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Chapter

Physicochemical Insights of the Organic Matter Particles Dispersed in Wastewaters Induced by Bio-Polyelectrolytes

Carlos A. Quintero Gonzalez, Eduardo A. López-Maldonado and Mercedes T. Oropeza-Guzmán

Abstract

The turbidity and color of the water are mainly caused by colloidal particles. These particles remain in suspension for a long time and can even pass through a very fine filter medium, since they do not have a tendency to agglomerate. Due to this, polyelectrolytes such as chitosan have been used in coagulation-flocculation processes because they dissociate into charged species in solution and these contribute to charges or dissociable groups which are covalently bound to its structure. With the zeta potential measurements (ζ) vs. pH and particle size, the ideal dose of bio-polyelectrolyte was determined with which, the isoelectric point (IEP) was reached, generating electroneutrality in the system, removing 92% of the chemical oxygen demand (COD). The results discussed here represent a sustainable alternative to the water reuse and sanitation problem of the fish processing industry. The use of bio-polyelectrolytes offers that the by-products obtained from the coagulation-flocculation process can be reused and recovered for other uses.

Keywords: turbidity, colloidal particles, chitosan, coagulation-floculation, isoelectric point, bio-polyelectrolyte

1. Introduction

The problems of water availability have their origin in the physiographic and climatic distribution, the contamination of surface and underground waters and the accelerated increase in demand for the different uses. For example, the reuse of water in agriculture is a well-known practice in the world; however, reuse in industry, municipal services, secondary uses, and aquifer recharge is only practiced to a limited extent. Given the imminent shortage of the resource in some areas of the country, the reuse of water is considered as an alternative supply; however, to reuse the water it is necessary to meet a certain quality.

Among the main parameters that define water quality are turbidity and color, attributed to the presence of colloidal particles and dissolved organic matter. These particles remain in suspension for a long time and can even pass through a very fine filter medium [1] since they do not have the tendency to agglomerate.

In particular, coagulation and flocculation processes have shown their usefulness in eliminating colloidal particles in water. On one hand, coagulation aims to neutralize the surface charges of suspended particles, and thus facilitate their agglomeration. In practice, this procedure is characterized by the injection and rapid dispersion of both chemical and organic products [2]; on the other hand, flocculation aims to favor, with the help of slow mixing, the contact between destabilized particles. Thus, the particle agglomerate forms a "floc" that can be easily eliminated by the decantation and filtration procedures [3].

Polymers have been used in coagulation-flocculation processes for water purification for at least four decades [4]; compared to alum, some of the advantages derived from the use of polymers in water treatment are:

- use of a lower dose of coagulant.
- less generation of sludge.
- less increase in the ionic charge of the treated water.
- cost reduction of 25–30%.

The polymers used in water treatment are soluble in water and mainly synthetic in nature, although some natural products may be of interest. Polymers are widely characterized by their ionic nature: cationic, anionic, and non-ionic. Strictly ionic polymers are called polyelectrolytes [5].

The most important characteristics of polymeric flocculants are their molecular weight (MW) and, in the case of polyelectrolytes, their charge density. All polymers used as flocculants in water treatment must be soluble in water.

In an aqueous solution, polymers very often assume a random folded configuration. The length of the polymer depends on the interaction between its segments, if there is an appreciable repulsion between segments then the polymer expands a little.

The best-known example is polyelectrolytes, where the segments are charged. In this case, the polymer can expand significantly and there are significant effects on ionic strength. At higher ionic strength, the repulsion between charged segments is "filtered" by ions in solution, so the expansion of the molecule would not be as great [6].

Due to this aspect, the polyelectrolytes are suitable for use in the coagulation-flocculation process and their use as coagulants in water treatment and sludge thickening. Thus, it is proposed to study the influence of bio-polyelectrolytes (BP), in the aggregation of particles of organic matter dispersed in water. The intention is to eliminate the contamination matrix that is generated in fish packing plants that currently lack water treatment systems. As an additional benefit, it is proposed that the residual sludge does not become waste for special handling, but rather has a reuse value taking advantage of its content. In this work, the performance of bio-polyelectrolytes as a sustainable alternative for the sanitation and reuse of treated wastewater is evaluated. The main factors that affect the performance of chitosan in destabilizing and aggregating colloidal particles of organic matter is discussed.

2. Experimental

The experimental protocol was proposed in three stages derived from taking a sample of the residual water generated in a fish packing company. In the first stage, the quality of the wastewater from the fish packing process was evaluated through measurements of chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), etc. In addition, the biodegradability of the contaminants contained in water was evaluated by means of a solid model. In the second stage, the coagulation-flocculation windows (ζ vs. pH) were determined and in the third part, the factors of pH, ζ and polyelectrolyte concentration were correlated in order to evaluate the organic matter separation process in the wastewater of the fish packing plant measuring turbidity, COD (Horiba Coda-500-A), COT (Hatch colorimetric measurement), TN (Hatch colorimetric measurement) and TP (NMX-AA-029-SCFI-2010).

2.1 Coagulants-flocculants agents

Polyelectrolytes of both natural and synthetic origin can flocculate colloids. Polyelectrolytes are polymers with a high molecular mass, which normally contain ionizable functional groups. Typical examples of polyelectrolytes are shown in **Table 1**.

In a simpler way, a polyelectrolyte (PE) can be defined as a polymer that dissociates into charged species in solution. Normally, the term polyelectrolyte is used for polymeric systems that consist of macroions, that is, macromolecules that carry charges or dissociable groups covalently bound to their structure, which in turn must be compensated for counter ions of opposite charges to guarantee the electroneutrality of the system [7].

2.2 Measurement of zeta potential (ζ)

In the zeta potential measurement, the Anton Paar Lite sizer 500 equipment was used, in which a small amount of sample (100 μL) is injected into a univette cell containing two electrodes that are used to create an induced electric field. Once the electric field is applied, the particles move towards the anode or the cathode depending on whether the surfaces are positively or negatively charged. The direction of motion indicates positive charge versus negative charge. The speed of the particle's motion is used to calculate the magnitude of the charge.

2.3 Measurement of particle size (DLS)

For the measurement of the particle size, the Anton equipment for lite sizer 500 was used, which uses the dynamic light scattering technique (DLS), which indicates the mean value of the intensity distribution called the "Z average" and the polydispersity index with which the width of the distribution is described.

2.4 Jar-test in fish packing wastewater

The jar technique was carried out in order to determine biopolyelectrolyte dosages among other parameters. In it, the coagulation-flocculation processes were simulated at the laboratory level. Its versatility lies in using a series of jars at the same time with variations in stirring speed (rpm). Chemical and hydraulic factors influence this process. Among these we have:

- pH;
- temperature;
- coagulant concentration;

- sequence of application of substances;
- degree of agitation;
- sedimentation time.

The pH plays a very important role in the study of the coagulation-flocculation phenomena. This is how a part of the charge of the colloidal particles that have absorbed OH- ions remains destabilized in the colloidal suspension.

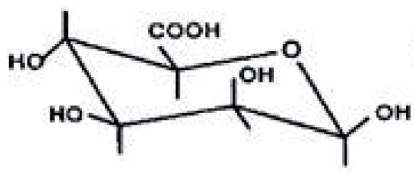
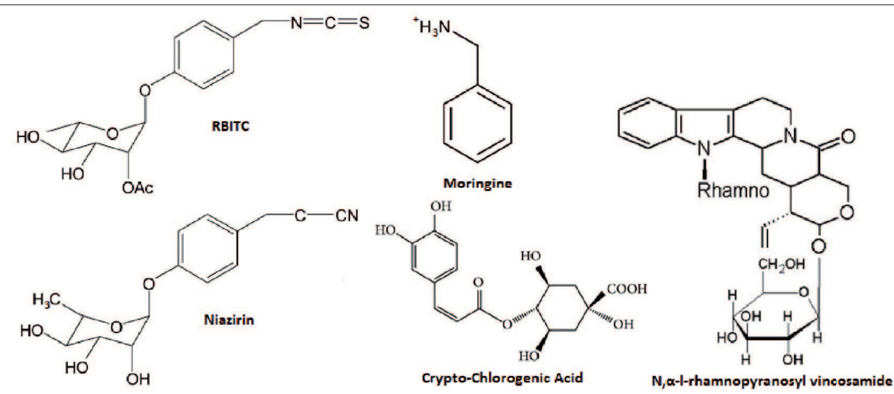
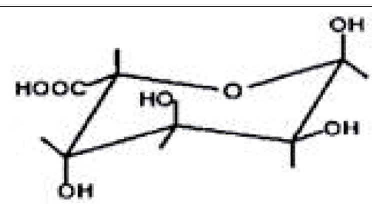
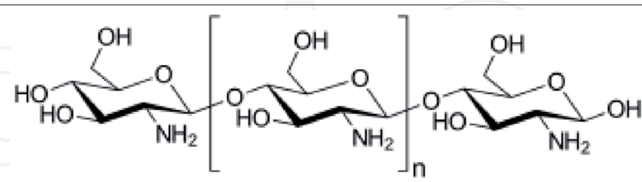
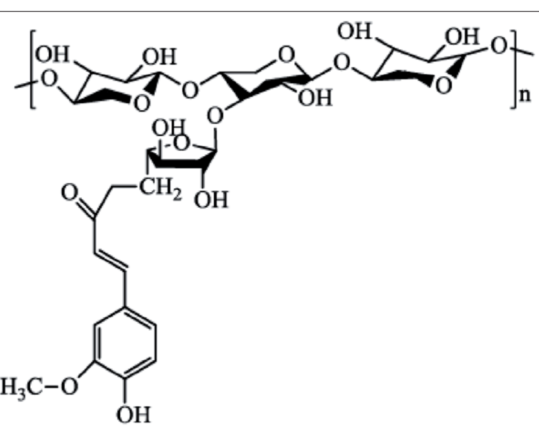
Organic flocculants	**Structure**
Manuranic acid	
Moringa	
Gluconic acid	
Chitosan	
Corn gum	

Table 1.
Organic flocculants.

Since the jar test is only a process simulation, it is necessary to maintain operating conditions such as rapid mixing, which aims to create turbulence or movement necessary to create the necessary contact between the bio-polyelectrolyte and the colloidal particles of the water, in order to neutralize their charges, destabilize them and make them agglomerate in a short period of time. The rapid mixing time is directly dependent on the nature of the coagulant. For example, polymers distribute more slowly than metal ions due to their chain length, therefore they will require a longer time or a greater speed gradient.

800 mL of residual water was taken, then additions of 20, 40, 80, and 100 mL of a chitosan solution were made at 1,000 ppm and the time and rpm that were used are 5–10 min, 30–100 rpm [8].

Generally, the slow mixing time does not exceed 15 minutes. Since an excessive time can create heating of the sample causing more efficient flocculation, but at the same time poor sedimentation, the release of gases dissolved in water occurs, forming bubbles that adhere to the flocs and make them float [9]. In this process, it is recommended 3–15 min., 20–40 rpm, finally, a rest of 30 min., which will allow the formed flocs to settle.

3. Results and discussion

The first strategic sampling area was carried out at the entrance of the process with water from the well, taking the NMX-AA-003-SCFI-2019 standard as a sample reference, the total hardness of this water was evaluated in order to identify the presence of salts of calcium and magnesium ions which are responsible for incrustations and can generate failures and loss of efficiency in the processes. In **Table 2**, the results are shown, which indicate that this concentration of salts will not generate any type of interference in industrial processes.

On the other hand, TOC and COD were measured in the wastewater from each process in order to quantify all the carbon present in the organic matter that dissolves or can be suspended in the water and thus, establish the amount of oxygen consumed in the total chemical oxidation of organic constituents present in the water through COD values. Complementary to the characterization of

Parameter	Well water	Waste water sanguaza	Waste water flour process
Temperature	20	4	30
PH	7.017	7.4	6.9
Zeta potential (mV)	1.8	−18.8	16.3
Turbidity (NTU)	12	386	737
Total suspended solids (mg/L)	7	302	517
Total handness (mg/L)	20–50	—	—
COD (mg/L)	—	305	434
TOC (mg/L)	—	209	317
TN (mg/L)	—	306	297
TP (mg/L)	—	284	227
Size particle(nm)	492	1.022	1.196

Table 2.
Physicochemical characterization of wastewater.

the wastewater, the parameters of TN and TP were also evaluated. Because the wastewater exceeds the maximum permissible limits of contaminants in water, a treatment must be carried out which reduces the degree of contamination, since it has a large contribution of essential nutrients for the growth of organisms, such as nitrogen and phosphorus. These can stimulate the growth of macro and photosynthetic microorganisms in harmful quantities, which would trigger a eutrophic environment in water bodies.

On the other hand, the parameter ζ was measured because it is directly related to the ionic properties of the dissolved solids present in the wastewater.

Solid/aqueous interfaces suffer from a pH-dependent surface charge, that is, they tend to have a positive charge at acidic pH and a negative charge at basic pH. The sign and magnitude of the surface charge govern the adsorption of ionic species in solution and the physical properties of dispersions (e.g., their stability against coagulation). That is why, in the coagulation process, the suspended solids are destabilized by varying the pH of the water and this tends to zero when it approaches the isoelectric point. A simple variation of pH could be enough to stabilize or destabilize the solids that are dissolved in the water [10]. Therefore, the pH value can control both the charge density of the bio-polyelectrolyte and the surface charge of the suspended particles (**Figure 1**).

The surface charge of both coagulants and colloids in water depend on pH and their behavior having a great influence and performance in the coagulation-flocculation processes, which is why ζ measurements are required to characterize the colloidal system and understand repulsion and aggregation between colloidal particles [11].

The dosing strategy was determined by measuring the ζ of both the organic matter colloids and chitosan, and also by the optimum pH value to reach the isoelectric point. The purpose of the chitosan dose is to reduce interparticle repulsion by neutralizing negatively charged particles of organic matter.

In general, the electro-neutrality zone for the chitosan-organic matter system is below pH 6 as shown in **Figure 2**. Working at this pH improves the efficiency of the coagulation-flocculation process, since chitosan achieves a higher charge density in an acid medium, therefore its concentration can be decreased.

The best clarification of the wastewater was at pH 5.9, at this pH the positive charges in the chitosan lead to an increase in the hydrodynamic diameter (Dh) due to the repulsion between the intramolecular protonated amino group and this is beneficial in the effect of dosing in turbidity removal efficiency [8]. Furthermore, at this pH, the system reaches the maximum surface contact between chitosan and organic matter in the wastewater [12].

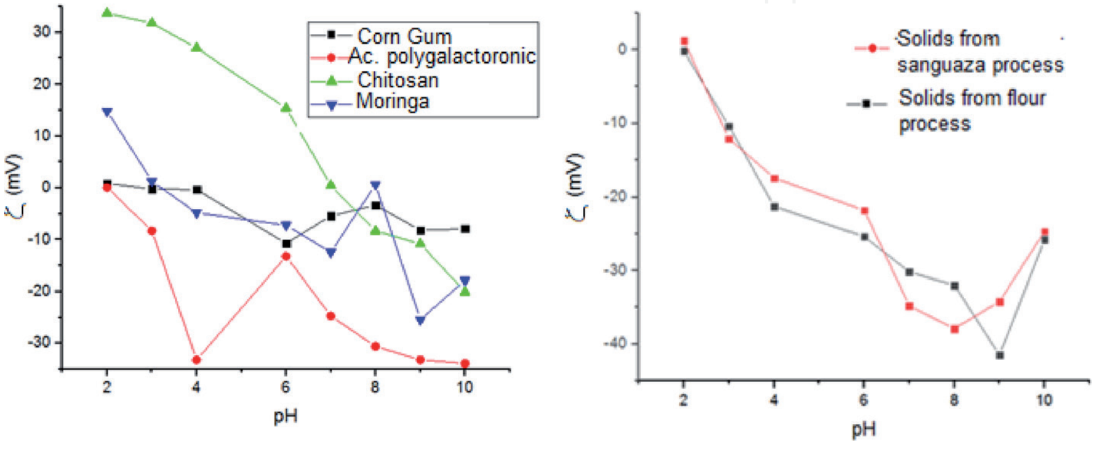


Figure 1.
Ionic behavior of different polyelectrolytes at different pH values.

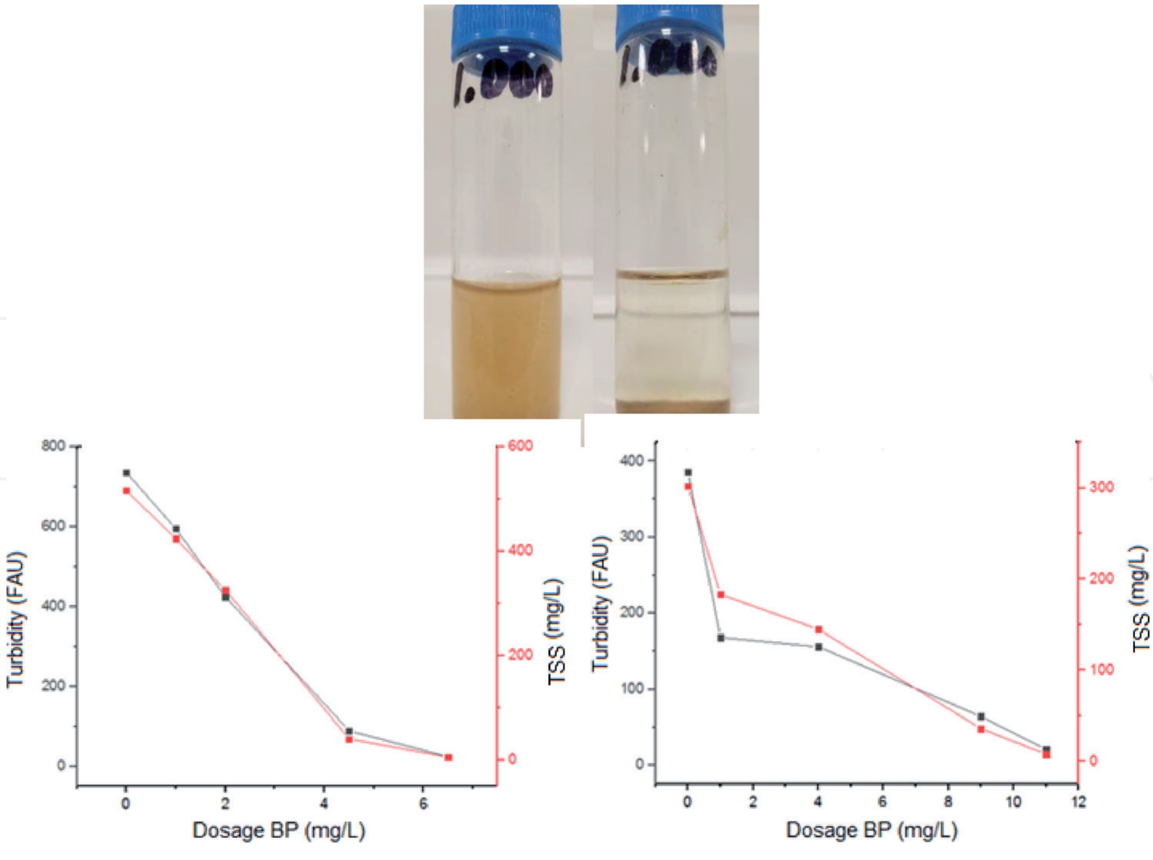


Figure 2.
Effect of chitosan dosage on turbidity removal efficiency. (A) Sanguaza process; (B) flour process. BP: Bio-polyelectrolyte, TSS: Total Suspended Solids.

The optimal dose of chitosan was 10 ppm, thus obtaining a turbidity removal efficiency of around 97% at this dose, the surface charges of the organic matter particles were neutralized by chitosan molecules resulting in a ζ value close to zero.

Particle size influences many properties of particulate materials and is a valuable indicator of their quality and performance. Larger, spherical particles will flow more easily than small ones, but smaller particles dissolve more quickly and result in higher suspension viscosities than large particles. Smaller particle sizes and a high surface charge (ζ) typically improve the stability of the particles in solution [13–15].

For the measurement of the particle size, the dynamic light scattering technique (DLS) was used, as can be seen in **Figure 3**, as the chitosan dose is increased, the size of the particles in solution increases due to the adsorption of organic matter by the active functional groups of chitosan and in turn the decrease in the ζ. This indicates that the system is unstable and that this in turn, as the dose increases, will reach the isoelectric point, generating electroneutrality in the system. Therefore, the suspended solids by gravity and their own weight will settle.

The performance of the coagulation-flocculation process was evaluated with different parameters such as COD, COT and TSS. In addition, different doses of polymer through profiles of ζ and pH were evaluated (**Figure 4**).

Electro-neutrality occurs at $\zeta = -0.3$ at pH = 5.7 and required a dose of 100 ppm of chitosan. At this point, the lowest turbidity was observed in the supernatant (4 FAU) compared to the original turbidity (369 FAU) in the wastewater suspension at room temperature. Furthermore, it can be observed that the floc formation is of higher quality when the isoelectric point is reached. For the COD measurements, the potassium permanganate ($KMnO_4$) procedure was chosen, in which a known amount of KMnO4 is added, which is assessed with a primary calcium oxalate standard. The excess KMnO4 reacts with the excess oxalate and finally, the excess oxalate is titrated with the permanganate and this reaction was carried out at elevated temperature to accelerate the process, obtaining an efficient coagulation-flocculation process, removing a total of 93% of total COD and 100% of TSS in jar tests (**Figure 5**).

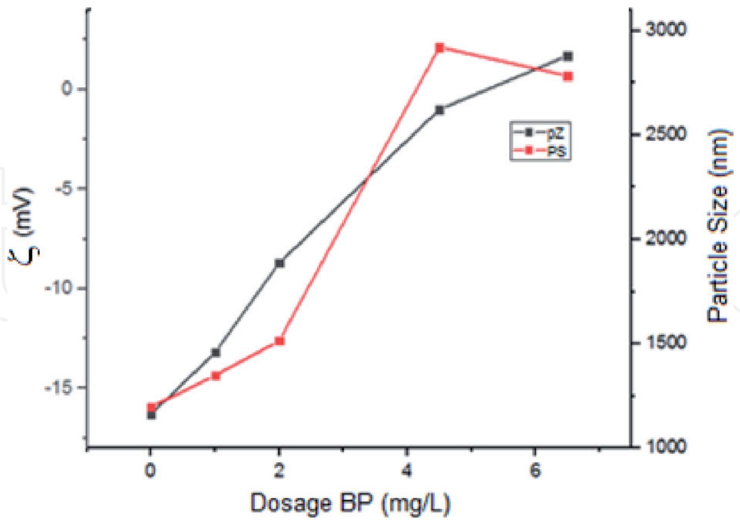


Figure 3.
Effect of chitosan dosage on particle size and Z potential.

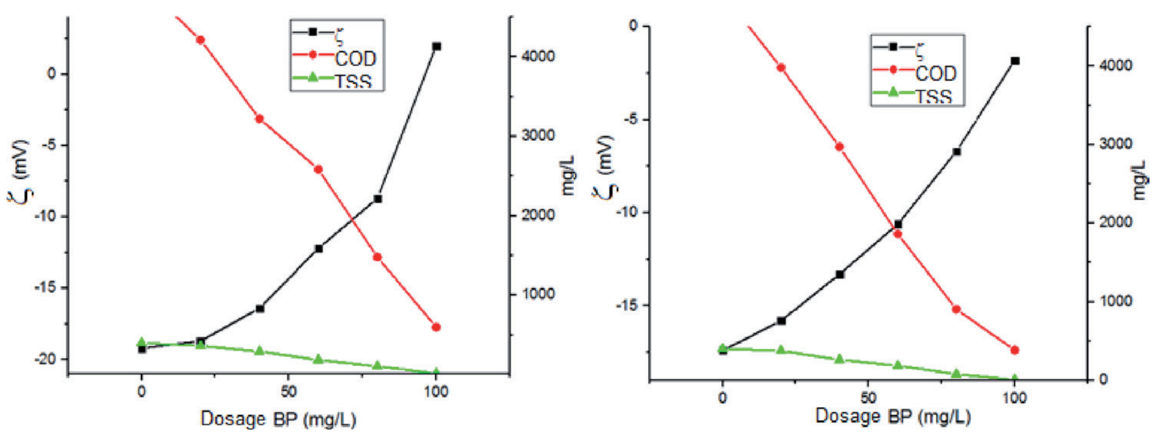


Figure 4.
ζ and evaluation of water quality parameters as a function of chitosan dose in jar tests. (A) Sanguaza process; (B) Flour process. z: zeta potential, BP: Bio-polyelectrolyte, Chemical Oxygen Demand, TSS: Total Suspended Solids.

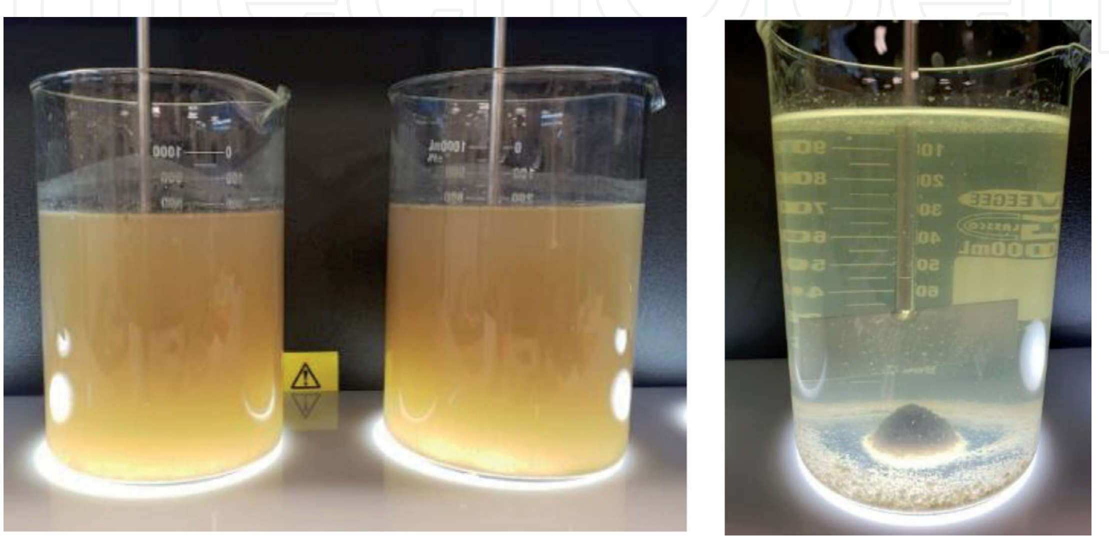


Figure 5.
Bio-polyelectrolyte contaminant removal efficiencies.

Parameter	Raw water	Filter water	Coagulation-flocculation treatment	% Removal
COD	12,800	4,920	385	92
TOC	2,394	976	198	76
TN	1,854	574	370	35
TP	1,620	487	164	66
TSS	579	397	0	100
Turbidity	595	405	0	100

Table 3.
Evaluation of the quality of the wastewater treated by coagulation-flocculation process.

The main objective of coagulation-flocculation, as it is a primary treatment in wastewater, is to eliminate the suspended solids present in the water as shown in **Table 3**. When carrying out a good dosage of polyelectrolytes, the removal efficiency can be as high as 100%. In the best dose of chitosan, the coagulation-flocculation stage leads to the sedimentation of the suspended pollutants, reaching 92% and 76% removal of COD and TOC, respectively. However, the effluent has a high content of TN and TP represents a risk of eutrophication in the environment, which makes it necessary to couple the coagulation-flocculation process to a secondary treatment.

4. Conclusions

For the treatment of wastewater containing organic matter in suspension, such as a fish packing plant, to be effective, it is necessary to know both the chemical and physical properties of the suspended solids and the water to be treated. The addition of chitosan to wastewater with a high content of organic matter (fish packing plant), triggers a series of processes that begins with the hydrolyzation of the chitosan, followed by the destabilization of the particles by simple specific adsorption of the hydrolysis products and finally sedimentation and separation of organic matter from water. It should be noted that the cationic behavior of chitosan chains allows a better interaction between suspended particles and chitosan itself. Considering the above, the use of biopolyelectrolytes in the coagulation-flocculation process efficiently removes the suspended solids allowing high efficiencies in the removal of COD and TOC, it is worth mentioning that an excess in the dose of bio-polyelectrolyte will re-suspend the settled solids increasing operating costs. This work contributes to the objectives of sustainable development allowing the sanitation and recovery of wastewater using coagulant-flocculating agents that are eco-friendly with the environment.

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References

[1] Comisión Nacional del Agua (CONAGUA) (2009), Situación del subsector agua potable, alcantarillado y saneamiento. Edición 2009, México, SEMARNAT, 167p.

[2] Conagua, Semarnat. Estadísticas del Agua en México. Edición 2013. México. 2014.

[3] Jiménez, B.; J.C. Durán, J. M.; Méndez, C. Calidad. En: Jiménez C., M.L. Torregrosa y L. Aboites (Eds.). El Agua en México: cauces y encauces. AMC-Conagua. México. 2014

[4] Acosta-Zamorano, D.; Macías-Carranza, V; Mensoza-Espinosa, L.; Cabello-pasini, A. Agrociencia 2013, 47, 767-779

[5] O.G. Zavala Garcia, M.T. Oropeza-Guzman, W.M. Arguelles Monal, E.A. Lopez-Maldonado, Design and mechanism of action of multifunctional BPÉs with high performance in the separation of hazardous metal ions from polluted water Part I: chitosan-poly(vinylcaprolactam) and its derivatives, Chem. Eng. J. 359 (2019) 840-851.

[6] Edeline, F. Tratamiento fisicoquímico del Agua; Red Hen Press: California, 1997; p 158.

[7] López-Maldonado EA, Oropeza-Guzman MT, Jurado-Baizaval JL, Ochoa-Terán A. Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements. Journal of Hazardous Materials 2014; 279: 1-10

[8] López-Maldonado, E.A., Oropeza-Guzman, M.T., 2021. Nejayote biopolyelectrolytes multifunctionality (glucurono ferulauted arabinoxylans) in the separation of hazardous metal ions from industrial wastewater. Chem. Eng. J. 423 (28), 130210.

[9] Stuart, M.; Lapworth, D.; Crne, E.; Hart, A. Review of Risk Potencial Emerging Contaminants in UK Groundwater. Sci. Total environ. 2012, 416, 1-21.

[10] Sze, A., Erickson, D., Ren, L. and Li, D., Zeta potential measurement using the Smoluchowski equation and the slope of the current-time relationship in electroosmotic flow, Journal of colloid and interface science, 261, pp. 402-410, 2003.

[11] Feng, X.; Leduc, M.; Pelton, R. Colloids and Surfaces A: Physicochem. Eng. Aspects 2008, 317, 535-542.

[12] Suarez, K; Ponce, S; Lopez, T, Eco-friendly innovation for najayote coagulation-floculation process using chitosan: evaluation through zeta potencial measurements. J. Chemical Engineering. 2014, 536-542.

[13] Sze, A., Erickson, D., Ren, L. and Li, D., Zeta potential measurement using the Smoluchowski equation and the slope of the current-time relationship in electroosmotic flow, Journal of colloid and interface science, 261, pp. 402-410, 2003.

[14] López-Maldonado, E.A., Zavala García, O.G., Cruz Escobedo, K., Oropeza-Guzman, M.T., 2017. Evaluation of the chelating performance of biopolyelectrolyte Green complexes (NIBPEGCs) for wastewater treatment from the metal finishing industry. J. Hazard Mater. 335, 18-27.

[15] E.A. López-Maldonado, M.T. Oropeza-Guzmán, A. Ochoa-Terán, Improving the Efficiency of a Coagulation-Flocculation Wastewater Treatment of the Semiconductor Industry through Zeta Potential Measurements, J. Chem. 2014 (2014) 1-10.