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Articles

Decontamination kinetics of tannery waters using bioflocculants

Cinética de descontaminación de aguas de curtiembre utilizando bioflocculantes

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Abstract

In this research, the kinetics of the reduction of the initial turbidity (1455 NTU) of wastewater from a tannery industry was evaluated by applying direct bioflocculants prepared from the algae *Chondracanthus chamissoi* (alginate) and the molts of the crustacean *Emerita analoga* (chitosan). The biological precursor material was collected on Lima, Peru's beaches; from this material, fibrous alginic acid was produced, and later sodium alginate. The processes of demineralization, deproteinization, and subsequent deacetylation were used to obtain chitosan from crustacean molts. The effect of pH, the doses of bioflocculants, and the equilibrium time of the process were evaluated. In addition, the kinetic order of the flocculation rate was determined using the jar test. The results indicated a turbidity removal of more than 99 % within the first 30 minutes for doses of 0.2 to 2 g/l of flocculants and acid pH (equal to 4); no significant differences were recorded at different pH values (4-12) and doses (0.2 to 2 g/l). The linear adjustment between flocculation time and turbidity generated significant first-order kinetic equations for both flocculants with rate constants k1 of the order of 10^{-4} (1/NUT.min) and reduction times of half of the particulate matter (average life: $T_{1/2}$) less than 10 minutes. This can be considered a criterion to measure the efficiency of the direct flocculation process in treating tannery industrial waters.

Keywords: Velocity Law, chitosan of *Emerita analoga*, alginate of *Chondracanthus chamissoi*, Average life, turbidity removal.

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Resumen

En esta investigación se evaluó la cinética de reducción de la turbidez inicial (1455 UNT) de aguas residuales de una industria curtiembre mediante la aplicación de biofloculantes directos elaborados a partir del alga *Chondracanthus chamissoi* (alginato) y de las mudas del crustáceo *Emerita analoga* (quitosano). Se recolecto el material biológico precursor en las playas de Lima, Perú, a partir de este material; se produjo ácido algínico fibroso y posteriormente alginato de sodio. Se usaron los procesos de desmineralización, desproteinización y posterior desacetilación para obtener el quitosano a partir de las mudas del crustáceo. Se evaluó el efecto del pH, la dosis de los biofloculantes, el tiempo de equilibrio del proceso. Además, se determinó el orden cinético de la velocidad de floculación mediante la prueba de jarras. Los resultados indicaron una remoción de la turbidez superior al 99 % dentro de los primeros 30 minutos para dosis de 0.2 a 2 g/l de floculantes y pH ácido (igual a 4); no se registraron diferencias significativas a distintos valores de pH (4-12) y dosis (0.2 a 2 g/l). El ajuste lineal entre el tiempo de floculación y la turbidez generó ecuaciones cinéticas significativas de primer orden para ambos floculantes con constantes de velocidad k_1 del orden de 10^{-4} (1/NUT.min) y tiempos de reducción de la mitad de material particulado (vida media: $\tau_{1/2}$) inferiores a los 10 minutos. Esto se puede

considerar como un criterio para medir la eficiencia del proceso de floculación directa en el tratamiento de aguas industriales de curtiembre.

Palabras clave: ley de la velocidad, quitosano de *Emerita analoga*, alginato de *Chondracanthus chamissoi,* tiempo de vida media, remoción de la turbidez.

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Introduction

The tannery industry is an important source of environmental pollution that often emits its discharges without any treatment, especially in developing countries. Its final discharge is detrimental to the quality of water resources, reducing their availability in the face of growing population demand (Doumic *et al*., 2015).

The effluent composition is linked to high organic material content, chemical oxygen demand-COD, which can exceed 10 000 mg/l (Mageshkumar & Karthikeyan, 2015; Doble & Kumar, 2005), and

biochemical oxygen demand (BOD_5 from 700 to 2 400 mg/l). High salinity levels, dissolved solids, extreme pH values (from 3.8 to 8.18, according to Chowdhury, Mostafa, Biswas, Mandal, & Saha, 2015), and high suspended solids content (1 168 mg/l; Siraj *et al*., 2012) have also been recorded; their mixture results in high final turbidity. Although various physicochemical techniques are practiced for the treatment of these wastes, more cost-effective methodologies are always sought (Nwabanne, Oguegbu, & Agu, 2018); treatments range from advanced oxidation processes, reverse osmosis, electrochemical, adsorption and coagulation, among others; the particularity of the processes, limits the total removal of not only inorganic but also organic agents. In wastewater, colloidal or particulate substances fail to sediment, as the gravitational forces result in lower particle size due to repulsive forces (Mageshkumar & Karthikeyan, 2015).

Coagulation and flocculation are among the most successful methods due to their simplicity, lower cost, and efficiency. No sophisticated equipment is required to eliminate soluble particles, colloids, and suspended material so that the aggregation of particles defines their sedimentation. Using conventional chemical coagulants such as aluminum sulfate or ferric chloride has successfully removed toxic agents, including color, from wastewater (Oladoja, 2015). This methodology has also been employed in the wastewater pretreatment stage (Gilpavas, Arbeláez-Castaño, Medina-Arroyave, & Gómez-Atehortua, 2018).

Nowadays, synthetic and natural polymeric coagulants reduce the pollutant load observed as turbidity. According to Nwabanne *et al*. (2018), the application of natural coagulants elaborated from vegetables, algae or exoskeletons, mollusk, or crustacean shells, represents a "green" treatment with great potential to destabilize colloids (Alba & Kontogiorgos, 2018; Matter *et al*., 2019). For example, crustacean skeletons and shells contain carbohydrate biopolymers that provide coagulants such as chitosan, derived from chitin (Menkiti, Nnaji, & Onukwuli, 2009), algae contain alginate precursors, and various plants have derived components that are often applied as natural coagulation adjuvants (Lozano-Rivas, 2012).

One of the most widely applied coagulants is chitosan; Roussy, Vooren, Dempsey, and Guibal (2005) studied the influence of chitosan of different molecular weights and different degrees of deacetylation (DD) to coagulate and flocculate bentonite suspensions (5g/l) in demineralized water (DW) and tap water (TW), subjected to pH values between 5 and 7. The results indicated that chitosan doses lower than 0.10 mg/l removed more than 95 % of TW or DW turbidity, whereas the decrease in turbidity was due to first-order kinetics. On the other hand, Takahashi, Imai, and Suzuki (2005) removed *p*-quinone from an aqueous phase using chitosan of different molecular weights and degrees of deacetylation (DD). The results indicated that chitosan was more effective in solutions with basic pHs, removing between 83.1 and 88.6 % of the contaminant. Likewise, Ariffin, Tan, and Zainon (2009) treated wastewater from the textile

industry, applying the coagulation and flocculation process and found optimal removal conditions using 30 mg/l of chitosan at a pH of 4 and with a mixing time of 20 minutes (250 rpm for 1 minute and 30 rpm at 20 minutes). Thus, they achieved a 72.5 % reduction in chemical oxygen demand (COD) and a 94.9 % removal of turbidity.

In the last decade, Li, Jiao, Zhong, Pan, and Ma (2013) evaluated the efficacy of chitosan, prepared under different molecular weights and degrees of deacetylation (DD), to coagulate-flocculate kaolinite suspensions with demineralized water (DW) and with tap water (TW). The results did not indicate significant effects of pH (3-9), but using a higher dose of chitosan for high values of initial turbidity achieved removals from 54.6 to 95.2 %. In addition, Al-Manhel, Al-Hilphy, and Niamah (2018) studied the effect of different doses of chitosan (0 to 1/100 ml) prepared from shrimp shell on physicochemical parameters, such as turbidity, electrical conductivity (EC), TDS and pH, of a wastewater sample, achieving removals of 50.5 % (turbidity), 27.2 % (EC) and 48.23 % (TDS) for each parameter, and establishing a linear relationship between the concentration of chitosan with each parameter.

Regarding the use of alginate, Vijayaraghavan and Shanthakumar (2018) removed 96.8 % of acid black dye from textile wastewater using 40 mg/l alginate and 6 g/l calcium (pH = 4.2) with the sedimentation of 30 minutes. They also studied the coagulation-flocculation kinetics, which corresponded to a second-order model. Likewise, Banerjeea, Tiwade,

Sambhav, Banerjee, and Bhaumik (2019) studied the nutrient absorption and adsorption kinetics of wastewater by applying different doses of alginate beads (AIMS), prepared with Ca-alginate beads reposed in an algae suspension, and solidified in a $CaCl_2$ solution; they further elaborated a BABS alginate blank, without using the algae suspension. They concluded that a dose of 3 % AIMS and BABS alginate was optimal to remove the contaminant.

Other kinetic studies were reported by Menkiti *et al*. (2009), who studied the coagulation-flocculation performance of a liquid system using a chitin derivative prepared from a periwinkle crustacean shell (PSC). The speed constant (K) and coagulation time for the disappearance of half of the pollutant ($T_{1/2}$) were applied to the coal-washing wastewater, and the kinetic order (α) was determined, among other parameters, achieving a reduction in total suspended solids within the first five minutes.

Kinetic studies have been conducted with different natural materials, for example, Okolo, Nnaji, Menkiti, Ugonabo, and Onukwuli (2014) established coagulation-flocculation kinetic models using *Xanthosoma spp.* to treat brewery wastewater, and two years later, Okolo, Nnaji, and Onukwuli (2016) studied the coagulation-flocculation kinetics of suspended particles (N) using *Detarium microcarpum* seed powder. On this occasion, the researchers determined the rate constant (K_{11}), graphing $1/(\sqrt{N})$ versus time, found the coagulation time $\tau_{1/2}$ and

the fast coagulation constant (K_R) to adjust the process variables and optimally predict effluent clarification.

In 2015, Nnaji *et al*. studied the coagulation-flocculation kinetics of a coagulant elaborated from pulverized snail shell (PSSC), subjected to different pHs and doses, to remove turbidity from wastewater from a quarry, determined the speed constant (K_{11}) and average coagulation time ($\tau_{1/2}$), among other parameters. They also reported a pH optimum of 6, with a dose of 800 mg/l PSSC, to achieve an optimum 98.5 % turbidity removal with $\tau_{1/2}$ times between 13.8 and 972 minutes. Likewise, Menkiti, Sekeran, Ugonabo, Menkiti, and Onukwuli (2015) optimized the coagulation-flocculation kinetics of brewery wastewater using a chitin-derived coagulant (CDC) to remove suspended and dissolved particles (SDP) from the effluent; optimal conditions were achieved at pH 5.5; a dose of 100 mg/l and 26.4 minutes. Under optimal conditions, the PDS is reduced from 98.18 % with a second-order velocity constant.

Turbidity and its relationship with colloids and material suspended in liquid medium

Colloids or colloidal suspensions in wastewater are a set of combined particles suspended in a continuous phase, possess dimensions as small as 1 nm to 1 mm, and generate an opalescence or turbidity in the liquid medium (Bajpai, 2018). There is a very wide range about the nature of colloids and suspended material, made up of inorganic (mineral particles) and organic (cationic or anionic polymers) groups, positive or negative charges are critical. Also, the influence of hydronium ion potential (pH) and temperature play a crucial role in the behavior of particulate material because they determine its stability in solution, causing turbidity (Katzourakis & Chrysikopoulos, 2019). In addition, these groups usually form micelles that agglomerate about 20 to 100 hydrophobic (non-polar) or hydrophilic (polar) molecules (Bajpai, 2018).

Thus, this reduction in the transparency of a liquid, known as turbidity originates from the scattering of light falling on the colloidal material suspended in the liquid; this phenomenon is explained through the Lambert-Beer law, Equation (1) (Acebo-González & Hernández-García, 2013; Mäntele & Deniz, 2017):

$$I = I_o e^{-\varepsilon c d} \qquad (1)$$

Where I represent the final intensity; I_o is the initial intensity absorbed by the test medium or liquid; ε is the molar absorptivity; c means the concentration of the light scattering material, and d is the

length of the optical path of the sample. It can be inferred that turbidity is related to the concentration of suspended particulate matter that diffracts light. In this context, both parameters can be related through the law of turbidity conservation described by Walski, Minnich, Sherman, Strause, and Whitman (2017) using a linear relationship between both parameters (Equation (2)):

$$C = f(T) \quad (2)$$

Where C represents the concentration of particulate matter expressed in units of mg/l, and T is the turbidity expressed in nephelometric turbidity units (NTU). Various authors have correlated suspended material content against turbidity (Al-Sameraiy, 2012) so that NTU units can replace concentration units (mg/l), and their measurement could be used as an effluent quality control parameter, reducing not only analysis time but also operational costs (Mucha & Kułakowski, 2016).

Coagulation-flocculation and direct flocculation

One way to eliminate suspended solids in wastewater is by applying the coagulation-flocculation method. Coagulation is a physicochemical process that produces the destabilization of colloids through the application of metallic salts $Al_2(SO_4)_3$ and $FeCl_3$, among other agents, which attract negatively charged particles to form very small but dense agglomerates. Flocculation, on the other hand, is given by polymers that present bonding bridges or act as electron donors, reduce the compression of the double layer or neutralize charges, producing larger flocs, which separate from the solution and complete the sedimentation process (Wang, Huang, Yang, Liu, & Liu, 2019; Mageshkumar & Karthikeyan, 2015; Jadhav & Mahajan 2013). In this way, the application of coagulant-flocculants achieves different efficiencies depending on the nature of the wastewater, its pH, electrical conductivity, and type of contaminants, among other factors.

Direct flocculation consists of applying the flocculant directly without the prior use of a coagulant. Thus, the separation of suspended solids is performed in less time, using cationic polymers of high molecular weight to neutralize the negative charges of colloidal particles or join such destabilized and agglomerated particles. Flocs are formed by very dense and compressed bridges that produce a smaller amount of sludge, which can be easily treated by biological methods (Lee, Robinson, & Chong, 2014).

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Direct bio-flocculants

These are polymers from renewable natural resources, such as plants, algae, and crustacean shells. These materials act as counter-ions, neutralizing the opposite charges of colloids or any particle with charge and large molecular structure, including various functional groups. They also lower the zeta potential and the electronic double layer of particles, especially in organic effluents such as textile and food industries (Chong, 2012). Among the most commonly used materials are alginate and chitosan, whose molecular structure is shown in Figure 1.

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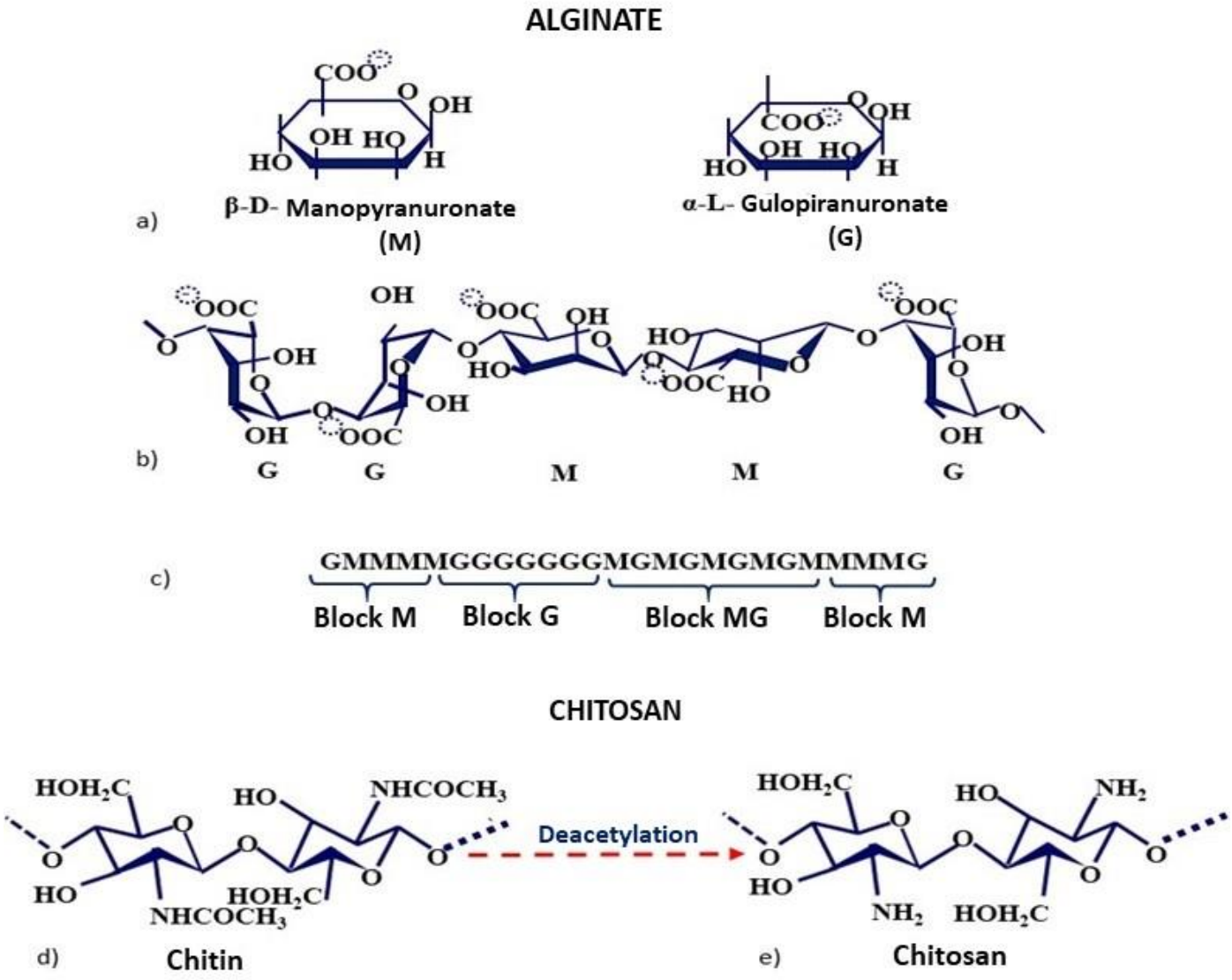

Figure 1. Molecular structure of alginate a) basic units of α-L-guluronic acid (G), β-D-manuronic acid (M); b) blocks of the essential acids; c) alternating sequences of the MG blocks; d) Molecular structure of chitosan chitin, and (e) chitosan.

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Sodium alginate

Alginates are linear polysaccharides and are produced in three stages. The first, from algae, extract in the form of alkaline salts; in the second, the supernatant is subjected to a reaction with a calcium salt producing insoluble calcium alginate. In the third stage, it is dissolved in acid-forming alginic acid, which is then treated with ethyl alcohol to form sodium alginate in paste form (Hernández-Carmona *et al*., 2012).

This biopolymer has revealed high flocculation property, more than 90 % color removal, and an 80 % reduction in chemical oxygen demand-COD (Lee *et al*., 2014). It has a complex structure, as the molecule is made up of two acidic structures, such as β-D-manuronic acid and α-L-guluronic acid, as shown in Figures 1a, 1b, and 1c. Both molecules are linked by glycosidic structures (1-4) through segments: D-manuronic (M), L-guluronic (G) and their conjugations: MM, GG, and MG (Hernández-Carmona *et al*., 2012). According to Kıvılcımdan, Ertesvåg, and Sanin (2016), a higher or lower proportion of these acids define the flocculation efficiency; a higher presence of the guluronic group would prove to be more efficient in the turbidity removal process.

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Chitosan

Chitosan is a biopolymer with free amino functional groups on its surface. It is widely applied for its low cost to treat wastewater due to the formation of gels with pollutants (Siraj *et al*., 2012). It is produced by the deacetylation of chitin extracted from shells rich in these components. Figure 1d shows the active amino groups (-NH_2) of chitosan, which can protonate (H^+) in water in the presence of a cationic polyelectrolyte; the molecule generates a static attraction and adsorption, managing to form larger flocs that eventually sediment (Lee *et al*., 2014).

The positively charged amino groups present form chelates that serve as ligands for charged ions or substances, including metal ions. The anti-bonding electronic pairs of nitrogen and oxygen atoms develop the same capacity, which acts as donors towards the positive charges (cations) through coordinated bonds (Bassi, Prasher, & Simpson, 2000). Abebe, Chen, and Sobsey (2016) applied chitosan at a dose of 5 to 30 mg/l in a wastewater filtration process to remove the microbial load and particulate matter, achieving turbidity below 1 NTU and confirming its removal efficiency.

Coagulation-flocculation mechanism for natural bio-flocculants

Due to its molecular structure of amino and hydroxyl groups, chitosan can act with its charge. Still, it can also generate protonic charges that neutralize the negative charges of contaminants, achieving flocculation due to the formation of hydrogen bridges (Li *et al*., 2013). This occurs during the removal of anionic dye residues, showing hydrophobic properties (Szyguła, Guibal, Palacín, Ruiz, & Sastre, 2009).

Regarding alginate, as an anionic type polymer, it does not flocculate pollutants with the same load but considering that wastewater, such as peeling water, contains a diversity of functional groups in suspended colloids, its application represents an opportunity for efficient removal and cost reduction (Suopajärvi, Liimatainen, Hormi, & Niinimäki, 2013).

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Particle collision kinetics in coagulation-flocculation

Flocculation is a sequential process of collision between particles, starting with a pericinetic (Brownian) flocculation due to the movement of molecules induced by the thermal energy of the fluid, followed by orthokinetic flocculation referred to the collision of particles due to the movement of water molecules, generating a velocity gradient. Finally, differential sedimentation occurs due to the collision between particles of different sizes; here, the larger ones descend slowly upon collision with the smaller ones, generating agglomeration.

Okolo *et al*. (2014) applied the equation of Smoluchowski (1917), who developed the first flocculation theory and limited the collision of particles under a laminar regime with Brownian motion to explain pericinetic flocculation (Equation (3)):

$$\frac{dN_m}{dt} = \frac{1}{2}\sum_{i+j=m} K_{ij} N_i N_j \; - \; N_m \sum_{i=1} K_{im} N_i \qquad (3)$$

Where K represents the coagulation rate constant for an order = *m* at a time *t*, and *N* is the total concentration of flocculated particles (mg/l). However, this expression by itself does not explain the actual process in

a water treatment, where velocity rates are applied in turbulent flow, with decreasing rate until reaching laminar flow or steady-state conditions, Menkiti *et al*. (2009) and Okolo *et al*. (2014) expressed the *N* aggregation of monodispersed particles for an initial stage as follows (Equation (4)):

$$-\frac{dN_t}{dt} = KN_t^m \qquad (4)$$

During wastewater treatment, the kinetic order "m" of the coagulation and flocculation velocity ranges between 1 and 2, the linearization of this formula is developed as follows (Equation (5)) (Okolo *et al*., 2014):

$$ln[dN_t/dt] = m \ln N_t + ln\, K \qquad (5)$$

The integral algorithm of Equation (4) for $m = 1$ during the initial conditions of time $t = 0$ and initial concentration N_0 is expressed as (Equation (6)):

$$\int_{N_0}^{N} \frac{dN}{N^m} = -K \int_0^t dt \qquad (6)$$

This equation, once solved, is very exact to explain the process in the initial stage during the first 30 minutes; its generic resolution corresponds to the form (Equation (7)) (Okolo *et al*., 2014):

$$\frac{N_{m(t)}}{N_0} = \frac{\left[t\,2\left[\frac{1}{KN_0}\right]\right]^{m-1}}{\left[1+\frac{t}{2\left[\frac{1}{KN_0}\right]}\right]^{m+1}} \tag{7}$$

Solving this equation for $m = 1$ results in (equations (8) to (12)):

$$\frac{N}{N_0} = \frac{1}{(1+[2(1/KN_0)]^2} \tag{8}$$

$$\frac{N}{N_0} = \left[1 + \frac{t}{(2(\frac{1}{KN_0})}\right]^2 \tag{9}$$

$$\sqrt{\frac{N_0}{N}} = \left[1 + \frac{t}{(2(\frac{1}{KN_0})}\right] \tag{10}$$

$$\frac{1}{\sqrt{N}} = \frac{1}{\sqrt{N_0}}\left[1 + \frac{t}{(2(\frac{1}{KN_0})}\right] \tag{11}$$

$$\frac{1}{\sqrt{N}} = \frac{1}{\sqrt{N_0}} + \frac{N_0 K t}{2\sqrt{N_0}} \quad (12)$$

From Equation (12), one can experimentally test the kinetic behavior in particle collision during direct flocculation, plotting $\frac{1}{\sqrt{N}}$ *versus* time t will produce a slope $\frac{K\sqrt{N_0}}{2}$ with an intersection equal to $\frac{1}{\sqrt{N_0}}$.

On the other hand, when dealing with a second-order equation $m = 2$, Equation (4) takes the form (Equation (13)):

$$-\frac{dN_t}{dt} = KN_t^2 \quad (13)$$

Whose integral formula is (Equation (14)):

$$\int_{N_0}^{N} \frac{dN}{N^2} = -K \int_0^t dt \quad (14)$$

The integration of equations (13) to (14) results in Equation (15):

$$\frac{1}{N} = Kt + \frac{1}{N_0} \quad (15)$$

Under experimental conditions, plotting $\frac{1}{N}$ against time t will produce a slope K (1/min) and an intersection on the coordinate axis (y) equal to $1/N_o$.

According to Okolo *et al*. (2014), the term $\frac{1}{N_0 K}$ appears in the above expressions, which is represented by the symbol τ indicating that the flocculation time is inversely proportional to the coagulation velocity constant (Equation (16)):

$$\boldsymbol{\tau} = \frac{\mathbf{1}}{\boldsymbol{N_0 K}} \tag{16}$$

From which, it can be determined that $\tau_{1/2}$ represents the reduction time of half of the contaminant during direct flocculation (Equation 17):

$$\boldsymbol{\tau_{1/2}} = \frac{\mathbf{1}}{\mathbf{0.5} \boldsymbol{N_0 K}} \tag{17}$$

Finally, τ' represents the time required to reach equilibrium (Equation (18)):

$$\boldsymbol{\tau'} = \mathbf{2\tau} \tag{18}$$

Likewise, *N* (mg/l) concentrations and turbidity (NTU) can be mutually replaced based on the Fick's law algorithm relationship and Equation (6) (Menkiti *et al*., 2009; Okolo *et al*., 2014), while coagulation-flocculation efficiency is expressed according to Okolo *et al*. (2014) (Equation (19)):

$$\boldsymbol{Efficiency} = \left[\frac{\boldsymbol{N_0 - N_t}}{\boldsymbol{N_0}}\right]\boldsymbol{x100}\ \% \qquad (19)$$

Materials and methods

The following equipment and materials were used in this experiment: Sartorios analytical balance; Daihan Scientific oven; Hanna turbidimeter, model: LP 2000-11, Hanna pH meter, model HL 8424; VELP programmable flocculation equipment, model F105 AO 109; Diab electric heating plate, model MS7-H550; Tyler sieves.

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Wastewater collection

Samples of tannery wastewater were collected at the liming process in three stages of industrial processing in the district of San Juan de Lurigancho in Lima-Perú and then mixed to obtain a composite sample, which was transported to the laboratory for treatment with bioflocculants.

Sodium alginate synthesis

The seaweed of the species *Chondracanthus chamissoi* belongs to the "*Gigartinaceae*" family (Calderón, Ramírez & Bustamante, 2010); it proliferates in the cold waters of the Peruvian coast, is popularly known as "yuyo" and is often used in coastal meals.

To develop the experiment, 5 kg of algae were collected at "Los Yuyos" beach in the "Costa Verde" in Lima. Once collected, they were washed with distilled water and dried in an oven at 50 °C, eliminating 91

% of humidity. Once dried, they were ground and sieved, separating particles smaller than 2.5 mm.

50 g of the dry material was weighed and leached for 2 hours with a solution of HCl (0.1 N); then, the particulate material was washed with distilled water and separated by filtration.

This solid material was deposited in a glass container and subjected to an alkaline extraction with Na_2CO_3 (1 N) at a temperature of 80 ºC for 2 hours, forming a suspension of sodium alginate. This material was washed with warm water (50 ºC), and then HCl was added to obtain fibrous alginic acid, which was washed and separated by filtration.

From this stage, a purification of the fibrous material was made in a 2-propanol solution for 30 minutes; the new precipitate formed was dried at 40 ºC for two days and finally treated with Na_2CO_3 solution converting all the alginic acid into sodium alginate, which was dried and pulverized until 125 µm particles were obtained.

Chitosan synthesis

Emerita analoga is a crustacean known on the coasts of Lima as "muy muy" the samples were collected at "Venecia" beach in Lima, and much of the material corresponded to molts collected along the coastline. This material was washed and dried in an oven at 70 °C, crushed, and sieved until particles smaller than 2.5 mm were obtained, achieving a 6.2 % recovery of dry material.

The dried material obtained from the *Emerita analoga* was treated with a solution of HCl (1M), at a ratio of 10 ml of HCl per gram of dried material (1:10 p/v), at an ambient temperature of 30 °C, for three hours, then deproteinized with a solution of NaOH (1M) for 32 hours at 65 °C, by constant stirring.

Deacetylation of the solid material was achieved by treating it with a 50 % NaOH solution in a ratio of 1 g of dried material to 40 ml of NaOH (1:4 p/v) for two hours at 60 °C. It was then dried in an oven at 150 °C for three hours and finally sieved until particles smaller than 125 µm were obtained.

Effects of pH, doses, and interaction time of bioflocculants

The effect of pH, flocculant doses, and suspended particulate matter flocculation time on the tannery wastewater samples' turbidity was evaluated. The pH was modified by adding HCl (1 N) to values of 4, 6, 9, 10, 11, and 12, whereas the doses of the bipolymers corresponded to 0.2, 0.4, 0.8, 1.2, 1.6, and 2 g/l of flocculant. Finally, times of 20, 30, 45, and 60 minutes were tested to determine the equilibrium time of the process, as well as the reduction times of 50 % of the initial turbidity.

Kinetic study of particle collision

A dose of alginate and chitosan at concentrations of 0.8 and 1.2 g/l at pH = 4 was used for each test, with stirring speeds for rapid mixing of 150 rpm for 1 minute, followed by 40 rpm of slow stirring for 45 minutes and a 30-minute rest for subsequent turbidity measurement.

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Statistical analyses

The statistical programs R. Core Team (2019), Jamovi (2019) and SSPS v.25 were used to analyze the significant differences between treatments.

Results

The sample initially had a pH of 12.35 and turbidity of 1455 NTU.

Table 1 shows the results obtained in the initial tests of the effect produced by the variations in pH and the doses of flocculants in the experiments. Accordingly, it can be seen that in the first 20 minutes, flocculation had already exceeded 98 % turbidity reduction. The doses applied presented similar removals. Although certain variations were observed in the case of pH, there were no significant differences ($p > 0.05$) between the removals achieved by both coagulants.

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Table 1. Results: pH, dose and flocculation time effects on wastewater turbidity reduction.

Parameter	Value	Final turbidity (NTU)	% turbidity removal (using Alginate)	Final turbidity (NTU)	% turbidity removal (using chitosan)
Time (min)	60	1.52	99.89	5.73	99.6
	45	1.65	99.89	5.47	99.62
	30	18.15	98.75	15.38	98.95
	20	23.01	98.43	22.18	98.49
pH	4	23.29	98.41	25.04	98.29
	6	725	50.24	670	53.92
	9	429	70.52	438	69.89
	10	586	59.73	595	59.07
	11	592	59.35	605	58.4
	12	331	77.26	402	72.35
Doses (g/l)	0.2	9.05	99.38	6.35	99.56
	0.4	7.92	99.46	5.77	99.6
	0.8	0.44	99.97	1.27	99.91
	1.2	1.52	99.89	5.73	99.61
	1.6	4.28	99.7	5.85	99.6
	2	4.32	99.71	5.91	99.6

According to Table 1, both flocculants had lower final turbidity in an acid medium (pH = 4); turbidity decreased to 0.42 NTU and 1.31 NTU when applying doses of 0.8 g/l of alginate and chitosan, respectively.

At this pH (4), the alginate was negatively charged in its totality, with COO^- ions attracting various cations, including $NH4^+$ ions, achieving high flocculation and turbidity removal. But, for pH values above 4, the residual turbidity was higher, fluctuating between 300 NTU and 700 NTU (pH = 6), suggesting an increase in carboxylate ions that generated strong interactions with the charges present in the medium (Banerjee *et al*., 2019). However, higher coagulant doses slightly decreased turbidity removal due to suspension reestablishment (Devrimci, Yuksel, & Sanin, 2012).

Coagulation-flocculation kinetics test results

Table 2 shows the final turbidity results obtained in the peri-kinetic test for both coagulants, using doses of 0.8 and 1.2 g/l at pH = 4.

Table 2. Results of the kinetic test applying alginate and chitosan in the liming wastewater.

	Alginate		Chitosan	
Time (minutes)	Dose (0.8 g/l)	Dose (1.2 g/l)	Dose (0.8 g/l)	Dose (1.2 g/l)
	Final Turbidity (NTU)	Final Turbidity (NTU)	Final Turbidity (NTU)	Final Turbidity (NTU)
8	16.42	12.32	18.2	23.04
15	14.62	11.56	17.12	16.78
22	12.11	10.85	15.77	10.17
29	10.37	4.79	10.84	5.76
36	5.88	2.76	5.17	2.61
45	2.34	1.13	3.87	1.41

Kinetic test results for both coagulants within 45 minutes showed a decrease in final turbidity content and higher removal upon increasing the coagulant dosage from 0.8 to 1.2 g/l.

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Discussion

Effect of contact time

The experimental runs were developed four times (Figure 2), and their effect was observed between 0 and 60 min, as shown in Figure 2a; the equilibrium time (constant turbidity) occurred at 45 minutes for both flocculants, with a dose of 0.8 g/l, with similar values of turbidity reduction, lower than 10 NTU. In general, it has been reported regarding turbidity removal efficiency or suspended solids removal, above 98 % in tests with alginate (Banerjee *et al*., 2019), in the case of Al-Manhel *et al*. (2016) reported values of 15.5 %. The application of a short mixing time at 150 rpm for one minute facilitated the collision of the particles with the polymers, but a subsequent slow agitation (40 rpm), given by a slower process, allows the formation of bonds or neutralizes the necessary charges; in either case, the formation of flocs is facilitated, maintaining the aggregation process.

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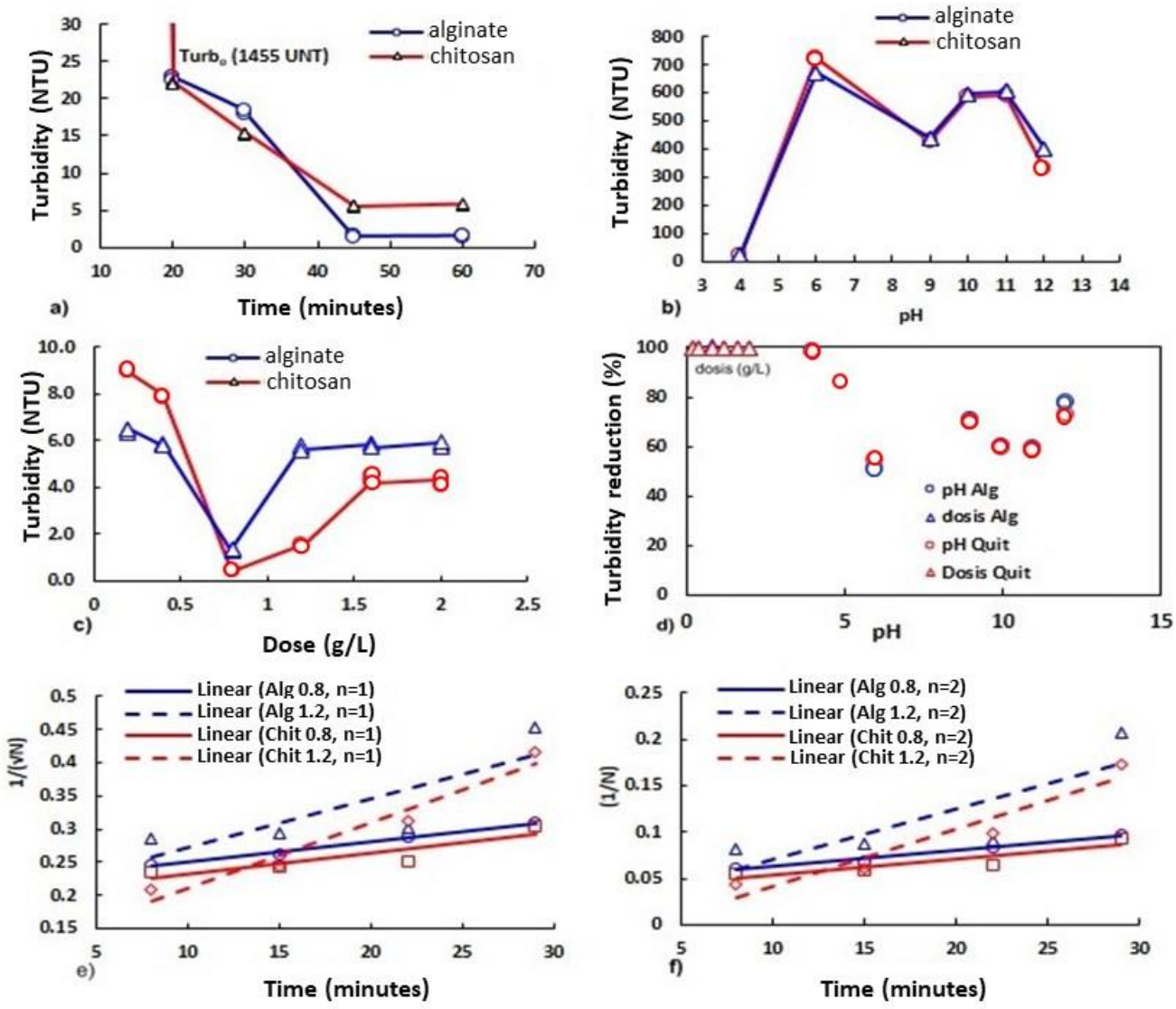

Figure 2. Effects of: a) time; b) pH; c) bioflocculant dose on the kinetic development of particle collision; d) turbidity reduction as a function of pH, particle collision kinetics during flocculation; e) first order, and f) second order.

Effect of pH

Figure 2b shows that both compounds acted efficiently on the colloidal material at acid pH = 4, subjected to a dose of 0.8 g/l, with turbidity values lower than 2 NTU. However, at higher pH values, higher turbidity was also observed. According to Melton, Xu, Williams, and McGillivray (2019), the electrostatic forces of the substances present influence rapid pH changes; for this reason, values higher than 4 generated an interaction between the different charges of the colloids present in the sample, decreasing the efficiency in turbidity reduction (300 - 700 NTU).

Regarding alginate, the minimal difference in pK_a values between its two main components, glucuronic acid (pK_a =3.38) and mannuronic acid (pK_a = 3.65), generates an abrupt change in turbidity, with changes in pH, causing protonation of carboxyl groups (COO^-), due to the presence of their conjugated MG blocks (Banerjee *et al*., 2019). Applying a pH equal to 4 overcame this condition, achieving a removal efficiency of 99.9 %. On the other hand, the decrease in chitosan solubility with increasing pH has been reported previously (Al-Manhel *et al*., 2016; Roussy *et al*., 2005), as it becomes insoluble at pHs higher than 6, which explains the

increase in turbidity recorded in this research for increasingly alkaline pH applications. The amino group involved in this process would act partially by decreasing the coagulation of organic-type suspensions (Takahashi *et al*., 2005).

Effect of bioflocculant doses

Dosage is a critical variable because too much or too little could adversely influence the expected pollutant removal efficiency; the optimum concentrations of flocculants were evaluated in terms of turbidity removal efficiency. Doses were tested in the range of 0.2 to 2 g/l of a sample, at pH equal to 4, with rapid agitation at 150 rpm for 1 minute, followed by slow agitation at 40 rpm for 30 minutes and a settling time of 30 minutes.

According to Figure 2c, a flocculant concentration of 0.8 g/l was efficient for the flocculation of the negative and cationic colloidal material present; however, the available sites for the fixation of the substances were exhausted with higher doses of the flocculant. Mahmoodi, Taghizadeh, Taghizadeh, and Azimi (2019) demonstrated that at higher doses of alginate, active sites were unsaturated, generating higher

aggregation and thus reducing the specific surface area available for adsorption. On the other hand, an increase in the doses would also generate a more significant presence of carboxyl groups (COO-), causing repulsion between the colloids and negatively charged ions (Nguyen *et al*., 2019). This would explain a slight reduction in turbidity removal for a dose between 1.2 and 2 g/l, with a slight increase in the final turbidity values (4 and 6 NTU). However, these turbidity reduction oscillations would not show significant differences ($p > 0.05$), since they all exceeded 99 %, demonstrating a high application potential. Figure 3 shows the proposed flocculation mechanism for alginate.

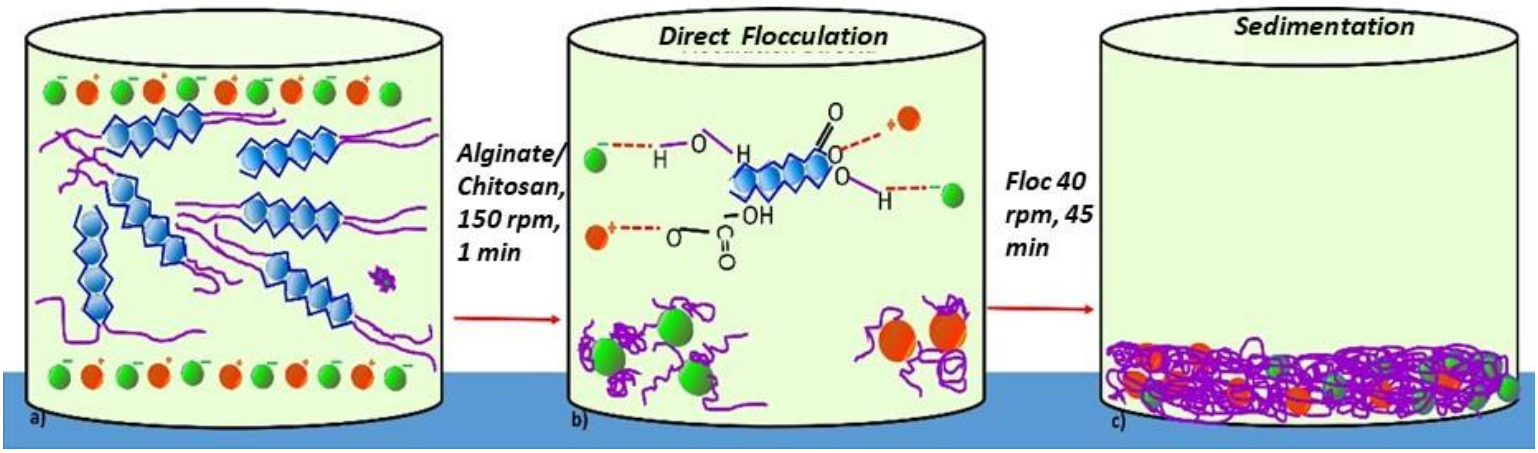

Figure 3. Proposed turbidity reduction process applying alginate: a) wastewater from liming loaded with particulate and dissolved organic and inorganic material, red spheres represent positive charges and green: negative; b) fast and short coagulation stage to destabilize

colloids and loaded surfaces; c) slow flocculation process with formation of aggregates that reach sedimentation.

Regarding chitosan, Figure 2c shows a trend similar to alginate ($p > 0.05$), with a more pronounced oscillation between two groups of doses, those lower than 0.8 g/l and those higher than this value. In the first case, an increase in flocculation would occur as the doses increased up to this value of 0.8 g/l, achieving turbidity of 1.3 NTU, a value that increased with excess chitosan. It happens that chitosan, on the one hand, possesses a multiplicity of its positive charge, with free amine groups capable of interacting chemically with negatively charged molecules of the wastewater, forming ligands or chelates. On the other hand, electron-donating atoms in its structure, such as nitrogen and oxygen, act on positive charges present in the solution (Al-Manhel *et al*., 2016). The removal achieved was higher than that recorded by Ariffin *et al*. (2009) in textile wastewater, who proved that doses of 0.03 g/l generated a 72.5 % turbidity reduction. This would explain the enormous potential of chitosan for diverse applications in organic-type effluents. It is known that higher doses prevent the formation of bridges between particles, allowing colloidal reestablishment or re-suspensions due to the repulsion of the electrostatic positive charges, as would occur for doses higher than 0.8 g/l.

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Coagulation-flocculation kinetics

The units of suspended solids concentration (mg/l) can be replaced by those of turbidity (NTU), as well as the second order constant k_2 (L.mg.min = 1/NTU min) (Ni'am, Othman, Sohaili, & Fauzia, 2007), under this principle, turbidity was applied in the linearized $1/\sqrt{N}$ model as a function of time (Villota, Camarero, Lomas, & Perez-Arce, 2015).

The solution of equation (4) for an order $m = 1$ generated equation (15) from which the corresponding points ($1/\sqrt{N}$) were plotted against time, and the coagulation-flocculation rate constants were found, as Nnaji *et al*. (2015) established. They correlated $1/\sqrt{N}$ *versus* equilibrium time and developed a first-order kinetic model in coagulation-flocculation using a powdered snail shell coagulant (PSSC); all their findings were supported by very high R^2 factors (> 0.9).

Under the same principle, two statistical parameters R_2 and the p-value with 95 % confidence, were used to evaluate the predominance of the main coagulation-flocculation model based on the precision of the obtained graph fit; based on the experimental data, doses of 0.8 and 1.2 mg/l at pH equal to 4 were tested to evaluate the pericinetic conditions.

The parametric results (Table 3) indicated first-order conditions, predominant in the tests, because a higher significant difference was achieved for alginate at 0.8 g/l (p-value = 0.01) and for chitosan at 1.2 g/l (p-value = 0.02), with R^2 values of 0.99 and 0.96, respectively. In contrast, the $m = 2$ showed no significant differences, except for the lowest doses of alginate applied (0.8 g/l), which produced an R_2 factor (0.98) somewhat lower than that of the first order.

Table 3. Pericinetic model of order $m = 1$ for flocculation with alginate and chitosan.

Flocculant	Order n	Dose (g/l)	K (1/NTU.min)	$\tau_{1/2}$ (min)	τ' (min)	R^2	*p*
Alginate	1	0.8	0.00016 ± 0.0	8.46 ± 0.0	16.91 ± 0.0	0.99	0.01*
Alginate	1	1.2	0.00039 ± $5.7x10^{-06}$	3.50 ± 0.047	6.99 ± 0.093	0.69	0.17
Chitosan	1	0.8	0.00016 ± $5.7x10^{-06}$	8.37 ± 0.152	16.74 ± 0.305	0.81	0.10
Chitosan	1	1.2	0.00052 ± 0.0	2.64 ± 0.015	5.28 ± 0.031	0.96	0.02*
Alginate	2	0.8	0.0017 ± 0.0	15.42 ± 0.0	30.84 ± 0.0	0.98	0.01*
Alginate	2	1.2	0.0055 ± $1.5x10^{-04}$	4.74 ± 0.129	9.48 ± 0.259	0.67	0.18
Chitosan	2	0.8	0.0016 ± $5.77x10^{-05}$	15.74 ± 0.556	31.49 ± 1.112	0.79	0.11
Chitosan	2	1.2	0.0061 ± $5.77x10^{-05}$	4.27 ± 0.04	8.55 ±0.08	0.91	0.05

The asterisk * represents a significant predominant difference.

Regarding the coagulation-flocculation velocity constants, the fits for m = 1 showed K_1 of the order of 10^{-4}, while for m = 2, the k_2 constants were of the order of 10^{-3}, half turbidity reduction times decreased as the K constant increased. The constants found in this investigation differ from those calculated by Nnaji *et al*. (2015) (K_{11} = 5.310x10^{-7}) for a 1 000 mg/l dose of PSSC. However, similar to other authors (Menkiti *et al*., 2015; Okolo *et al*., 2016) also reported the inverse relationship developed between the velocity constant and the coagulation time ($\tau_{1/2}$), which means that the constant (K_{11}) increases when the $\tau_{1/2}$ is lower.

On the other hand, the velocity constant derived from the linearized equation (15) in the m = 1 model suggests that a dose of 0.8 g/l of chitosan and alginate at pH = 4, generates a velocity constant (K = 1.6x10-^{4} 1/NTU.min) that reflects an optimal turbidity removal. According to Menkiti *et al*. (2015), lower doses of coagulants would be associated with insufficient amounts that do not achieve good destabilization of colloids, which is reflected in their removal percentage. In contrast, for a higher dose of 1.2 g/l, a higher velocity constant K in coagulation-flocculation is generated for both coagulants (3.9x10^{-4} L/NTU.min for alginate and 5.2x10^{-4} L/NTU.min, for chitosan).

Unlike Menkiti *et al*. (2015), the kinetics of higher or intermediate coagulant doses were not tested in this research to evaluate the reversibility of the process, such as peptization of alginate or protonation

of functional groups, as pointed out by Chuang *et al*. (2017) and Banerjee *et al*. (2019) for low pHs (lower than 4).

Conclusions

The removal results between the application of alginate and chitosan in water samples of liming water were similar, producing an effective reduction of colloidal material of more than 99 %. The efficiency was high, demonstrating the peri-kinetic nature with a time of 8 minutes after the particle collisions, which were significantly adjusted to first-order kinetics.

It was demonstrated that this application offers significant advantages by requiring short settling times to treat tannery wastewater.

Nomenclature

NTU = Nephelometric Turbidity Units.

COD = Chemical Oxygen Demand.

BOD5 = Biochemical Oxygen Demand.

AIMS = Alginate Immobilized Microalgae Systems.

BABS = Alginate Blank.

PSSC = Pulverized Snail Shell Coagulant.

EC = Electrical Conductivity.

TDS = Total Dissolved Solids.

DD = Deacetylation.

DW = Demineralized Water.

TW = Tap Water.

PSC = Periwinkle shell a crustacean.

N = Suspended Particles.

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