Chapter 7

Innovation of Coagulation-Flocculation Processes Using Biopolyelectrolytes and Zeta Potential for Water Reuse

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Additional information is available at the end of the chapter

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Abstract

The coagulation-flocculation process is one of the conventional technologies used for the treatment of different types of industrial wastewater. The zeta potential is a key parameter that allows to determine the effective pH, the type and the correct biopolyelectrolyte dose to return the water quality using coagulation-flocculation. In this chapter, we present the application of a natural cationic biopolyelectrolyte (chitosan) to make the separation and recovery of cellulose fiber more efficient and to increase the reuse of treated water from the pulp and paper industry. The result of the coagulation-flocculation test at pH 5.4 and a chitosan dose = 10 mg/L shows that the treated water has the following values: biochemical oxygen demand = 150 mg O_2/L, turbidity = 5 FAU, total suspended solids = 2 mg/L, chemical oxygen demand = 200 mg/L and hardness = 250 mg $CaCO_3$/L. The quality of water obtained allows its discharge to a natural water body, in which it is possible to continue with a biological treatment stage, or to reuse the treated water for the manufacture of paper. Additionally, this coagulation-flocculation process can be coupled to an advanced oxidation process to increase the quality of the water and mineralize the content of organic material.

Keywords: zeta potential, wastewater treatment, biopolyelectrolytes, coagulation-flocculation

1. Introduction

The issue regarding the quality and use of water has several aspects: the first option is the most common and of greater importance, than a simple view, which becomes the vital liquid to survive and perform daily activities. Its quality directly affects the health and well-being of society [1]. The second corresponds to the use of water as the main raw material for the manufacture of some products and the operation of production processes. The interaction of water with the environment is influenced by the water quality that both society and the industrial sector confer on water.

Each type of industry has a particular interest in the care of water quality and its reuse, which is why day by day, they require new strategies to treat and recycle the wastewater they generate in the different production processes [1]. Water quality is affected by various chemical substances that dissolve in water used in each stage of the manufacturing process.

In general, the main pollutants that are identified in the industrial wastewater are suspended particles, organic matter, heavy metals, the hardness of the water and fats and oils [2]. One of the pollutants frequently present in the industrial wastewater is suspended particles or solids. According to the nature of the production processes, the particles in suspension can be organic and inorganic and can be present in different particle sizes. The content of organic matter in industrial wastewater is attributed to the organic compounds (colorants, additives, nutrients, carbohydrates, etc.) that can be biodegradable or difficult to be degraded, and that are incorporated into the water at the time of use [3]. The levels of concentration in which these contaminants or undesirable substances are present in the wastewater are directly related to the operating conditions of the productive processes. The presence of these pollutants in the water causes an impact on the efficiency of the production processes, limits the reuse of water, increases the consumption of clean water, the discharge of the wastewater generated contaminates the water bodies, and this implies sanctions to the industry for exceeding the maximum permissible limits at the effluent discharge point [3].

There is an urgent need of environmentally friendly and cheaper technologies to eliminate the chemical toxicants from wastewater to improve the water quality.

Several methods that have been developed to eliminate these present pollutants from wastewater are as follows: reverse osmosis, solvent extraction, coagulation-flocculation, membrane separation, chemical precipitation, advanced oxidation processes, ion exchange, evaporation, electrolysis [4–6], photochemical [7], activated sludge [8], anaerobic and aerobic treatment [9, 10], electrodialysis [11], ultrasonic treatment [12], magnetic separation [13] and adsorption [14–16].

As part of the integral management of water in the industry, the development of environmentally friendly technologies is involved. In this chapter, we propose one of the strategies to restore the water quality (decontaminate, purify, remove undesirable substances for a specific use), which consists of the application of natural functional polymeric materials in physicochemical/electrochemical systems for the elimination of contaminants [17]. One of the simple and efficient methods for the separation of various types of contaminants is coagulation-flocculation, in which chemical substances are used as synthetic coagulant-flocculating agents (polyelectrolytes) [18]. However, in order to employ the different renewable sources, which are rich in polymeric materials and available in the region, as shrimp waste from the fishing industry will be used as a raw material for the production of functional polyelectrolytes and give it an added value. Due to the type of interactions that occur at a molecular level between the contaminants and the polyelectrolytes in the coagulation-flocculation processes, the zeta

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potential measurements are key to determine the best operating conditions and understand the mechanisms of interface (contaminant-biopolyelectrolyte). In this chapter, the physicochemical characterization of six types of industrial wastewater is presented. Due to the complexity and variety of the contaminants present in these types of wastewater, only the wastewater treatability results of the pulp and paper industry are presented.

2. Experimental

2.1. Wastewater sampling

In this chapter, the physicochemical characterization of six types of industrial wastewater and how to develop a treatment strategy for water recovery and how to add value to the byproducts formed are presented. The wastewater sampling protocol was followed as recommended by Mexican sampling standard (NMX-AA-003-1980). Residual water samples were taken from the nixtamalization industry (nejayote) that is dedicated to the manufacture of corn products and their derivatives. Another sample was collected from a candy factory that generates wastewater with a high content of dyes and suspended particles. The third case corresponds to a company dedicated to the recycling of cellulose and paper, which uses well water for its paper and cardboard manufacturing process. Another type of water sample was collected from the industry that is dedicated to the collection of hazardous waste that contains a greater proportion of oil and water. Finally, there is the sector dedicated to the metalworking industry and the semiconductor industry. Tested parameters were: total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), turbidity, color, particle size, electrical conductivity (EC), zeta potential (ζ), total phosphorous (TP), biological oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC) and total nitrogen (TN). Tests were carried out following the current Mexican standard procedures that are equivalent to those published by EPA (AWWA standard methods, respectively).

2.2. Extraction of chitosan biopolyelectrolyte

Chitosan (Ch) was obtained from waste shrimp shells using the adapted method proposed by the authors Goycoolea et al. [19].

2.3. Zeta potential = f (pH) profiles of the industrial wastewater and chitosan

Zeta Potential from wastewater and biopolyelectrolyte data was recorded on a Stabino Particle Charge Mapping (Microtrac). The measurements were done at ambient temperature in Teflon cuvettes. Influence of pH on the zeta potential behavior of each biopolyelectrolytes was studied within a pH range of 2–11 with 0.1 M NaOH and 0.1 M HCl [20].

2.4. Wastewater coagulation-flocculation tests using chitosan

The performance of cationic chitosan biopolyelectrolyte in the coagulation-flocculation of wastewater from the cellulose and paper recycling industry was carried out using 20 mL of residual water at pH 5.4 and in different doses of chitosan extracted from the shrimp shells.

After each addition of chitosan, the mixture of residual water with chitosan was stirred at 200 rpm for 2 min and subsequently at 50 rpm for 20 min. For the evaluation of the quality of the treated water, a sample of the supernatant was extracted [21].

3. Results and discussion

Tables 1 and **2** show the physicochemical characterization of the six types of industrial wastewater. The values of the main residual water quality parameters such as BOD_5, COD, alkalinity, hardness, pH, electrical conductivity, content of dissolved and suspended solids, settleable solids, temperature, turbidity, nitrogen and total phosphorus, heavy metals are shown. Of these normative parameters, the environmental legislation dictates which ones must comply, considering the type of industry and body of discharge of residual water. Additionally, other non-regulated parameters, which are fundamental to understand and operate the coagulation-flocculation process, such as particle size, turbidity, total organic carbon, biodegradability and zeta potential [21]. The measurement of these parameters is key to implement the design and sequence of an industrial wastewater treatment train to achieve the best quality of treated water.

In all types of wastewater, the regulated parameters exceed the maximum permissible limits, both for their discharge to the water receiving bodies and for their reuse. One of the main pollutants present in industrial wastewater is the content of dissolved and suspended solids, where these can be organic and inorganic depending on the source of the wastewater. Generally, the first stage of a wastewater treatment train consists of the elimination of the suspended particles; this is where the coagulation-flocculation processes are applied. Considering the main interactions that occur between the suspended particles and the coagulant-flocculant agents, the zeta potential is a key parameter to determine the surface charge density of the suspended particles and the polyelectrolytes, as well as the optimum dose to perform the solid-liquid separation of the suspended particles.

Figure 1 shows the $\zeta = f$ (pH) profiles of each type of industrial wastewater, metalworking, candy factory, nejayote, recycled oils, recycled cellulose and paper. These profiles show that all the wastewater has negative zeta potential values at pH > 5, while at pH <5, zeta potential values are close to neutrality or positive. With exception, the wastewater from the electroplating processes shows positive zeta potential values at pH <6.0, and at pH > 7.0 presents negative zeta potential values. As expected, in order to carry out a coagulation-flocculation process in an efficient way, it is necessary to add a polyelectrolyte with a positive charge to neutralize the negative charge of the wastewater from the pulp and paper industry. The monitoring of the zeta potential value with respect to the polyelectrolyte dose in the wastewater allows to construct the coagulation-flocculation operation curves, and this ensures that the operators of the wastewater treatment plants avoid the problem of overdosing of coagulant-flocculant agents and save on the consumption of chemical substances [22]. In this chapter, the capacity of a biopolyelectrolyte extracted from the shrimp waste for the clarification of wastewater from the cellulose and paper recycling industry was evaluated. This was done with the aim of increasing the reuse potential of the treated water and improving the efficiency of solid-liquid separation processes for the recovery of cellulose fiber present in industrial wastewater.

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Parameter	Nixtamalization wastewater	Parameter	Candy Industry wastewater
Temperature (°C)	38	Temperature (°C)	26
Sedimentable solids, SS (mL/L)	850	SS (mL/L)	25
Total Dissolved Solids, TDS (mg/L)	47,200	TDS (mg/L)	12,743
Total Suspended Solids, TSS (mg/L)	2000	TSS (mg/L)	2342
Turbidity (FAU)	1500	Turbidity (FAU)	1676
Alkalinity (mg/L $CaCO_3$)	1025	Alkalinity (mg/L $CaCO_3$)	500
Electric conductivity, EC (mS/cm)	5.42	EC (mS/cm)	1.30
ζ (mV)	−10.5	ζ (mV)	−25.7
Particle size of dissolved part (nm)	100–600	Particle size of dissolved part (nm)	300–800
Color (Pt-Co)	8580	Color (Pt-Co)	6572
pH	10.0–12.0	pH	6.7
Chemical Oxygen Demand, COD (mg O_2/L)	28,450	COD (mg O_2/L)	786
Total Organic Carbon, TOC (mg C/L)	9836	TOC (mg C/L)	250
Biochemical Oxygen Demand, BOD_5 (mg O_2/L)	2700	BOD_5 (mg O_2/L)	653
Total Phosphorus, TP (mg P/L)	1321	TP (mg P/L)	142
Total Nitrogen, TN (mg N/L)	418	TN (mg N/L)	120
Biodegradability (BOD_5/COD)	0.27	Biodegradability (BOD_5/COD)	0.83
Parameter	**Recycled cellulose and paper wastewater**	**Parameter**	**Recycled oils wastewater**
Temperature (°C)	35	Temperature (°C)	28
Chlorides (mg/L)	900	Zn (mg/L)	10.2
Total hardness (mg/L)	3800	Cu (mg/L)	12.2
Alkalinity (mg/L $CaCO_3$)	850	Alkalinity (mg/L $CaCO_3$)	100
Fats and oils (mg/L)	11	Fats and oils (mg/L)	6732
TSS (mg/L)	500	TSS (mg/L)	15,000
TDS (mg/L)	3500	TDS (mg/L)	3500
SS (mL/L)	438	SS (mL/L)	438
Turbidity (FAU)	560	Turbidity (FAU)	350
EC (mS/cm)	1.00	EC (mS/cm)	2.00
ζ (mV)	−25.8	ζ (mV)	−2.1

Parameter	Recycled cellulose and paper wastewater	Parameter	Recycled oils wastewater
Particle size (nm)	500	Particle size (nm)	750
Color (Pt-Co)	3000	Color (Pt-Co)	2340
pH	5.4	pH	7.63
COD (mg O_2/L)	8000	COD (mg O_2/L)	43,650
TOC (mg C/L)	1890	TOC (mg C/L)	5200
BOD_5 (mg O_2/L)	4000	BOD_5 (mg O_2/L)	17,500
Total Nitrogen, TN (mg N/L)	88	Biodegradability (BOD_5/COD)	0.4
Total Phosphorus, TP (mg P/L)	16		
Biodegradability (BOD_5/COD)	0.5		

Table 1. Physicochemical characterization of industrial wastewater: Nixtamalization, recycled cellulose and paper and recycled oils wastewater.

Parameter	Electroplating wastewater	Parameter	Metalworking wastewater
Temperature (°C)	25	Temperature (°C)	32
Sn (mg/L)	4854	Zn (mg/L)	7.78
Pb (mg/L)	1044	Ni (mg/L)	41.57
Fe (mg/L)	683	Cr (mg/L)	7.44
TSS (mg/L)	4510	Cd (mg/L)	0.47
Turbidity (FAU)	2990	SS (mg/L)	9
EC (mS/cm)	74	Fats and oils (mg/L)	465.66
ζ (mV)	26	TSS (mg/L)	3352.63
Particle size (nm)	346	Turbidity (FAU)	2990
Color (Pt-Co)	6742	EC (mS/cm)	327
pH	0.8	ζ (mV)	−10.0
COD (mg O_2/L)	1432	Particle size (nm)	678
TOC (mg C/L)	125	Color (Pt-Co)	2500
BOD_5 (mg O_2/L)	30	pH	7.36
TN (mg N/L)	50.6	COD (mg O_2/L)	64,800
Biodegradability (BOD_5/COD)	0.02	TOC (mg C/L)	3858
		BOD_5 (mg O_2/L)	2857
		TN (mg N/L)	316.8
		Biodegradability (BOD_5/COD)	0.04

Table 2. Physicochemical characterization of industrial wastewater: Electroplating and metalworking wastewater.

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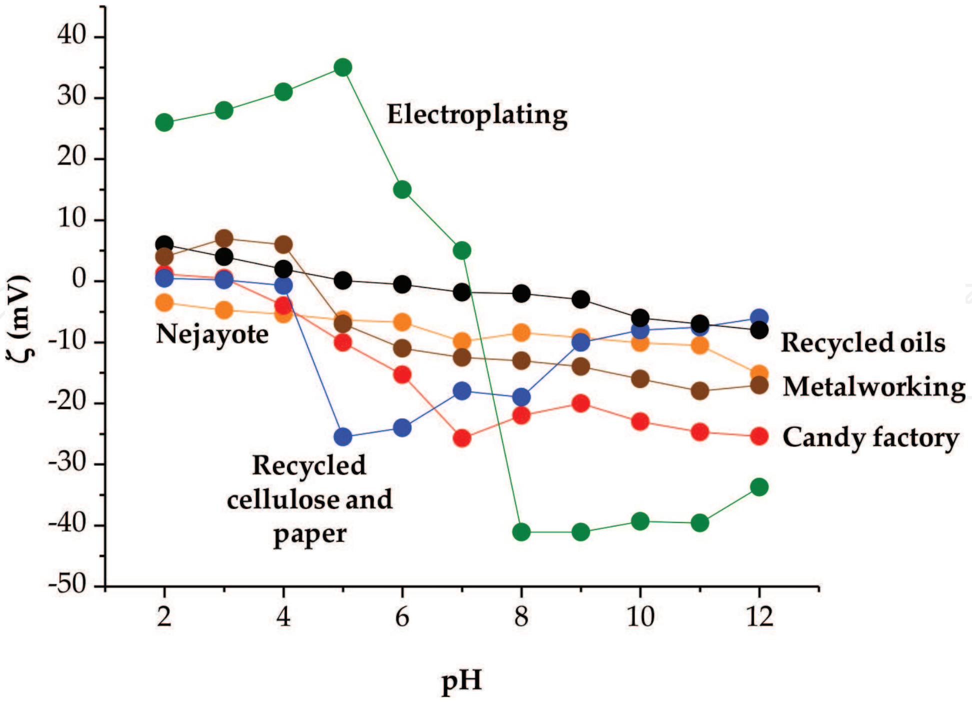

Figure 1. ζ = f (pH) profiles from industrial wastewater: Candy factory, metalworking, recycled oils, nejayote, electroplating and recycled cellulose and paper.

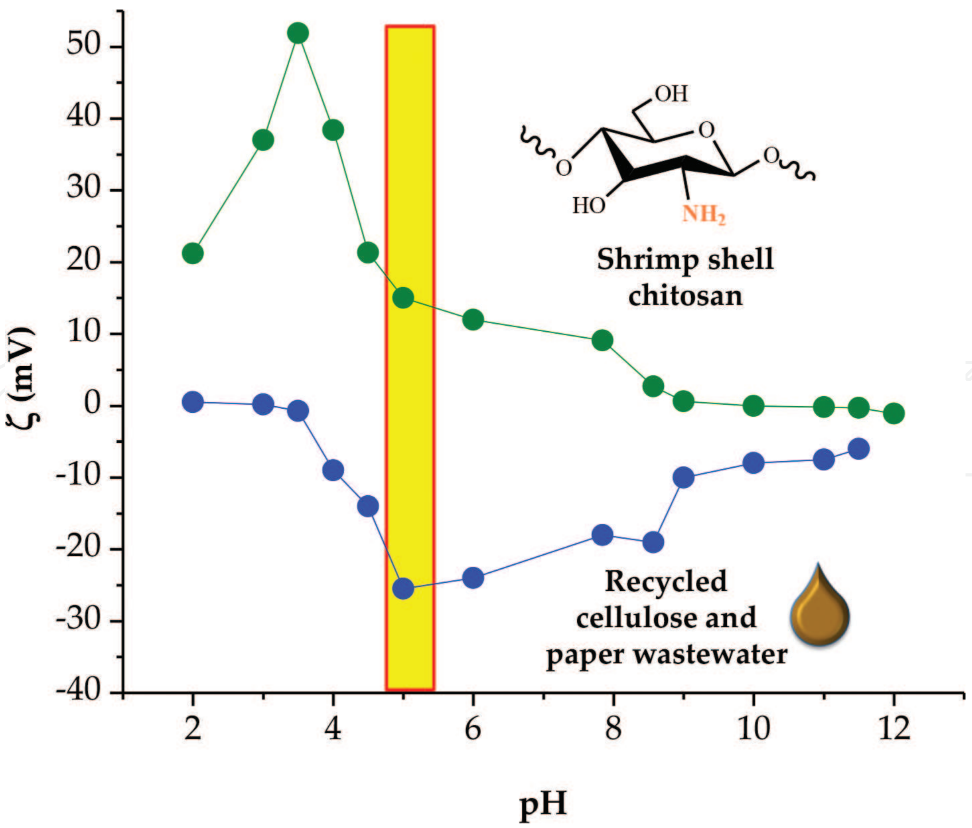

Figure 2. ζ = f (pH) profiles of recycled cellulose and paper wastewater and chitosan.

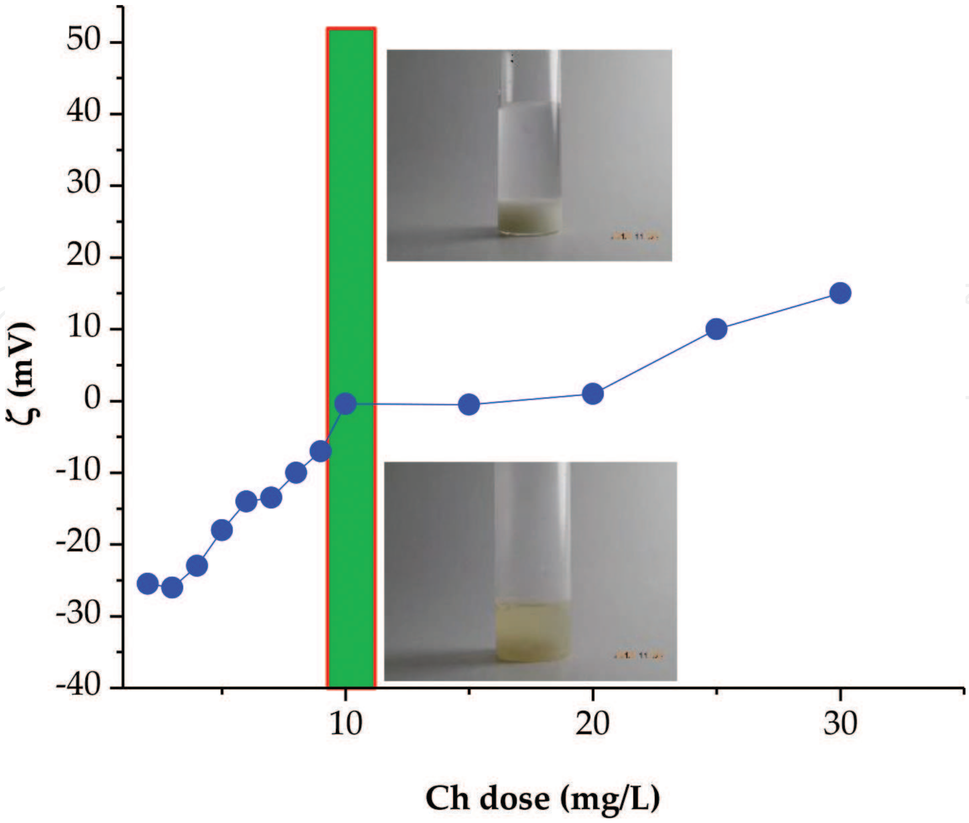

Figure 3. ζ = f (chitosan dose) in coagulation-flocculation tests from recycled cellulose and paper wastewater.

Figure 2 shows the variation of zeta potential with respect to the pH of the wastewater and chitosan. The zeta potential value of the wastewater shows that the suspended particles have a negative surface charge density at pH 5–9. The ζ = f (pH) profile shows that at pH = 4.0 and pH > 10.0, the wastewater has two isoelectric points (ζ = 0). The stability of the particles to remain suspended is due to the value of the negative zeta potential (ζ = −25.5 mV). In order to destabilize the dispersion of cellulose fiber particles, the addition of a cationic coagulant-flocculant agent that allows the neutralization of the negative surface charge is necessary. The wastewater at pH 5.4 has a ζ = −25.5 mV and the chitosan ζ = 15.0 mV, the dosage of chitosan at this pH by pure electrostatic interaction ensures its reaction.

In **Figure 3**, it is shown that the zeta potential value of the wastewater from cellulose and paper industry increases linearly as the dose of chitosan increases (ζ = −25.5 mV to ζ = −5.1 mV), reaching the isoelectric point at a dose of 10 mg/L chitosan. The water treated at pH 5.4 with chitosan has a value of BOD_5 = 150 mg O_2/L, turbidity = 5 FAU, TSS = 2 mg/L, COD = 200 mg/L and hardness = 250 mg $CaCO_3$/L, and the treated water with these physicochemical characteristics can be discharged into the municipal sewer system or reused as process water.

4. Conclusions

The wastewater generated by industries is becoming more complex and difficult to treat to restore its quality and reuse it. The coagulation-flocculation process has become one of the most used technologies to remove suspended particles, dyes and heavy metals; however, one of the trends consists of the substitution of synthetic coagulant-flocculant agents with biopolyelectrolytes. This leads to the development of environmentally friendly technologies, and take advantage of the waste that contains biodegradable polymeric materials and with high potential for its application in the elimination of toxic pollutants from industrial wastewater. In this chapter, the wastewater treatment of the cellulose and paper industry was carried out through a coagulation-flocculation process using a dose of 10 mg/L chitosan at pH 5.4. Through the zeta potential measurements, the pH = 5.4 at which the chitosan and the wastewater have an opposite electric charge was determined, and the best dose of chitosan to maximize the recovery of cellulose fiber and obtain the best quality of treated water.

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Conflict of interest

The authors state that there is no conflict of interest.

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