Coagulants and Natural Polymers: Perspectives for the Treatment of Water

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Abstract

The waste generated by modern society, when discarded in nature can make the water unfit for human consumption. Thus to obtain drinking water is necessary to perform a physical-chemical treatment, which allow the removal of the turbidity and organisms harmful to health. These coagulant chemicals and related products, although efficient, physical and chemical characteristics of water, complicate the disposal of sludge generated, and make the water have a high cost, which is passed on to consumers. In view of the replacement or Reduction of chemical coagulants used in water clarification, natural polymers and coagulants are effective, productive, free from physical and chemical changes in the treated water, and add value to their sources of origin. In this perspective, this review encompasses the most natural products Studied and Reported in the scientific and applied in water treatment.

Keywords

Water Clarification; Polyelectrolytes; Natural Sources

Introduction

Water is a vital substance and of great importance in all natural and anthropogenic activities. It regenerates shape and oceans and seas, rivers, lakes and forests, becoming part of the identity of environments and landscapes and of paramount importance for the development of ecosystems and human life. But while in the past has been considered an infinite good, currently misuse, coupled with growing demand, has made reserves of fresh water and clean decrease (TELLES; COSTA, 2007).

Because of its ability to solubilize the pure water is not found in nature. Dissolved impurities comprise minerals, organic compounds and gases that alter the physical characteristics (turbidity, color, temperature, electrical conductivity), chemical (chemical and biological demand for oxygen, pH, alkalinity, total organic carbon) and biological water, whose effect depends on the composition, concentration and chemical reactions between pollutants (RICHTER; NETTO, 2003).

The quality of water that reaches the consumer is determined by parameters that establish the maximum concentration of substances contained in the product, which must be respected (DI BERNARDO; DI BERNARDO, SON, 2002). In Brazil, these parameters are the burden of the Ordinance of the Ministry of Health n □ 2914 to December 12, 2011, where they are established procedures for control and monitoring of drinking water, and its potability standards to which all water distributed the population must obey in order to adapt it to the parameters microbiological, physical, chemical and radioactive level that does not provide health risks, and subject to monitoring water quality (BRAZIL, 2011).

In this context, water treatment is the removal of suspended and colloidal particles, organic matter, micro-organisms and other substances that are deleterious to health, seeking the lowest cost of deployment, operation and maintenance, and reduced environmental impacts to the surrounding region (LIBANIUS, 2008).

In the water treatment step involving coagulation is conducted by physico-chemical modification of colloidal particles that characterize the color and turbidity by adding coagulant chemicals, reduce the forces responsible for keeping the particles apart and suspended (RICHTER, 2009). In water treatment plants (WTP), coagulation affects the performance of the other stages of the treatment, favoring microbiological quality of the final product increasing the lifetime of filters and reducing the final cost of the treated water (LIBANIUS, 2008).

Coupled coagulation, flocculation step constitutes conditions of time and agitation where the particles from colliding and coagulating destabilized by forming flakes could be eliminated by sedimentation. When the flocculation is inefficient and increases the uptake of particulate filtration units, favoring the deterioration of filtered water and increasing the need for washing the filters, making the costly water treatment (LIBANIUS, 2008).

Subsequently flocculation, sedimentation occurs, a physical process which, by gravity, particles denser than water will settle on the bottom of a surface. The flakes that do not have weight to decantarem are retained in filtration, a physico-chemical process where they are separated from impurities suspended in water, due to passage through a porous filter media such as sand, anthracite, garnet sand, granular activated carbon , among others. Finally, the water resulting from all of these processes had undergone disinfection, and distributed to the consumer (RICHTER, 2009).

Currently, the need for better quality water for everyday activities and economic, increased the number of treatment units, and the lack of financial investments for the treatment and supply of this product, especially in developing countries, has stimulated research that render the coagulation and flocculation processes more efficient, allowing increasing the production of water without change in physical body of ETAs and the application of natural polymers as coagulants and coagulant aids primary or flocculation (Richter, 2009; GRAHAMA; GANGA; FOWLER; WATTS , 2008).

Coagulants Metal: Efficient, but Controversial

According Libânio (2008), to be used in water treatment, the metal needs coagulant in aqueous solution, undergoing a process called hydrolysis, where the cations form strong bonds with oxygen and can coordinate with up to six water molecules. Thus, there is formed a precipitate of hydrolysed forms of the metal. With the rapid mix process (coagulation) hydrolysed species of positive charge, come into contact with impurities in suspension, predominantly negative charge, destabilizing them. With the collision of these particles occurs later flocculation.

The action of these coagulants occur by mechanisms such as compression of the double layer, where trivalent ions reduce electric potential around the particle, allowing the approach of other molecules; adsorption-neutralization, which after the addition of coagulant for the formation of hydrolyzed species charge positive, which adsorb on the particle surface, destabilizing them, and scanning more common in conventional water treatment plants, where depending on the dosage of the coagulant and the pH of the medium, are adsorbed colloids and suspended particles enveloped by the hydroxide precipitate salt (Libanius, 2008; DI BERNARDO; DI BERNARDO, SON, 2002).

The definition of the type of coagulant being applied to the process relates to the suitability raw water treatment technology, the cost of coagulant and products associated with it, the quantity and quality of sludge generated (LIBANIUS, 2008).

In Brazil, the main metal coagulants used are aluminum salts (aluminum sulfate) and iron (ferric chloride). However, considering the prospect of replacing these products, poly aluminum (PAC) is among the most promising and available in the domestic market (SON; WAELKENS, 2009).

The aluminum and iron salts act as diprotic acids in solution and consume alkalinity and may necessitate the addition of an alkalizing the coagulation process so that the hydrolysis reactions occur. Due to the reduction in pH, after the addition of the alkalizing process is also necessary to confer the pH mildly basic water treated in order to preserve the supply pipes. Both processes entail additional costs to treatment (MATILAINEN; VEPSÄLÄINEN; SILLANPÄÄ, 2010; DI BERNARDO et al., 2002; LIBANIUS, 2008).

Although recognized the efficacy of chemical coagulants, there are disadvantages associated with the use of these products, such as the inefficiency of low water temperatures, as well as aluminum, in this case, increasing the residual cation in solution, causing health problems and distribution water; costs relatively high, the large volume production of sludge; action on the pH of the treated water, and possible, although not yet fully characterized, harmful effects on human health, as evidence of aluminum in the development of neuropathic diseases, as Alzheimer's disease, and toxicity on aquatic organisms. Thus it is desirable to replace these chemical coagulants for products that do not generate such drawbacks, such as natural polymers and coagulants (Yin, 2010; MATILAINEN; VEPSÄLÄINEN; SILLANPÄÄ, 2010, YANG et al. May 2011).

Coagulants and Natural Polymers: New Perspectives

Historically, natural vegetable coagulants were applied to the clarification of drinking water before the advent of chemical synthetic base aluminum and iron. There is evidence of the use of nirmali (AS. potatorum) to 4000 years, and nuts from 400 AD., India, for this purpose, in the sixteenth century was used as coagulant almonds soaked beans in Egypt and Sudan to improve water quality (Libanius, 2008; NDABIGENGESERE; NARASIAH; TALBOT, 1995; BABU; CHAUDHURI, 2005).

Synthetic polymers used in water treatment arose after World War II, but began to be used effectively after the 1960 U.S.. Compounds are composed of long chains of a number of chemical units that repeat joined by covalent bonds, so-called monomers. When have electrical ionizable sites are called polyelectrolytes, and according to the load that has classified as cationic (positively charged), anionic (negative charge) or non-ionic (neutral) (RICHTER, 2009; LIBANIUS, 2008).

The natural coagulants act, in most cases, via the mechanism known as adsorption, neutralization, where the formation of hydrolysed species of positive charge in the compound, the adsorption occurs at the surface of this particle suspension, destabilizing it. This attraction results from interactions such as hydrogen bonds, coordination reactions, covalent reactions and ion exchange (LIBANIUS, 2008, p. 124).

When employed, the polymers act enabling the formation of chemical bridges, through hydrogen bonds or van der Waals forces, where the colloidal particles are adsorbed in the chain of the compound, it must be long in order to avoid the repulsive effect of the double and allowing the adsorption layer on its surface, as shown in Fig. 1 (LIBANIUS, 2008, p. 125-126).

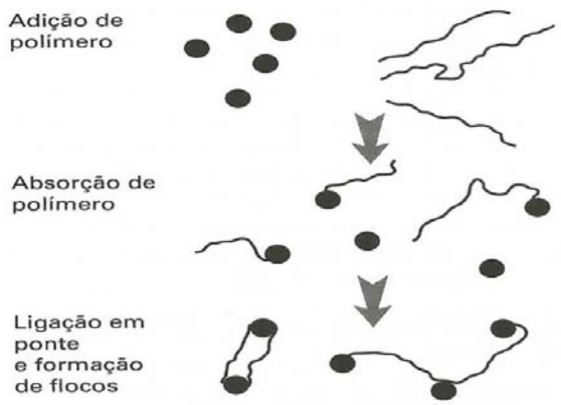

FIG. 1 FLOC FORMATION WITH THE USE OF POLYMERS SOURCE: RICHTER, 2009.

However, an excessive dose of polymer prevent the formation of these linkages due to the lack of ionizable sites available (LIBANIUS, 2008, p. 125-126).

The application of polymers for the clarification of raw water offers several advantages, such as elencam Richter (2009) and Libanius (2008):

- Adding size, density and strength of the flocs formed;
- Increase the production of treated water and the size reduction of flocculation and decantation units in an ETA;
- Contain the dosage of coagulant metal employed in water treatment and their respective drawbacks;
- Applied as coagulation or flocculation auxiliaries, increase the rate of sedimentation of the flocs and increase their resistance to the effect of shear forces caused by hydrodynamic flow of fluid;
- Increased filter life;
- Reduction of sludge volume and better conditions of dehydration this;
- Reduced spending alkalinizing to correct the final pH of the water, since lower doses of coagulant metal minimize pH drops clotting.

The polymers also exhibit the best effect in removing dissolved organic matter when compared to metal coagulants, and do not have action dependent on pH and not raise the conductivity of the water is clarified, since the load of dissolved ions is less (CHANG; CHIANG; TANG; CHAO; HSING, 2005).

For synthetic polymers, the fact that no investigation into their effects on living organisms, and reported drawbacks such as the relatively high cost of production and low biodegradability of the compound, limited their application in water treatment. Moreover, there is concern about the toxicity of the main polyelectrolyte monomer, since, during manufacture, these substances can acquire impurities such as acrylamide monomer, which can cause adverse health. Countries like Japan, Switzerland not allow the use of polymers in water treatment, as France and Germany governing its use at low doses, since the polymers are almost totally removed from the water during treatment. In the case of acrylamide, the residual content in water should not exceed 0.05%, for polyDADMAC (polydiallyldimethyl-ammonium chloride) the maximum allowable monomer content is 0.5% and the polyethyleneimines are not generally used to treat drinking water, being reserved for effluent treatment (RICHTER, 2009; Libanius, 2008; GRAHAMA; GANGA; FOWLER; WATTS, 2008; NDABIGENGESERE; NARASIAH; TALBOT, 1995).

Already coagulants and natural polymers are mainly polysaccharides or proteins, often derived from sources medicinal popular. In water treatment are productive, highly biodegradable and capable of providing treated water without pH change. Use these coagulants goes back a long time ago, and now scientists have identified several types of plants for this purpose as well as for the treatment of industrial effluents (YIN, 2010).

When introduced in water treatment, being of natural or synthetic origin, attention should be paid to possible residues of these compounds in the water that is carried to the consumer. Thus, natural polymers are alternatives to replace potentially dangerous products public health as well as being readily obtained without the use of complex chemical processes and present a generally low cost (DI BERNARDO; DI BERNARDO, FROLINNI, 2000).

The following are the main sources of natural polymers and coagulants, coagulants used as primary or auxiliary, the process of clarification of raw water in water treatment.

Nirmali

AS. potatorum (nirmali) is a small-sized tree, found in central and southern India, where it is used to clarify surface water for over 4000 years, indicating that the first natural coagulant used for water treatment and is still used today in villages India for this purpose (BABU; Chaudhuri, 2005; Yin, 2010).

Chaudhuri and Babu (2005), the test performed with seeds nirmali as coagulant, indicate that seeds of S. potatorum contain materials which can serve as a coagulant, removing turbidity, bacteria and viruses from water.

Seed extracts nirmali are anionic polyelectrolytes destabilizing the particles in water through chemical bridges. Studies have established that the extract contains lipids, carbohydrates and alkaloids presenting the carboxyl and hydroxyl groups, which increase the clotting ability. It is believed that the presence of hydroxyl groups along the polymer chain provides abundant adsorption sites leading to formation of chemical bridges (YIN, 2010, p. 1 439).

Moringa Oleife+ra

The Moringa oleifera is the most studied natural coagulant on scientific research, being used as a clarifying agent in water treatment in lieu of metal coagulants such as aluminum salts and iron. It comes from a tropical tree found in Asia, Africa and Latin America, whose seeds contain an edible oil and water-soluble substance. African rural communities use their raw seed to clear cloudy water of the river. In previous studies, the moringa oleifera proved to be an effective natural coagulant and can be used in water treatment by applying a peel or dried seeds, which is extracted from the edible vegetable oil and coagulant (YIN, 2010; NDABIGENGESERE; NARASIAH , TALBOT, 1995; RICH et al., 2010).

Ndabigengesere, Narasiah and Talbot (1995) in a study with moringa, ascribe its activity cationic coagulant proteins densely charged and water soluble having a molecular weight of about 13 kDa, acting through the mechanism of charge neutralization and adsorption .

Extracts from the seeds of Moringa Oleifera may reduce from 80.0 to 99.5% of the turbidity and suspended solids from raw water, in addition to removing the bacteria in the order of 90 to 99%, and 90% of cercariae (Schistosoma mansoni) water used by inhabitants of the Sudan (MUYBI; e VISION, 1994, apud RICO et al., 2010; OLSEN, 1987, apud RICO et al., 2010; KALOGO et al., 2001). Added to these effects, the jug hardly affects pH, conductivity, and alkalinity concentrations of cations and anions of water; to perform, requires no adjustment of pH and alkalinity of the medium, such as coagulants metal; does not cause corrosion problems piping, and produces less volume of sludge compared to alum, reaching a level of up to 5 times lower than the metal salt (NDABIGENGESERE; NARASIAH, 1998; RICH et al., 2010).

According to the researchers, the greatest obstacle to effective adoption of Moringa in treating drinking water and wastewater is a lack of adequate supply of seeds for this purpose. The solution to this problem could be the tree intensive cultivation in tropical countries and can therefore be consumed worldwide (NDABIGENGESERE; NARASIAH; TALBOT, 1995).

Tannins

Tannins are plant secondary metabolites occurring in leaves, bark and fruit polyphenol compounds being obtained from plants such as acacia. Have been used to treat drinking water, and wastewater and industrial wastewater. However, reports on the effect of tannins on human health has limited its application as natural coagulants for water treatment, where the tannins could replace coagulating due to its chemical structure phenolic groups of anionic nature which can be deprotonados and form phenoxide stabilized resonance, allowing coagulation (YIN, 2010; OZACAR; SENGIL, 2003; SCHOFIELD; MBUGUA; PELL, 2001).

Studies with tannins as coagulant applied to the clarification of raw water reveal that the effectiveness of these substances is dependent on the chemical structure of the plant from which it was extracted and the degree of modification of tannin (OZACAR; SENGIL, 2003).

When comparing the results of tannins applied to the process water clarification as coagulant aids and as the coagulation aluminum sulphate, there was a greater effect of these compounds when used as aids in coagulation than as a primary coagulants, since possible to reduce the amount of metal salt applied in the process significantly, and their ability to form sludge more easily when applied as an auxiliary make the process more effective filtration (OZACAR; SENGIL, 2002).

In surveys, Sciban et al. (2009) used chestnut oak and for the clarification of muddy water, with 80% efficiency and 70% respectively in low turbidity water. Already Beltran-Heredia and Sánchez-Martín (2008) proceeded clarification of raw water from a treatment plant using flocculant derived tannins, commercially called TANFLOC belonging to Brazilian company TANAC. The product is obtained from the bark of the acacia tree common in Brazil, and tannin-based compound, consisting of flavonoid structures with an average molecular weight of 1.7 kDa, and positively charged nitrogen in its structure, as shown in Fig. 2. In the research, the efficiency of TANFLOC in water clarification process not related to the temperature; allowed the effective removal of BOD, COD, turbidity levels (up to 80%), with application of 40 mg L-1, and removing about 30% of anionic agent tensioativo, and generate little sludge volume and being biodegradable.

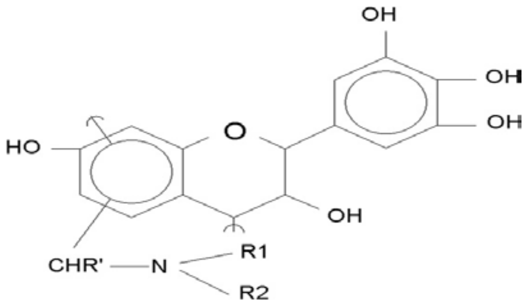

FIG. 2 POSSIBLE STRUCTURE TANFLOC, A TANNIN. SOURCE: SÁNCHEZ-MARTÍN; BELTRÁN-HEREDIA; SOLERA-HERNANDEZ, (2010)

Cactáceos

The application of species of cactus for water treatment is quite new in comparison with other natural coagulants such as nirmali and Moringa oleifera (Yin, 2010). According to Zhang et al. (2006), cactáceos have received great attention in recent years due to their chemical and structural composition, nutritional components and medical applications, such as protein, amylose, malic acid, resins, vitamins and cellulose.

The most studied genera of cacti for water treatment are the Opuntia, associated with its medicinal properties and source of food, and the cactus latifaria, which has also been used successfully as natural coagulant (YIN, 2010).

Saenz, Sepulveda and Matsuhiro (2004) attributed the clotting ability of Opuntia the presence of mucilage, a complex with viscous large water retention capacity, made of carbohydrate molecules such as arabinose, galactose, lrhamnose, xylose and galacturonic acid, and stored in internal and external parts of the cactus. Cactáceas having cladodes (modified stems that can make the gas exchange with the environment, since the leaves are adapted for minimal loss of water in photosynthesis) containing mucilage.

According to Miller et al. (2008), the ability Opuntia spp coagulation occurs through the mechanism of forming chemical bridges, through hydrogen bonds or dipole interactions. The flakes formed in the study are long and thin, mucilage derived from the common species of cactus, aloe vera and okra. The authors attribute the polygalacturonic acid, component present in mucilage, as responsible for the formation of chemical bridges in flocculation.

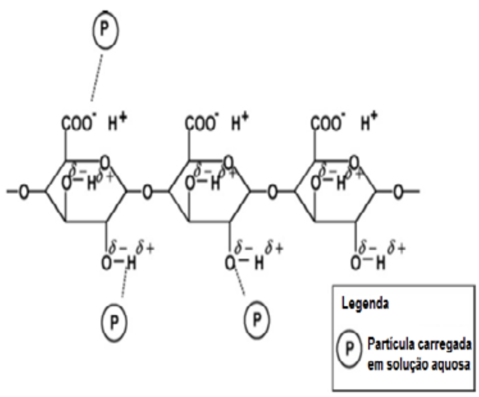

FIG. 3 STRUCTURE OF GALACTURONIC ACID, POLYSACCHARIDE CONSTITUENT SPECIES CACTÁCEOS. (FEATURED IONIZABLE SITES FORMED IN AQUEOUS SOLUTION) SOURCE: YIN (2010)

The polygalacturonic acid structure, shown in Fig. 3, indicates a chain anionic be due to partial deprotonation of the carboxyl and hydroxyl groups in aqueous solution, involving chemisorption between the charged particles and these groups (YIN, 2010).

Diaz et al. (1999) used the cactus latifaria as the primary coagulant for the removal of turbidity from synthetic water, obtaining good results. In this study, the authors made a comparison of the use of moringa, prosopis juliflora and aluminum sulfate polymer with cactus, getting in the latter case the best results.

A study by Zhang et al. (2006), using polymer extracted from cactus opuntia as the primary coagulant, concluded that this presents great turbidity removal efficiency, which can be compared to the action of moringa as a coagulant. Compared to metallic aluminum chloride coagulant, the authors obtained better results than removal of turbidity and total organic carbon in the polymer cactus, for the same dosage of the coagulant metal. With the results, the authors attribute the cactus as a substitute for aluminum chloride in water treatment process, and indicate cactáceos as potential application in large scale, even though its development is limited to laboratory scale.

Lenz, Zara and Thomazini (2011) studied the efficiency in terms of removing turbidity of raw water from the river, the extract obtained Mandacaru cactus (Cereus jamacaru), as an aid to coagulation and flocculation aluminum sulfate. The polymer added to the process mixture rapidly, after the metal coagulant, allowed the removal of turbidity higher than that obtained by the aluminum sulphate without the use of the extract.

The use of cactus extract Mandacaru possible the formation of flakes of larger size than that shown by aluminum sulfate, increasing the settling velocity of the aggregate material. Thus, it is expected to reduce the time of flocculation and decantation in an ETA, making the process faster and greater production of treated water. The use of the extract also caused no significant variation in pH and alkalinity of the clarified water (LENZ; ZARA; THOMAZINI, 2011).

The authors emphasize that the extract Mandacaru is viable as an aid in the treatment of water. Developed from a natural source of cheap and abundant in the country, this product can generate socio-economic impacts, such as generating income for small farmers and alternative planting in the Brazilian semiarid region.

Other Natural Coagulants

The gumbo was employed by Lima (2007) as an aid flocculation and filtration treatment of water and wastewater, enabling better quality of water decanted. Made it possible to reduce the dosage of aluminum sulphate, and the cost of applying the polymer okra is less than the cost of other natural and synthetic polymers used as assistants or flocculation and filtration, water treatment and sewage.

Chitosan is a compound biodegradable, not toxic and is a linear polymer of high molecular weight cationic, derived from chitin from shrimp shells and the shells of marine crustaceans, and shows an effective coagulant for the treatment of drinking water of low turbidity, requiring lower dosages than for alum. The sludge generated does not contain potentially harmful metallic elements living species, facilitating the process of disposing of it (SPINELLI; SENS; FÁVERE, 1999).

Chitosan is efficient in cold water at very low concentrations, producing reduced volume of sludge, which is easily degraded by microorganisms. Act by two coagulation mechanisms: a charge neutralization (has positively charged amino group) and bridging. Results already described in the literature indicate that chitosan can be a potential substitute for metallic salts and synthetic polyelectrolytes in treating drinking water and waste (RENAULT et al. 2009).

Bernardo study by Di, Di Frollini and Bernard (2000) using corn starch and cationic cationic waxy cassava (essentially 100% amylopectin), and cationic synthetic polymer, demonstrated that cationic waxy cassava starch was more efficient than the other two polymers in removing turbidity and apparent color, the settling velocities studied. Furthermore, the cationic cornstarch generated better results than those obtained with the cationic synthetic polymer. The authors attribute the good results obtained with the cationic tapioca starch for its high molecular weight, and mechanism of action have been the predominant adsorption and bridging.

Conclusions

Coagulants and polymers obtained from many natural sources, when applied as coagulants primary or auxiliary coagulation / flocculation present as viable and inexpensive alternatives for the replacement or reduction of the dosage of the coagulant metal employed in the process of treating water, and respective drawbacks associated with these salts.

In general, these products have efficiency in removal of turbidity of water, comparable or superior to that achieved by metal coagulants, spending a lower dosage. These products proved not dependent on temperature or pH correction and alkalinity of the water to work efficiently.

In terms of action on the physicochemical characteristics of the clarified water, the natural polymers and coagulants show cause little variation in pH, alkalinity, conductivity and concentration of cations and anions, and allow more effective removal of BOD and COD, and , in some cases microorganisms.

Being from natural sources, these compounds can generate value-added products, presenting itself as a new source of income.

However, despite all the associated benefits, natural coagulants and polymers should be effectively applied to the process of water clarification in scale only after undergoing tests where certifying its non-toxicity, biodegradability and viability.

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