of large and dense floccules, which means fast and efficient water purification from inorganic and organic impurities. In a cost-saving technology, direct flocculation, which is a non-coagulative purification process, is used. In this simplified method, cationic or anionic polymers play a dual role: they neutralize the charge of the particles and unite them through the formation of bridges. This process is effective over a wide pH range (unlike coagulation) and is primarily used to remove relatively high levels of organic contaminants.

Schematically, coagulation and flocculation are presented at Fig. 1. As a rule, coagulation proceeds very quickly (< 10 s), while flocculation takes much longer (20–45 min) (Romero et al., 2018). During coagulation, the sizes of aggregates are relatively small in the presence of salt; in this case, a plateau is quickly reached after a short-term increase in their size. Flocculation with high molecular weight compounds usually leads to the formation of larger aggregates; after they reach the maximum size, a certain decrease is observed, associated with a change in the configuration of the active groups or the irreversible destruction of the resulting aggregates (flakes).

According to recent studies, the flocculation process in the presence of polysaccharide flocculants is performed due to two main mechanisms: charge neutralization and the formation of polymer bridges (Van der Lee, 2020). These two pathways depend on the adsorption of the polymer on the surface of the particles as a result of electrostatic interactions, hydrogen bonding, hydrophobic interactions, complexation, or binding of ions to macromolecules (Van der Lee, 2020). A detailed explanation of these mechanisms must be based on detailed studies at the molecular level, since flocculation is a rather complex multi-stage process involving several competing physical phenomena and chemical reactions. Understanding these processes makes it possible to find the relationship between the properties of the used flocculants and the flocculation efficiency, which is practically important.

A verification of the flocculation mechanism has been presented relatively recently (Fan et al., 2020). Briefly, there is an optimum flocculant concentration at which large flakes capable to settle are formed (the so-called flocculation window). Exceeding this concentration limit re-stabilize suspended particles. The influence of temperature, which is critical for thermo-

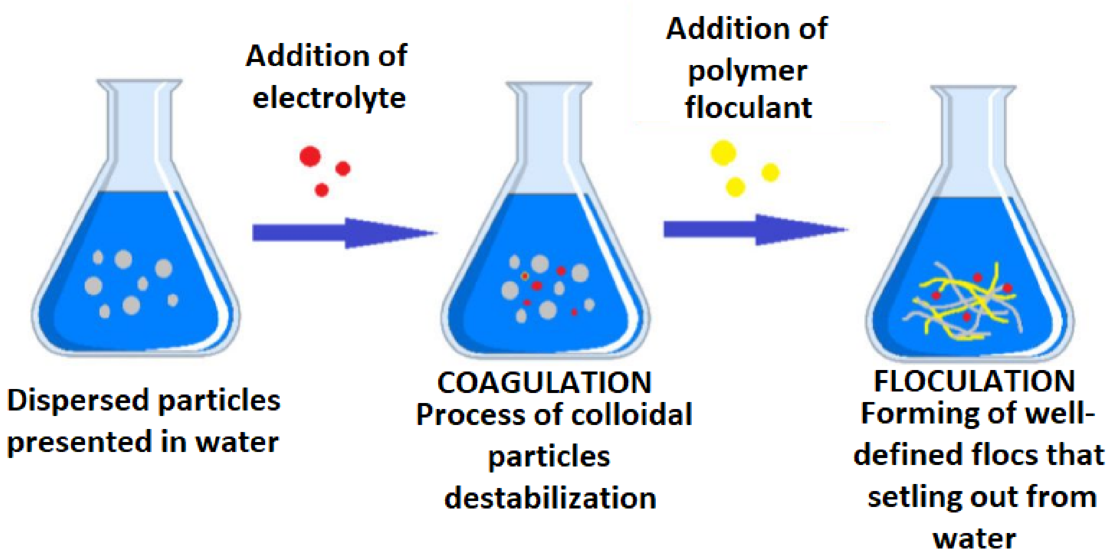

Fig. 1. Processes of coagulation and flocculation.

sensitive polymers, has also been studied. Such substances not only undergo re-conformation under the influence of a certain temperature, but also change their hydrophilic nature to hydrophobic. As a result of subsequent changes in molecular interactions, partially or completely reversible aggregation may form.

A detailed description of the mechanisms of flocculation, supported by theoretical considerations, been published has recently (Al-Manhel et al., 2018; Tran et al., 2020). Simulation of the process made it possible to determine the adsorption and aggregation times, which are different for Brownian diffusion and flocculation. For example, the aggregation time is 16 s and 180 s in shear and diffusion processes in a suspension of charged silica particles flocculated polyacrylamide, respectively.

Both mechanistic and kinetic experiments have been considered in the recent review (Sun et al., 2019). The paper also discusses the role of physicochemical processes in particle aggregation, the stability of flakes, the interaction of molecules, the mechanisms of destruction of aggregates, and transport processes, including particle collisions during laminar and turbulent motion.

Charge neutralization

Charge neutralization may take place if the charge of the polymer is opposite to the charge on the surface of the colloidal particles. In this case, molecules' adsorption decreases the electrokinetic (or zeta) potential (ζ), which is the potential difference between the dispersed particles and the medium. In other words, this is the electric potential on the shear plane, i.e., at the boundary between the adsorption and diffuse layers of particles in a colloidal solution. A decrease in the ζ-potential contributes to van der Waals forces to appear, which facilitates the aggregation and sedimentation of the formed floccules (Al-Manhel et al., 2018).

The described mechanism is especially effective for low-molecular weight polymers ($< 10^5$ Da). The so-called electrostatic patch model is a variation, which assumes partial charge neutralization occurring in the presence of a polyelectrolyte of medium-molecular weight. In this case, neutralization does not occur completely, when and negatively charged fragments form on the surface of the same molecule. Such spots or "islands" with different charges cause attraction and sedimentation of neighboring particles. The formed flakes bind more strongly than during conventional charge neutralization.

Another type of charge neutralization is described in combination with the transfer of colloidal particles to the precipitate (Lu et al., 2020). First, the negative charge of colloidal particles is neutralized, then, positively charged large aggregates are formed (settling floccules). Mutual attraction between the aggregates and the remaining colloidal particles leads to their adhesion and precipitation. This non-selective process takes place mainly in the presence of inorganic coagulants (Al/Fe salts) and at neutral pH; in this case, the floccules are aggregates of $Al(OH)_3$ or $Fe(OH)_3$. Other water-soluble impurities may also be associated with or captured by the flakes. Other factors affecting this process are the presence of various anions in water and the concentration of colloidal particles (Lu et al., 2020). This phenomenon may also occur in the presence of bio-based polymeric flocculants.

Formation of polymer bridges

During the bridge forming, part of the polymer segments is adsorbed on the surface of colloidal particles, resulting in forming loops and tails in the solution; these loops and tails may attach to neighboring particles and so form larger aggregates-floccules. The polymer may be adsorbed by van der Waals forces, hydrogen bonding, or a chemical reaction between functional groups of macromolecules and colloidal particles. This process is especially effective for high molecular weight polymers ($> 10^6$ Da), which have the same charge as colloidal particles. This method is also applicable to dispersed uncharged particles, even if they are relatively far apart, i.e., at a distance exceeding the effect of electrostatic attraction forces, which may take place at very low concentrations.

The effectiveness of polymer flocculants is due to the formation of networks of macromolecules that may physically capture particles, as well as due to the possibility of changing the conformation in solution. Due to this, the shape of the polymer chains comes into agreement with the surrounding or attached colloidal particles. Adsorbed macromolecules may undergo a relaxation process: when they become too flat on the surface of the pollution particles, they lose the ability to combine with other particles (Jiang et al., 2020). Polymer blends are used to prevent unwanted inactivation of the polymeric flocculant. In this case, one polymer provides adsorption sites for another or it promotes a more elongated conformation of the adsorbed macromolecules.

In order to launch flocculation by the bridge forming, the macromolecules' size must exceed more than twice the thickness of the electrical double layer of the colloidal particle. The calculated minimum molecular weight of a linear non-ionic polymer (PAA) is about $3 \cdot 10^6$ Da. Aggregates formed in the presence of polymer flocculants are stronger and larger than in traditional method of coagulation with inorganic compounds.

Effectiveness of various flocculation mechanisms

When proceeding through the bridge forming, the flocculation efficiency depends not only on the chemical structure and molecular weight, but also on the degree of branching of the macromolecules. However, this issue is still debated. On the one hand, there is evidence that linear molecules improve process effectiveness (Tonhato et al., 2019; Zhao et al., 2020). On the other hand, hyperbranched cationic polyacrylamide is found to exhibit increased flocculating activity compared to its linear counterpart, which is explained by increased interaction of branches with suspended particles. In the presence of this new branched polymer, shorter settling time and large deposited flocculant sizes are observed (Wang et al., 2019).

It is worth noting that the polymer chain will wrap individual colloidal particles (which will restore a stable suspension) under certain specific conditions (for example, in a highly diluted solution). An intense mixing may cause similar effect, when the bridges between the colloidal particles break up, especially if they have formed due to the action of weak dispersion forces. However, in some cases, the reversibility of flocculation may be a positive aspect. Both breaking and re-growth of flocs lead to forming a dense compact sludge and to more efficient separating even with a reduced dose of flocculant. If neutralization is the primary mechanism, both breakdown and re-growth of the aggregates eventually result in forming of larger flakes that begin to repel themselves due to the accumulated charge. In bridging, smaller aggregates may fully recover, which increases flocculation efficiency (Peng et al., 2020).

The dominant flocculation mechanism is usually predetermined by the type of flocculant: an agent with a high-electrical charge density acts via neutralization, while high-molecular weight, but low-charged compounds flocculate predominantly by bridging. If traditional neutralization technology is not sufficient, and it does not provide high water quality standards, enhanced coagulation (or optimized coagulation) may be applied in order to increase the settling rate and to remove by-products completely. This may be achieved by using an excess of coagulant, a combination of coagulants or other additional agents (e.g., oxidizer and activated carbon), adjusting the pH, and controlling the hydraulic regime (Tian et al., 2019). Additional benefits of enhanced coagulation include significant sludge dewatering and reduced water treatment costs.

Methods for assessing the flocculation efficiency

Turbidity is the main sign indicating the presence of impurities in drinking water; therefore, the most important methods for measuring the content of impurities are based on the determination of this physical parameter. The principle the water turbidity measuring is based on the assumption that light penetrates freely a layer of pure water (completely transparent), and the presence of suspended particles causes its scattering or absorbing (Tyndall effect). The turbidity varies depending on the size, shape, concentration, chemical composition, and refractive index of the particles in the solution.

Measuring the intensity of scattered or transmitted light (transmittance) is the basis of methods used both in water treatment plants and in laboratory tests. At present, the standard method is to measure the scattered light at a 90° angle of incidence on the system to be cleaned. They use nephelometers (turbidity meters); the measurement result, depending on the technology used, may be expressed in nephelometric turbidity units, formazine turbidity units, or formazine attenuation units. Instruments based on transmitted light measurements are more useful for measuring turbidity caused by the presence of larger particles (> 1 μm in diameter) in water (Tian et al., 2020).

Instead of measuring a single reflection at an angle of 90°, modern turbidity meters register a series of reflected rays in the entire range of angles (360°) around the cuvette with the water sample under study, which ensures greater accuracy.

In some cases, for example, when the water is turbid due to the presence of metal ions (Fe^{2+} and Fe^{3+}), measuring the conventional absorbance in the 600–800-nm range are used in addition to nephelometry. After particles are deposited due to sedimentation, the transmittance increases, so the absorption of light tends to zero. Assessing the removal of fluorine, nitrate, and phosphate ions from aqueous solutions has been also performed by ion chromatography methods (Romero et al., 2018).

Absorption and UV/visible spectroscopy is a common method for determining flocculation efficiency (Zhao et al., 2018). It allows one to determine the concentration of impurities of a certain type (for example, metal cations) that absorb in the UV/visible range. The effectiveness of different flocculants and validity of the proposed methodology may be compared by measuring the absorption (or transmission) of water samples before and after treatment. For example, effective viscosity (η_{eff})

has been calculated to assess the effect of organic substances on flocculation performed using various flocculating agents (Nakamura et al., 2020). In addition, absorption spectroscopy is used to evaluate the water color. For example, determining the absorbance at 465 nm may accurately detect a bluish color that cannot be seen with the naked eye.

The criteria for evaluating the flocculation efficiency by measuring turbidity or light absorption are either the parameters of the solution depending on the concentration of the added flocculant, or the minimum settling time leading to the desired level of purification. Strictly speaking, the flocculation efficiency is the higher, the shorter the settling time and the lower the dose of flocculant (Zhao et al., 2020). The latter term is also referred to as the optimum dose (in the case of a polymeric agent, the optimum polymer dose) at which the lowest level of contamination may be achieved.

In some works, a flocculation index is proposed (Ghimici and Constantine, 2018). This parameter reflects the size of suspended particles (the greater the degree of aggregation, the higher the index). For example, equipment for continuous monitoring of flocculation based on a slurry flow meter using 900 nm light has been proposed (Ghimici and Nichifor, 2018).

The content of colloidal microparticles of certain sizes in an aqueous suspension, determined before and after treatment, is another criterion for the flocculation efficiency; according to some authors, it is preferable to assess turbidity. In this case, microscopic methods or even visual observation may be applied. The size and shape of the flakes, as well as their changes after the flocculant has been added, provide important information about the process progress. Determining the size of the precipitated particles makes it possible to predict whether they may be finally removed during the conventional filtration process.

The size, number, and size range of colloidal particles in a solution may be determined by the light scattering. Such measurements allow both to evaluate the flocculation efficiency and to contribute to the refinement of its mechanism, depending on the system and conditions used. For example, three cationic polymers (homopolymer of diallyldimethylammonium chloride and two of its copolymers with acrylamide) of different molecular weights (1.1–3.0 × 10^5 g/mol) and charge density (10%, 40%, and 100%) are used as flocculants for silica aggregates (Buenaño et al., 2019). The experiments on wastewater flocculation and sludge dewatering have been performed in an apparatus designed for aggregation (mini-thickener), after which the static charge density of sludge particles has been assessed, as well as ζ-potential of the agitated suspension at 22 °C and pH = 5.5. In this case, the flocculation mechanism is mainly predetermined by the charge density: bridging predominates at low charge density (10%); at a high charge density (100%), the electrostatic spot flocculates; and moderate charge density (40%) causes mixed-type flocculation, when both charge neutralization and bridge formation take place.

In another study, the flocculation has been analyzed using an advanced image analysis method using a CCD camera and associated software (Maćczak, et al. al, 2020). The cyclicity of the process of combining floccules, the growth of the combined agglomerates, their destruction and reconnection of floccules using synthetic and natural flocculants have been observed.

Since the ζ-potential decreases during flocculation by neutralizing the electric charge, this parameter is also a measure of the process effectiveness. Based on the ζ-potential changes, it is possible to determine both the degree of neutralization and the corresponding dose of flocculant The ζ-potential has been measured with cationic and anionic polyelectrolytes during the treatment of wastewater (containing Sn, Pb, and Fe cations) obtained from semiconductor production (Mao et al., 2020). It is concluded that this parameter plays a key role in assessing the effectiveness of coagulation-flocculation. The dependence of the ζ-potential on pH and the dose of flocculant has been determined; in turn, these parameters affect the turbidity and particle size.

The Jar test is the most common method for assessing the flocculation efficiency in practice. This important laboratory-based research tool may be used to simulate large-scale coagulation/flocculation during water treatment in wastewater treatment plants. There is no simple definition of this procedure, or even standard equipment for it. This experimental method aims to evaluate the minimum flocculant dosage and process conditions required to achieve a certain water quality. It is usually carried out in a shaker, in which 3–6 flasks are placed at a time.

There are modifications of this method allowing more accurate and reproducible studies. For example, the trial flocculation method has been modified by adding six turbidity meters in combination with a computerized data acquisition system. This makes it possible to determine the settling time of suspended particles of various masses (Nakamura et al., 2020).

Factors affecting flocculation efficiency

Many factors may affect flocculation process and its effectiveness: these are the chemical structure and properties (including the charge) of both the removed substance and the flocculant (in the case of polymers, the average molecular weight and its distribution are also important), their concentration, medium pH, temperature, mixing speed, and mechanism of the process.

The pH of the feed water is one of the most important parameters affecting the flocculation efficiency. It should be considered that contaminants (for example, hydrolysable salts) affect the level of acidity. In an alkaline environment, an increase in the dose of a flocculant does not improve the productivity of the process, but acidification of the medium is recommended in this case (Loganathan et al., 2020). When the pH changes from 8.5 to 12.0, the flocculation efficiency of chitosan obtained from microalgae *Chlorococcum* sp. is higher than in conventional coagulation with aluminum sulfate and ferric chloride (Diab et al, 2020). After microalgae-mediated flocculation, water is suitable for their repeated cultivation, since it does not contain contaminating metal compounds.

The effect of pH on the surface charge of an adsorbent based on chitosan has been studied as well (Hasan and Fatehi, 2019). The point of zero charge (the pH value at which the total surface charge of the particle is 0) is 6.15, while the adsorbent acquires a positive charge and can react with the anions present in the solution at pH = 3.

The effect of the initial pH and dose of another chitosan-grafted copolymer has been studied for the treatment of water contaminated with acid blue, Ab-113 (Vakili et al., 2019). The copolymer has been prepared by ultrasonic-initiated grafting with acrylamide and 3-acrylamide chloride neutralizing the charge. This new type of flocculant is used in combination with kaolin to improve flocculation efficiency (Djibrine et al., 2018). The dye removal rate reached a maximum (91.9%) at a flocculant amount of 25 mg/L at an optimum pH = 5.0, indicating a neutralizing flocculation mechanism. The improved flocculation effect in the presence of kaolin is also due to the binding of dye and flocculant molecules.

Similar studies have been carried out for tannin flocculants, lignin-grafted copolymers, and other plant agents (Feng et al., 2020). These works show the importance of pH, which influences the ζ-potential and allows the flocculation mechanism to be modified from neutralization to bridging.

The stability of flakes required for their settling depends on the strength and number of interfacial interactions between agglomerated particles. If the points of contact are sparse and weak, the flakes may easily break into smaller and more separate pieces. Intensive mixing at high shear rate causes effective fragmentation and erosion of the flakes (Djibrine et al, 2018). However, a consequence of this process may be reconnection (re-growth), when smaller flakes coalesce together after the shear forces are reduced again, and so re-flocculation occurs. The flakes disintegrate and grow simultaneously until a steady state is reached. The destruction of the flocculation may be fully or partially reversible, depending on the type of flocculating agent applied.

The flocculant concentration (strictly speaking, its optimal dose) is another factor that has a significant impact on the flocculation process. Both insufficient and too high concentration make the process inefficient. Appropriate flocculation time is also a significant factor, which depends on the type and amount of impurities in the solution and on the type of flocculant.

Since the size, shape, density, and settling rate of flocs change over time, changing floc hydrodynamics also affects the course of flocculation.

The degree of turbidity, which depends on the type and size of suspended particles in the water, may also affect the effectiveness of the process (Zhu, 2018). Sometimes, higher turbidity is easier to remove even with a small amount of flocculant due to the high potential for particle collision, while fine particles or dilute solutions with lesser turbidity may be more difficult to flocculate.

Finally, the effect of temperature should be mentioned. As a rule, at low temperatures, chemical reactions and physical processes proceed more slowly; however, a noticeable effect of thermosensitive flocculants is observed only at large temperature differences (Loganathan et al., 2020). Temperature increase accelerates the movement of molecules in solution, increasing the likelihood of their collisions and aggregation, which leads to flocculation rate increase.

Flocculants based on chitosan

In a wide range of high molecular weight organic polymers of biological origin suitable for the flocculation process, polysaccharides are of unflagging popularity. These compounds are particularly attractive for wastewater treatment due to a number of their advantages: biodegradability, availability, and structural features that facilitate their chemical modification. These characteristics make polysaccharides important agents for reducing COD, removing turbidity, microorganisms and many other contaminants present in water. Chitosan is one of the most common and effective polysaccharide flocculants.

Chitosan is the second most abundant biopolymer in the world after cellulose. It still attracts significant attention of researchers as a promising coagulant and flocculant[2] due to its precipitating properties. The presence of chitosan in the shells of crustaceans (crabs, shrimps, and spiny lobsters) gives them flocculating properties. *Portunus sanguinolentus* shells have been used in the treatment of wastewater from slaughterhouses, fish ponds, and a palm oil refinery (Saxena et al., 2018). Due to its unique properties, chitosan is widely used in industry (Salehizadeh et al., 2018). Although the disadvantage of chitosan is its insolubility at pH ≥ 7, its role as a flocculant is steadily increasing. There is scant information in the literature about the production of chitosan from another raw material of animal origin-powder of crushed fish bladders (Feng et al., 2020).

Chitosan is a deacetylated chitin derivative consisting of a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine (Fig. 2). It is highly valued for use in water and/or wastewater treatment due to its amino and hydroxyl functional groups, which may react with impurity particles (Djibrine et al, 2018). Many experiments have been carried out on flocculation using chitosan, which made it possible to achieve promising results (Molino et al., 2020; Salehizadeh et al., 2018). The complete mechanism of chitosan-mediated flocculation is not well understood yet; however, the bridging mechanism predominates during this process (Ang et al., 2020). The flocculation ability, like other properties of chitosan, depends on the degree of its deacetylation, as well as on the pH of the medium. Chitosan is soluble in an acidic environment (where the amino groups are protonated), but it is insoluble in neutral and alkaline environments.

Due to its chemical structure and complexing ability, chitosan has a high affinity for many classes of dyes, so it may be a universal sorbent for metals and surfactants, as well as microalgae do. However, like starch, it is insoluble in water and needs to be modified to improve usability and flocculation. There are only a few reports on the use of this polymer in its unmodified form. Chitosan dissolved in acetic acid has been tested to purify a water from a local river (Wei et al., 2019). In this study, high flocculation efficiency of chitosan has been found, as evidenced by a reduction in water parameters such as turbidity or total dissolved solids. Similar studies were carried later (Grenda et al., 2020) in a series of Jar tests on surface water samples comparing the flocculating abilities of chitosan and commonly used inorganic coagulants (aluminum sulfate and ferric chloride). As the concentration of the polysaccharide increased, the turbidity of the water decreased, which served as the main indicator of the effectiveness of the biopolymer used.

[2] Hereinafter, instead of the words "coagulation/flocculation" and "coagulant/flocculant" the terms "flocculation" and "flocculant" are used.

Due to the high consumption of chitosan, there were attempts to combine it with synthetic polymers to create biodegradable and more efficient flocculants, for example, a water-soluble terpolymer chitosan-acrylamide-fulvic acid, CAMFA (Vajihinejad et al., 2019). Flocculation tests were carried out on solutions of model dyes (reactive black 5 (Rb-5), acid blue 113 (Ab-113), and methyl orange); a measure of the flocculation efficiency was the change in the water color. High effectiveness of the CAMFA terpolymer in removing Rb-5 and Ab-113 dyes was observed, reaching more than 90%, although at a very high dose (almost up to 300 mg/L) in a wide pH range.

The use of grafted chitosan copolymers is increasingly proposed in the wastewater treatment process. A series of grafted chitosan flocculants were synthesized (Lu et al., 2020). A high content of methacrylate-ethyltrimethylammonium chloride (DMC) resulted in a better flocculation ability than that of acrylamide-grafted chitosan. The combination of chitosan and DMC monomer had an increased number of positive charges capable of neutralizing opposite charges on the surface of particles suspended in water.

The next type of modified chitosan flocculant has been synthesized by the reaction of carboxymethylchitosan (Chito-CTA) with a quaternary ammonium reagent (3-chloro-2-hydroxypropyltrimethylammonium chloride) (Djibrine et al, 2018). The resulting amphoteric polymer has a high solubility, which increases its applicability as a flocculant in water purification.

There are also some examples of new, environmentally friendly flocculants (Zhang et al., 2019), such as graft copolymers of chitosan and acrylamide or [2-(acryloyloxy)ethyl] trimethylammonium chloride obtained by copolymerization initiated by UV radiation. The resulting materials are characterized by a porous structure, which promotes the best flocculation efficiency in the water purification from zinc phosphate (recovery degree of about 99%).

There are also modifications of chitosan with xanthate and sulfonic acid group. This polymer, also obtained from the photochemical reaction of carboxylated chitosan, has proven to be very effective in removing heavy metal ions such as Cr and Ni from water, when the overall removal effectiveness in both cases exceeds 99% (Zhang et al., 2019). In this work, we study molecular interactions at the interface (on a microscale). In addition, the relationship between the chemical structure of the flocculant and the flocculation efficiency was established using FTIR, NMR, XRD, and SEM analyses. The network structure of modified and grafted flocculants is the most effective for wastewater treatment in various industries.

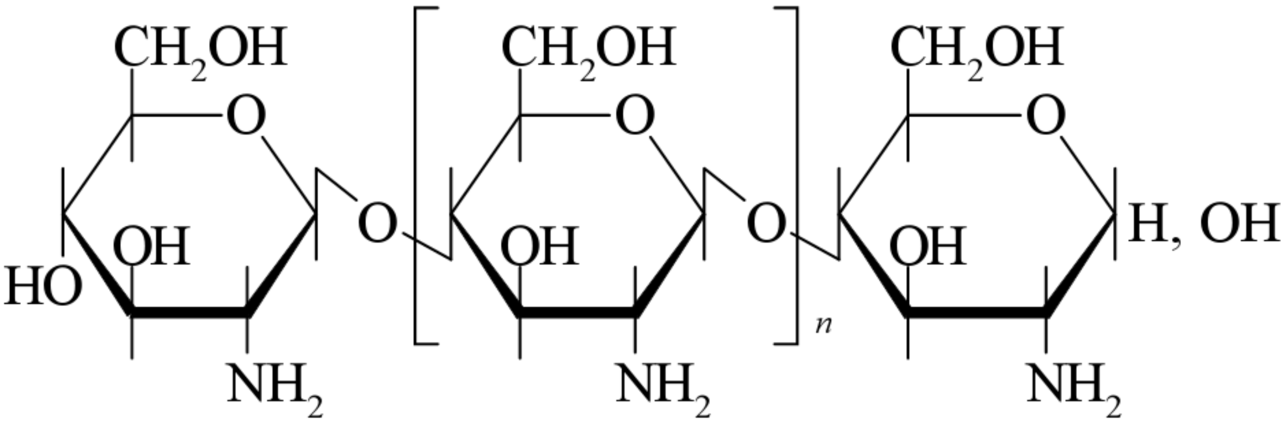

Fig. 2. Chemical formula of chitosan, a copolymer of D-glucosamine and N-acetyl-D-glucosamine.

The copolymerization of chitosan with acrylamide and 3-acrylamide propyltrimethylammonium chloride initiated by ultrasonic waves is another modification (Chen et al., 2020). The resulting cavitation[3] increases the formation of free radicals and initiates the copolymerization reaction. The obtained flocculant (CTS-g-PAA) has been used to purify water from acid blue (Ab-113) at 80% efficiency with optimal dose of 25 mg/dm^3. Adding the kaolin particles to the solution increases the flocculation efficiency up to 91.9% by increasing the surface area of the flakes adsorbed by CTS-g-PAA.

The combination of properties of chitosan and starch leads to promising results in wastewater treatment. The synthesis and properties of a new flocculant based on cationic starch-chitosan cross-linking copolymer (CATCS) are reported in details (Nakamura et al, 2020). Studying the suspension of kaolin at a concentration of 5 g/dm^3, the authors prove that CATCS exhibits better flocculation properties (both in acidic and alkaline conditions) than cationic starch and chitosan used separately.

Chitosan is proposed for the coagulation of pollutants entering wastewater during the production of chitin (Nakamura et al., 2020). The purification process is a two-stage process: (1) initial precipitation at pH = 4–11 (turbidity is reduced by 80%), then (2) coagulation with chitosan (99.4% of total turbidity removed at pH 10.6 and a dose of 86.4 mg/dm^3). It is worth emphasizing that the residue obtained by coagulation is rich in protein (55 mg/g) and thus may be used as an additive to animal feed or plant fertilizers.

A water-soluble chitosan derivative has been developed for removing the dye (reactive brilliant red) from textile wastewater (Noor et al., 2020). The modification of chitosan is based on the esterification reaction with a cationic agent (2,4-bis(dimethylamino)-6-chloro-(1,3,5)-triazine). The authors point out that the wastewater treatment process produces a large amount of sludge that is harmful to the environment, but, at the same time, textile dyeing effluents often contain azo dyes, which may be a valuable raw material. Recovery of these compounds is proved to be very advantageous. Once freed from flakes, they may be used to produce nitrogen-doped carbon materials by carbonization. The proposed method reduces the amount of toxic substances in solid residues after processing. At the same time, the resulting material may be applied as a supercapacitor due to its high electrochemical capacity and long-term stability.

When continuing the research described above, textile sludge containing chitosan has been used to create graphene-like carbon nanosheets, developed as an electrode material for supercapacitors (Noor et al., 2020). The desorption of the azo dye has been controlled by adjusting the pH of the medium. Thereafter, the product has been subjected to pyrolysis in the presence of a Fe(III) salt as a graphitization catalyst.

Regard must be paid to unmodified chitin used as a flocculant. In terms of its qualities, chitin is not inferior to aluminum sulphate as a coagulant (Noor et al., 2020; Zhao et al., 2020). Moreover, it is stable in all pH ranges (Zhao et al., 2020). The possibility of using chitin is environmentally beneficial, since it allows the disposal of seafood waste, but does not require the use of chemical reagents that burden the environment, as in the case of obtaining chitosan.

[3] Cavitation is formation and rapid disappearance of gas bubbles in the liquid, accompanied by sudden changes in pressure, leading to the release of a large amount of energy.

Conclusions

Flocculants are used in a number of technological processes, which require water purification from various types of suspended particles (inorganic, organic, and microbial). In particular, flocculants are used in the dairy, oil and gas industry, mining, metallurgy, paper industry, in the treatment of drinking water, municipal wastewater and mining waters. At present, much attention of the scientific community is drawn to obtain the bioflocculants of plant of animal origin (less commonly). The mechanism of flocculation with biopolymers is relatively well known, but it is not understood in details yet. Various factors, such as pH, ionic strength or shear rate, impurity concentration, and flocculant content, affect this process significantly. According to the worldwide published data, biopolymers have great potential to become effective flocculants for water purification, although their use in industrial practice is not wide so far. Obtaining new biomaterials and their modification in order to optimize the flocculation process are main directions of future researches.

Our study focuses on the use of readily available, safe, and cheap biodegradable, naturally occurring polymers (e.g., polysaccharides). In order to improve the flocculation efficiency, polysaccharides are subjected to chemical modification (e.g., graft copolymerization with synthetic monomers) or physical mixing with inorganic agents. Biomaterials obtained by biosynthesis in the presence of microorganisms have promising properties as well.

ORCID

E.V. Ulrich 0000-0003-4107-7277
A.S. Barkova 0000-0002-2602-6810

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