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Eco-friendly innovation for *nejayote* coagulation–flocculation process using chitosan: Evaluation through zeta potential measurements

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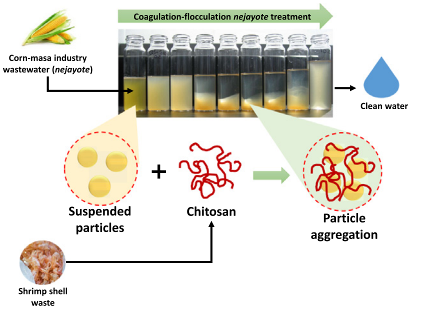
HIGHLIGHTS

- Novel coagulation–flocculation treatment of *nejayote* wastewater using chitosan.
- Zeta potential measurements is a useful technique for water treatment diagnosis.
- Chitosans of low and high molecular weight in flocculation performance were compared.
- ChL_{Mw} has broader flocculation window at pH 5 with high turbidity removal efficiency.
- ChL_{Mw} flocs grew and settle faster than $ChH_{Mw.}$

GRAPHICAL ABSTRACT



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ABSTRACT

The main objective of the present paper is to discuss the convenience of using chitosan as a non-hazardous substance to improve the coagulation–flocculation (CF) efficiencies in *nejayote* (wastewater treatment containing high levels of total organic carbon, TOC = 9836 mg/L). For first time, two different molecular weight of chitosan in the wastewater treatment of the tortilla industry, were used as study models. The conditions here reported showed that both chitosans can be effectively used as adsorbent at pH 5.5 (mixing at 800 rpm for 1 min followed by a slow mixing at 200 rpm for 5 min) and at dosage of chitosan less than 3 g/L for colloidal *nejayote* (without settleable solids). Both chitosan showed the highest performance under these conditions with more than 80% efficiency in turbidity removal, thus accomplishing the Mexican environmental regulation for free urban sewage discharge (NOM-002-SEMARNAT-1996). The zeta potential (ζ) of the *nejayote* supernatant before and after the CF treatment was used as a guiding parameter to evaluate each procedure. In addition, author suggest that the width of the flocculation window, for both chitosans in *nejayote* treatment, is attributed to their physical properties as molecular weight, deacetylation degree, dynamic viscosity and chemical properties as hydrogen bond, hydrophobicity and van der Waals interactions, as well as electrostatic forces that traditionally explain CF of colloids.

1. Introduction

In general, aqueous colloids pollutants (dp $\leqslant 1\ \mu m$) are very stable particles owing to hydration phenomena and/or electro-

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static surface charges. Even when suspended particles are close enough due the Brownian motion, charged colloids can resist the aggregation by repulsion effect due to their high surface potential [1]. The surface charge of colloidal particles can be approached by zeta potential (ζ) measurements. Accordingly, purification of aqueous colloidal pollutants can be achieve by coagulation–flocculation (CF) techniques. The first one is related with the destabilization of colloidal suspensions by neutralizing electric forces among suspended particles; and the second one is caused by the addition of minute quantities of macromolecules (commonly synthetic polymers), destabilizing the colloid by adsorption and interparticle binding. After that, bigger floccules appear and the precipitate can be removed by filtration, centrifugation or flotation [2].

Maize tortilla is the main food in Mexico and Central America and derivative products like corn chips and tortilla chips have widely penetrated the market in United States, Asia and Europe [3]. These products usually require high water volume, for example 50 kg of maize needs 75 L of water and a similar amount of wastewater is discarded [4]. This effluent is known as *nejayote* and is usually disposed in the urban sewage system dragging significant amounts of organic (parts of corn kernel like pericarp, germ and endosperm) and inorganic matter (excess of calcium and magnesium coming from lime used in the process). From the physicochemical point of view *nejayote* is commonly composed by slurry and settleable solids. At the same time, the slurry fraction of *nejayote* is composed by colloidal particles making it a complex pollutant to remove in this kind of food industry wastewaters [5]. Both impact mainly in the quantity of biochemical oxygen demand (BOD_5) and pH in water, exceeding the Mexican environmental regulation (NOM-002-SEMARNAT-1996). For this reason *nejayote* is currently considered a water pollutant and it is estimated that around 1.2 million of m^3 are generated each month, only in Mexico [6].

Until now, some water purification methods for *nejayote* have been reported to remove organic matter. For example, activated sludge and aerobic/anaerobic reactors have proven to be effective to degrade organic matter [7,8]. Nevertheless, the high pH, calcium content and the presence of bacterial inhibitors like phenolic compounds in *nejayote* make difficult the application of these technologies. Other studies suggest to re-use *nejayote* in the traditional corn-masa processing, however, this practice just increases the BOD_5 in wastewater [9,10].

Due to the fact that *nejayote* is an organic nutrient-rich product [11,12] specially in phenolic, ferulic acid and antioxidant content [4,6], new research to recover the solid fraction in *nejayote* have been explored [13–15]. To our knowledge, there are very few published reports about CF for *nejayote*, one of them deals with an enzymatic treatment in combination with chitosan that can be useful to reduce BOD_5 by bio-oxidation [16]. In this paper, the proposal is to investigate a CF process to allow full recovery of nutrient rich matter diminishing BOD_5 and chemical oxygen demand (COD) in nejayote.

Nejayote possess negative surface charge [17] that can be neutralized by adding cationic species, namely aluminum ions, ferric ions and synthetic polymers such as polyacrylamide [18]. Accordingly to Dong et al., using these chemicals may have several environmental consequences: (1) presence of acrylamide and metal residues in water that leads to human health risks; and (2) generation of large volume of toxic sludge. For both reasons, biopolyelectrolytes (BPEs) have been considered for environmental applications and low-cost byproduct eco-friendly alternative [19].

Chitosan is a deacetylated derivate of chitin, with β-(1→4) linked polysaccharide conformed by D-glucosamine residues with *N*-deacetylated alternation along the backbone chain [20] Chitin is the second most abundant biopolymer in nature, it is also widely distributed especially in marine invertebrates, insects, fungi and yeasts [21]. However its application is limited because it is not soluble in aqueous media; in contrast, chitosan is readily soluble in acidic solutions due to amino groups ionization.

Among BPEs, chitosan has characteristics of both coagulant and flocculants, i.e., high cationic charge density, long polymer chains, bridging of aggregates and precipitation in neutral and alkaline conditions [19,22] making this chitin byproduct the best option for the purposes of nejayote treatment.

For the above exposed, this paper presents an innovative eco-friendly procedure to approach *nejayote* treatment, since the separation mechanism is based on the use of a natural byproduct with non-toxic residues. The main objective is to separate solids (colloids) and recover water and valuable byproducts, with nutritional, and nontoxic properties. First of all, a diagnostic of *nejayote* using ζ measurements were done and the use of two different kinds of chitosan for CF test on real *nejayote* slurry wastewater. The aim is to employ ζ measurements to know and understand the behavior of the BPE in this kind of wastewater treatment. Finally, the CF windows may serve as the basic information to scale up an innovative wastewater treatment for *nejayote*. On the other hand, this study pretends to relate molecular level interactions with macroscopic phenomena as the solid–liquid separation in an ecofriendly CF waste water treatment procedure using a real model as that encountered in *nejayote* and chitosan physicochemistry.

2. Materials and methods

2.1. Materials

In this study we use two different biopolymers: chitosan powder of high molecular weight (dynamic viscosity of 2.35 Pa/s and deacetylation degree (DA) of 85%), and low molecular weight (dynamic viscosity of 0.39 Pa/s and DA degree of 95%). They were purchased from BioLog Biotechnologie and Logistik GmbH and Sigma–Aldrich, respectively. Commercial testing water quality reagents from HACH® were used. All other reagents were analytical grade and were used without further purification. Milli-Q grade water was used in all the experiments.

2.2. Methods

2.2.1. Wastewater sampling in the corn masa industry

Nejayote was provided by a local tortilla-making industry. The wastewater sampling protocol was followed as recommended by Mexican sampling standard (NMX-AA-003-1980). 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), total carbon (TC), inorganic carbon (IC) and total nitrogen (TN).

2.2.2. Preparation of wastewater slurries

Raw *nejayote* samples were centrifuged at 3500 rpm for 15 min at 25 °C using an Eppendorf, 5804R centrifuge to remove the settleable suspended solids and to carry out the physicochemical analysis.

2.2.3. Physicochemical analytic techniques

After sample preparation, TS, TDS, TSS, BOD_5 tests were carried out following the current Mexican standard procedures (NMX-AA-034-SCFI-2001 and NMX-AA-028-SCFI-2001) that are equivalent to those published by EPA (2540-C and 2510-B AWWA standard methods respectively). TOC, TC, IC and NT were analyzed in a Shimadzu instrument with TOC-L and TNM-L analyzer units respec-