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Preparation of new biocoagulants by shrimp waste and its application in coagulation-flocculation processes

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ABSTRACT

Chitin is a natural biopolymer produced from shrimp waste. Chitin has low solubility in usual organic and inorganic solvents. In the present work, it was possible to solubilize the extracted raw materials (biomaterials) through the chemical treatment steps that comprise the chitin extraction process. These biomaterials were characterized and solubilized in green solvents, producing four biocoagulants that were used in surface water treatment. The characterization of biomaterials confirmed a reduction in ash content and an increase in crystallinity when passing through chemical treatment steps, increasing the content of chitin and reaching the purity of 82.3% dry basis. The absorptions in the infrared spectra indicated the presence of the characteristic functional groups of the chitin before and after solubilization. The scanning electron microscopy images revealed chitin fibers randomly distributed. The energy-dispersive X-ray spectroscopy pointed out the presence of elements C, O and N. Biocoagulants were applied to the coagulation/flocculation of surface water, and the performance was investigated by the percentages of turbidity and organic material removal at pH 6.0. The biocoagulant composed of demineralized shrimp waste (DMSW), with a dosage of 200 mgDW L^{-1}, presented the best results for both removals; the turbidity reached more than 95% and the organic matter was 80%. Based on results, the processing and application of solubilized shrimp waste could promote environmental and economic benefits.

1. Introduction

Access to drinking water and the depletion of non-renewable resources are considered major challenges today. The water treatment technologies of the future must promote the use of renewable materials that protect the planet and do not generate toxic by-products. Among the available water treatment methods, coagulation/flocculation is the most widely used technique. As related by Bratby (2016), it is a low cost, simple and low power process. In this process, coagulants are added to destabilize the impurities present. The coagulants more used are based on metal salts, such as aluminum and iron salts, and polymers are also used as flocculation aids. According to Walton (2013), the consumption of treated water with residual aluminum has been attributed to serious health problems, such as the development of Alzheimer's disease. Several researchers proposed alternative compounds to decrease the amount of inorganic salt-based coagulants. Dao et al. (2016) presented a review of the use of various synthetic polymers and modified natural polymers. Oladoja (2016) summarized a study with several natural compounds, such as pectin, tannin, clay minerals, starch, plantain peelings ash extract and others, which were successfully used in water and wastewater treatment. Salehizadeh et al. (2018) presented a review with current trends in preparation and chemical modification of polysaccharide bio-based flocculants.

Chitin is a natural polymer as abundant as cellulose, which is found in arthropods, such as crab, shrimp, crustaceans and insects. According to FAO (2017), shrimp waste is the main source of chitin due to its high chitin content and large annual production. The waste account for around 60% of the shrimp total weight, and they are constituted (in dry basis) by chitin (20—30%, w/w), proteins (30—40%,

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w/w), mineral matter (30–50%, w/w) and pigments, according to Rødde et al. (2008). Chitin is a polysaccharide composed of 2–acetamide–2–deoxy–β–D–glucopyranose and 2–amino–2–deoxy–β–D–glucopyranose units. This biopolymer is renewable, biocompatible, friendly environmental, biodegradable and biofunctional. Chitin has strong hydrogen bonds (intermolecular and intramolecular), making its dissolution difficult; it is insoluble in usual solvents, such as water, organic solvents and acidic or basic solutions, as presented by a review published by Duan et al. (2018). Chitin has not been fully explored due to its insolubility, which limits the research and development of chitin-based materials from laboratory to industrial scale. Researcher has been performed by some authors to solubilize chitin, using different solvent combinations. Silva et al. (2017) and Chen et al. (2018) used ionic liquids; Chen et al. (2015) investigated CaCl2/methane; Feng et al. (2019) considered deep eutectic solvents and Ding et al. (2012) explored alkali/urea aqueous solutions. Zhang and Yan (2016) studied the combination between liquefaction and formic acid to get another compost by depolymerization of chitin. The solvents mentioned are mostly flammable, toxic or corrosive, like formic acid, methane, deep eutectic solvents and alkali. Other solvents are also difficult to recycle, such as ionic liquids, being economically unviable. Simple and safe processes to synthesize chitin-based materials from shrimp waste are still a challenge, but they are essential for the development of new products and for large-scale production.

Considering what was discussed previously, this work has considered the importance of addressing new bio-based coagulants to overcome the issues of using metal salts coagulants. In the present work, new biocoagulants were developed from shrimp wastes, which encompassed not only the environmental aspects regarding the transformation of shrimp wastes into added-value products, but also the water quality aspects to assure the efficiency and scalability of the new bio-based coagulants. These biocoagulants were obtained using an unprecedented way of solubilizing shrimp wastes containing chitin in low-cost and environmentally friendly solvents. Afterward, the coagulation/flocculation processes in surface water were performed, using the different biocoagulants obtained. The effects of dosage, pH and biocoagulant type on coagulation/flocculation efficiency were investigated to elucidate the best experimental conditions and to discuss the possible mechanisms involved in treatment.

2. Materials and methods

2.1. Preparation of biomaterials and biocoagulants

Shrimp waste (*Penaeus brasiliensis*) was used as raw material to obtain the different biomaterials and, afterward, to produce the biocoagulants. Fig. 1 presents the steps for production of the different biomaterials and biocoagulants. The chitin extraction conditions were determined according to Moura et al. (2006).

The solubilization and the biocoagulants production processes are protected under the patents BR102018072441-0 A2 and BR102018068760-3 A2. Briefly, the biocoagulants production followed these steps: addition of acetic acid solution (1%) and glycerol in the proportion of 1:1 v/v; addition of each dried biomaterial (2% w/v); the mixture was stirred at room temperature (25 ± 1 °C) for 48 h. Four biocoagulants(products) were obtained: SW (shrimp waste); DMSW (demineralized shrimp waste); DPSW (deproteinized shrimp waste) and CT (deodorized shrimp waste or chitin). The biocoagulants dosage was expressed as dry solid weight by water volume (mgDW L^{-1}).

2.2. Characterization of biomaterials and biocoagulants

The biomaterials were characterized by moisture content, ashes content and total nitrogen content (Kjeldahl nitrogen) (AOAC, 2016). The determinations of chitin and protein contents were performed according to the method proposed by Díaz-Rojas et al. (2006) and Rødde et al. (2008). The method considers that all the nitrogen detected is protein or part of the chitin structure, in stoichiometric ratios.

The crystallinity of each powder sample (biomaterials) was determined by X–ray diffraction (XRD) method (Bruker XRD D8, UK), coupled with the Brag Bentano rotating beams at a step size of 0.02 s^{-1}. The surfaces morphologies of biomaterials were analyzed using a scanning electron microscope (SEM) (Jeol JSM 6610LV, Japan), under an applied voltage of 10–15 kV with energy–dispersive probe X–ray (EDS), being the samples metalized with carbon on vacuum chamber (Denton Vacuum, Sputtering DeskV, USA). SEM analysis of the biocoagulants was performed after the evaporation of excess solvent using a drying oven at 60 °C. The presence of functional groups in the biomaterials was determined using a FTIR spectrophotometer (Shimadzu Prestige 210045, Japan). The diffuse reflectance technique in KBr pellets was used for the biomaterials, and the attenuated total reflectance (ATR) was used to obtain the biocoagulants spectra.

2.3. Surface water

The surface water used in coagulation/flocculation assays was obtained from the São Gonçalo channel, located in the city of Rio Grande–RS (Brazil). The water was characterized by pH, turbidity, temperature, alkalinity, chemical oxygen demand (COD), total solids, suspended solids and sedimentable solids. All the analyses were carried out according to the Standard Method of Water and Wastewater (APHA, 2012).

Turbidity is an important parameter to monitor water quality because it affects organoleptic properties; also, it provides a suitable environment for pathogens proliferation. Turbidity was measured in terms of nephelometric turbidity units (NTU) using a calibrated turbidimeter (HI 93703, Portable turbidimeter, Hanna, Brazil). The organic compounds are commonly found in surface waters, and these compounds include degradation products, humic substances, lignin, tannin, aromatic compounds or that have double bonds in their structures. All the above mentioned compounds strongly absorb ultraviolet (UV) radiation at 254 nm. The measurements of organic matter (OM) were performed using a UV–Vis spectrophotometer (UV–2550, Shimadzu, Japan) at 254 nm (Díaz-Rojas et al., 2006). The water pH was measured using a calibrated pH meter (Mars, MB10, Brazil).

2.4. Coagulation/flocculation experiments

Coagulation/flocculation experiments of surface water were performed with the four biocoagulants obtained, and they were evaluated through the removal percentage of turbidity and the removal percentage of organic matter present in the water. The shrimp waste (SW) was used in the coagulation/flocculation of the surface water as control sample, and no turbidity or organic matter was removed.

The coagulation/flocculation assays were performed in a jar test (Milam, JT303M/6, Brazil) using 1 L of water, with rapid stirring at 200 rpm for 2 min, followed by slow stirring at 50 rpm for 10 min, and sedimentation for 30 min. After sedimentation, 10 mL of water sample was collected approximately 2 cm below the surface to measure final turbidity and organic matter content. All the experiments were performed at pH 6.0, because this pH was the real condition of the surface water. No compound was used for pH adjustment. All experimental analyses were performed in triplicates at room temperature (25 ± 1 °C). The dosage is one of the

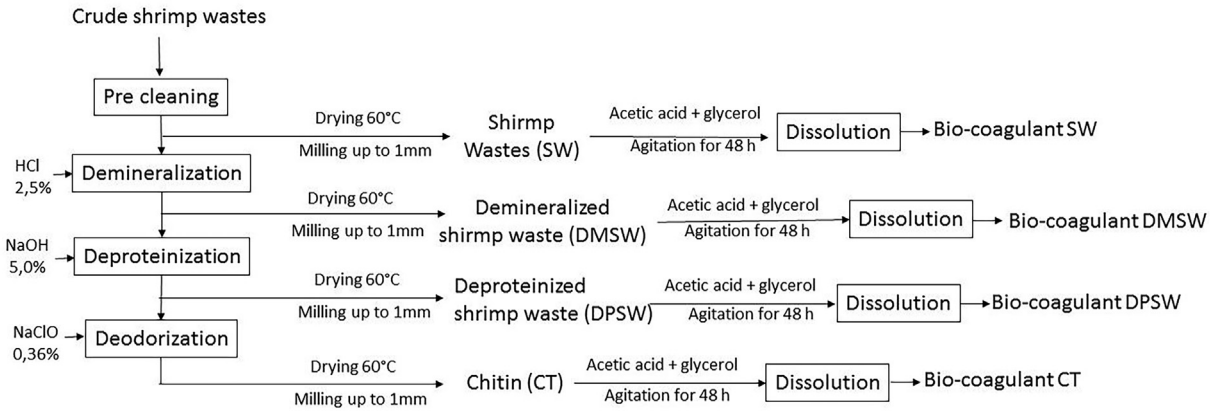

Fig. 1. Steps for biomaterials production to synthesize the biocoagulants.

most important factors, which should be considered to establish the optimal condition for the biocoagulants in coagulation/flocculation processes. The dosage was studied in the range from 50 to 400 mgDW L^{-1}.

3. Results and discussion

3.1. Characterization of biomaterials and biocoagulants

Table 1 presents the characterization results for the powder biomaterials after drying/milling. The moisture contents of the dried samples were between 8 and 14% (w/w); the ashes contents, which represent the mineral content, such as carbonates, phosphates and other impurities, ranged from 0.2 to 29.0% (w/w). The ashes content was reduced at each step of chemical treatment. The lipids content was not detected for each biomaterial. Moura et al. (2006) found that the shrimp waste from *Penaeus brasiliensis* species were composed of chitin, protein, ashes and moisture, and did not contain significant values for lipids. The amount of total nitrogen in each biomaterial also decreased at each step, except for the value found for the dried shrimp waste. The total nitrogen contents were found to be 7.32 ± 0.93% (w/w) for SW, 12.36 ± 1.51% (w/w) for DMSW, 7.70 ± 0.10% (w/w) for DPSW and 6.15 ± 0.10% (w/w) for CT. The DMSW showed high protein content (Table 1). This could be related to the fact that after the acid treatment, the mineral content that maintained the rigid structure was removed and the protein became more available. The DPSW, which is the shrimp waste after the deproteinization step, reduced drastically the protein content and raised the chitin content. The CT (Table 1), after the deodorization step, presented chitin content with purity in dry basis of approximately 82.3%.

Fig. 2 shows the FTIR spectra of the powders from shrimp waste after the various treatment steps (biomaterials), dried and milled, according to presented in Fig. 1. All samples presented similar spectra. The bands in the range 3550–3200 cm^{-1} were relative to the N–H and O–H stretching. The C–H stretching was observed at 2900 cm^{-1}. The stretching vibration of C=O was identified at 1730 cm^{-1}. At 1550 cm^{-1} was found the stretching vibration of amine. The band at 1430 cm^{-1} can be attributed to the angular deformation of C–O–H. The bands in the range from 1150 to 1030 cm^{-1} can be associated to the CH_2 bend and C–C stretching, respectively. The band at 1200 cm^{-1} could be assigned to a C–O stretching. The N–H bending was observed at 620 cm^{-1}. All absorption ranges found are in agreement with Silvestein et al. (2005).

Fig. 3 shows the XRD patterns for all the powder biomaterials. For the SW, a small diffraction peak was observed at $2\Theta = 20°$. After demineralization, deproteinization and deodorization steps, this peak enhanced in intensity, which indicated the increase in the index of crystallinity, IC, (from 10% to 57%). According to Moussout et al. (2016), this peak is related to the N-glucosamine sequences through the polymer chain. The crystallinity increase can be associated with the removal of ashes, proteins and pigments, which increased the chitin portion through the samples. The powders morphology was obtained by SEM (Fig. 4) in increments of 100 × . The surfaces showed a certain roughness for all the powder biomaterials.

Fig. 5 shows the EDS analyses that were used to identify the elements present in the powder biomaterials. In the SW, it was possible to observe the presence of C, N, O, Na, Cl, K and Au. The impurities were removed after each chemical treatment, which agrees with the reduction in ashes content shown in Table 1. For the purified chitin (CT) (Fig. 5d), only the constituents of the polymer chain C, N and O remained in the sample.

The biocoagulants were obtained from the biomaterials dried powders. FTIR analysis was used to evaluate the functional groups in all the biocoagulants. FTIR spectra (Fig. 6) pointed out that the four biocoagulants had very similar spectra because they had the same functional groups. This result shows that the solubilization of biomaterials into biocoagulants did not compromise their functional groups, which are important for coagulation/flocculation purposes. The band in the region between 3500 and 3000 cm^{-1} was wider for the biocoagulants than for the biomaterials due to

Table 1
Characterization for the dried powder of each biomaterial.

	Moisture content (%, w/w)	Ashes content (%, w/w)	Protein content (%, w/w)	Chitin content (%, w/w)
SW	8.92 ± 0.23	28.97 ± 0.48	33.36 ± 2.54	28.75 ± 1.70
DMSW	13.95 ± 0.11	3.45 ± 0.37	45.65 ± 3.40	36.95 ± 2.26
DPSW	11.12 ± 0.21	1.44 ± 0.34	18.34 ± 0.24	69.10 ± 0.90
CT	12.00 ± 0.10	0.20 ± 0.03	15.33 ± 0.26	72.47 ± 0.39

Mean value ± standard deviation (n = 3). SW (shrimp waste); DMSW (demineralized shrimp waste); DPSW (deproteinized shrimp waste) and CT (deodorized shrimp waste or chitin).

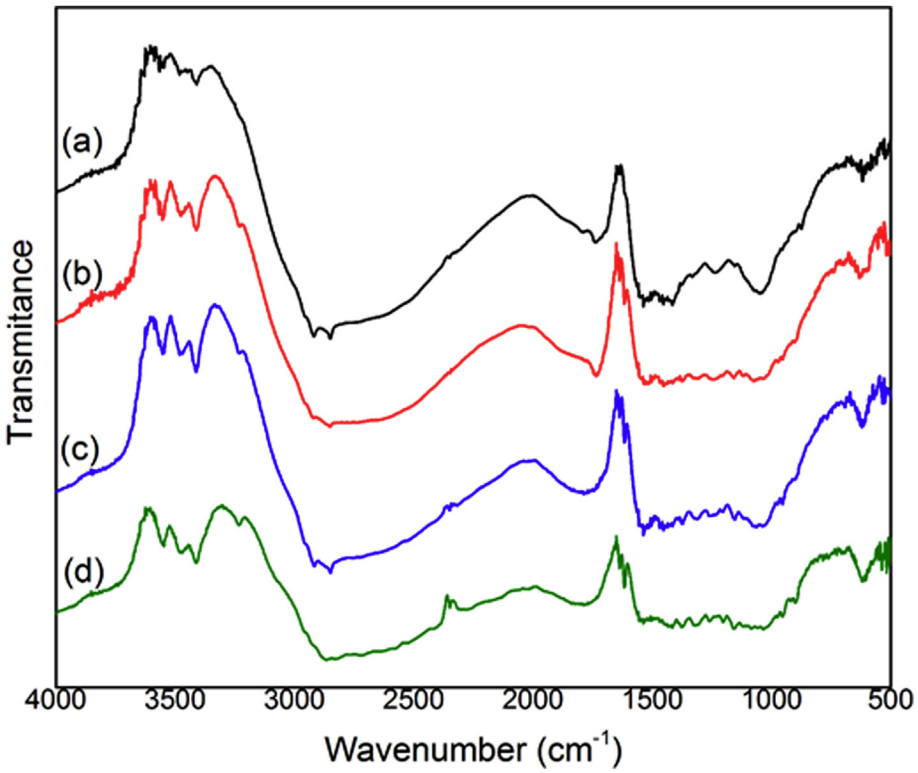

Fig. 2. FTIR spectra for the biomaterials powders: (a) SW (shrimp waste); (b) DMSW (demineralized shrimp waste); (c) DPSW (deproteinized shrimp waste) and (d) CT (chitin).

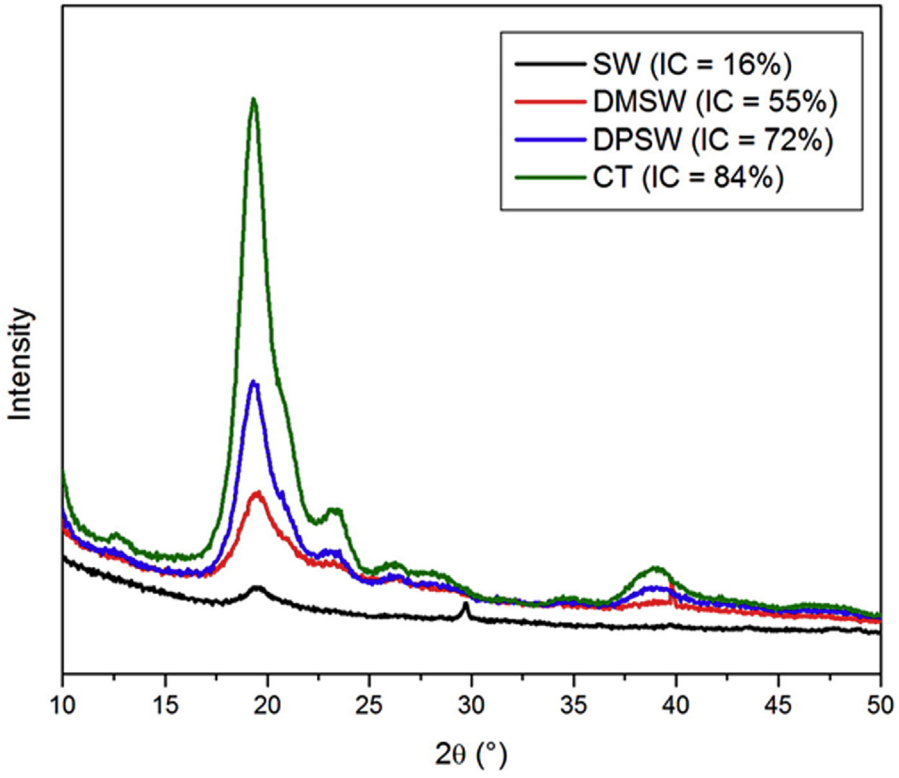

Fig. 3. X−ray diffractograms (XRD) for the all biomaterials.

solvent contribution. The carbonyl peak shifted to a lower wavenumber with greater intensity. The angular deformation bands of C−O−H at 1430 cm^{-1} and C−O elongation at 1215 cm^{-1} were also identified.

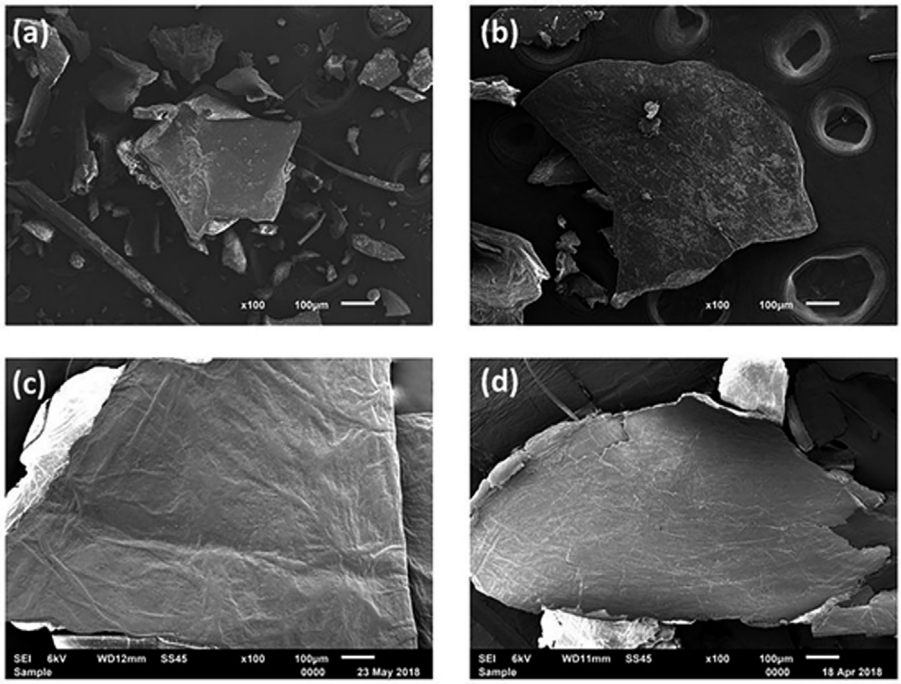

Fig. 4. SEM images for the all biomaterials: ((a) SW (shrimp waste); (b) DMSW (demineralized shrimp waste); (c) DPSW (deproteinized shrimp waste) and (d) CT (chitin).

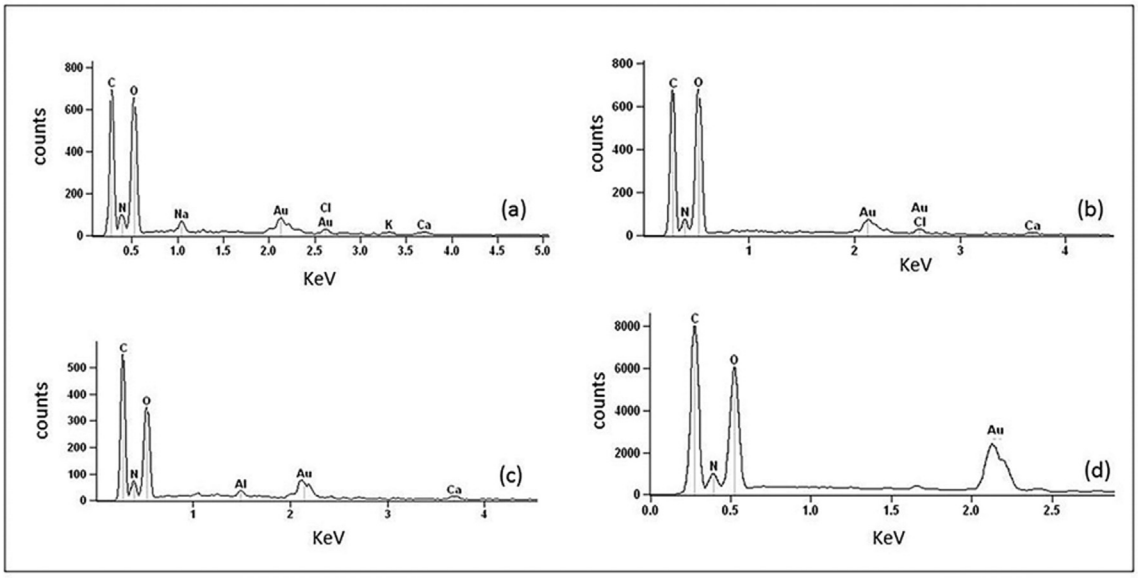

Fig. 5. EDS for the all biomaterials: (a) SW (shrimp waste); (b) DMSW (demineralized shrimp waste); (c) DPSW (deproteinized shrimp waste) and (d) CT (chitin).

Fig. 7 shows the images of biocoagulants surface at 1000 × . The images revealed high roughness, but they were similar to each other.

3.2. Coagulation/flocculation results

Table 2 shows the surface water characteristics used in this work. The biocoagulants were tested at different dosages determined by previous studies. The effect of biocoagulants dosage was investigated to obtain the best removal percentage of turbidity (Fig. 8) and the best removal percentage of organic matter (Fig. 9), at pH 6.0.

The biocoagulant produced from the shrimp waste (SW) showed a removal percentage of turbidity very low (Fig. 8), between 5 and 20%, for all the dosages studied. The low removal efficiency could be attributed to the high ash content (Table 1). The removal percentage of turbidity for the deproteinized biocoagulant (DPSW) enhanced as the dosage increased from 50 mgDW L-1 to 100 mgDW L-1; but with the increase in dosage, the percentages decreased to low or zero values. For the deodorized biocoagulant (CT) (purified chitin) the highest percentage of turbidity removal was 20% (100 mgDW L^{-1}). According to Table 1, the percentage of proteins in CT was low (around 15%), which could justify the low

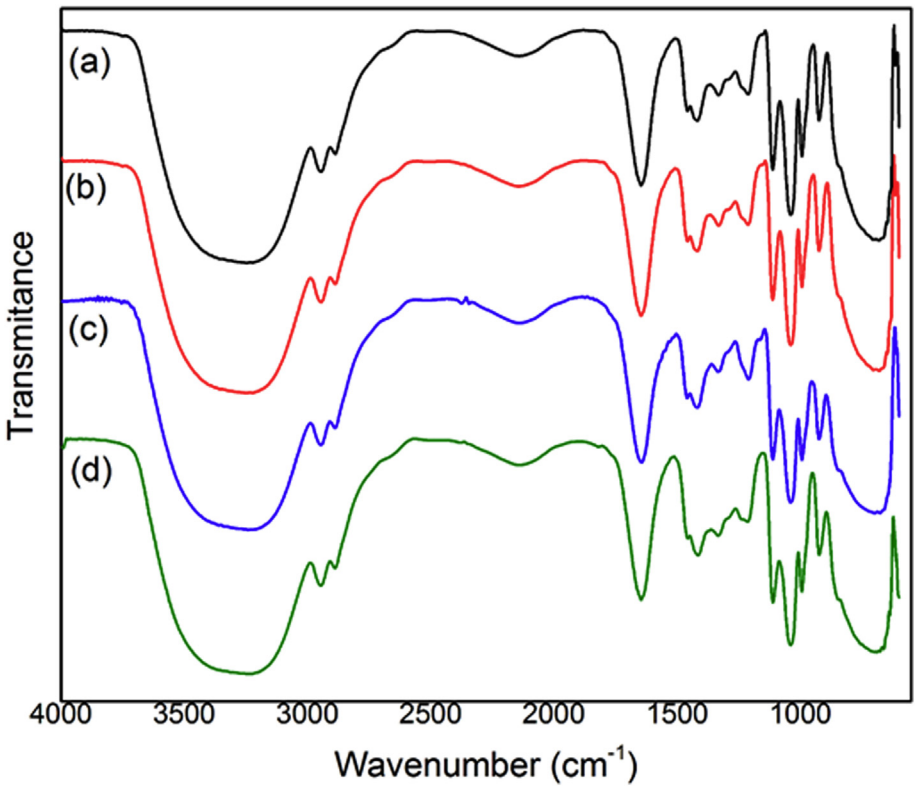

Fig. 6. FTIR spectra for the biocoagulants: (a) SW (shrimp waste); (b) DMSW (demineralized shrimp waste); (c) DPSW (deproteinized shrimp waste) and (d) CT (chitin).

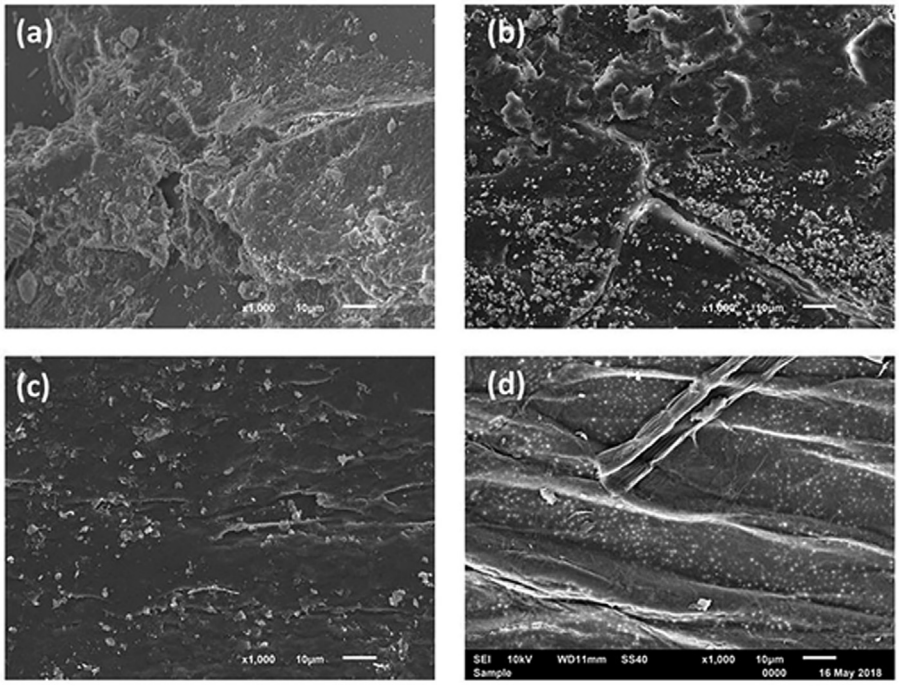

Fig. 7. SEM images for biocoagulants: (a) SW (shrimp waste); (b) DMSW (demineralized shrimp waste); (c) DPSW (deproteinized shrimp waste) and (d) CT (chitin).

interaction of this biocoagulant with the impurities. At higher CT dosages, there was an increase in turbidity, which is also reported by Cheng et al. (2005) and Meraz et al. (2016) using chitosan. This behavior was not observed for all the biocoagulants.

For the demineralized biocoagulant (DMSW), the removal percentage of turbidity increased with the increase of biocoagulant dosage until close to 100% at a dosage of 200 mgDW L-1. For biocoagulant dosages higher than 200 mgDW L-1, the removal

Table 2
Physical-chemical characterization of water.

Parameter	Values
pH	6.0 ± 0.2
Turbidity (NTU)	31.2 ± 1.7
Temperature (°C)	25.8 ± 0.1
Alkalinity (mg_{CaCO3} L^{-1})	31.0 ± 1.1
COD (mg_{O2} L^{-1})	57.0 ± 0.7
OM (abs 254 nm)	0.418 ± 0.003
Total solids (mg L^{-1})	70.5 ± 7.5
Suspended solids (mg L^{-1})	9.4 ± 1.4
Sedimentables solids (mg L^{-1})	nd

Mean value ± standard deviation (n = 3). nd: not detectable. NTU: nephelometric turbidity units; COD: chemical oxygen demand; OM: organic matter.

percentages of turbidity were around 80–90%. The high efficiency of DMSW may be related to the higher protein content, according to the values presented in Table 1. The amino acids that comprise the protein chains can have enhanced the amines groups content, already present in small portions through the chitin structure. These functional groups could have interacted with the impurities in surface water, which can lead to the greater destabilization of the colloidal particles. Hameed et al. (2016) used a tannin-based coagulant to treat municipal wastewater (52 NTU), achieving up to 87% removal of turbidity.

UV absorption (254 nm) was used to measure the percentage of organic matter removal. The dosage related results of the four biocoagulants are shown in Fig. 9. For all the biocoagulants studied at dosages of 50 and 100 mg_{DW} L^{-1}, the removal percentage of organic matter had values between 0 and 20%; but the SW biocoagulant was an exception, because it caused an increase in organic matter to almost all dosages, proving to be ineffective in the treatment. The DPSW and CT showed similar performance, with removal percentage of organic matter between 0 and 35% at dosages from 50 mgDW L-1 to 300 mgDW L-1, presenting intermediate behavior to those obtained with SW and DMSW. For the DMSW, the removal percentage of organic matter had similar behavior to that obtained for turbidity. The dosage of 200 mgDW L-1 was the most efficient because it resulted in larger values regarding the removal percentages of organic matter and turbidity. At dosages higher than 200 mgDW L-1, the removal percentage of organic matter decreased slightly but remained higher than those obtained with the other biocoagulants (SW, DPSW and CT). The removal percentages of turbidity and organic matter had similar behavior, which suggests that the turbidity was caused mainly by organic matter. The SW biocoagulant presented a much lower performance than the other biocoagulants (DPSW, DMSW and CT). The DPSW and CT presented the best removals for both parameters studied at dosages of 100 mgDW L-1 and 300 mgDW L-1, respectively. The best dosage for DMSW was of 200 mgDW L-1, for both parameters studied. Camacho et al. (2017) achieved up to 90% turbidity and 40% organic matter removals for initial turbidity water of 30 NTU using Moringa oleifera extract; but coagulant-free water reduced more than 60% of turbidity and 20% of organic matter. Comparing the DMSW with coagulants in the literature, it is reasonable to argue that this biocoagulant promotes greater removal for both parameters.

4. Conclusion

In this work were developed four biocoagulants from shrimp waste, which were the raw shrimp waste (SW), demineralized shrimp waste (DMSW), deproteinized shrimp waste (DPSW) and deodorized shrimp waste or chitin (CT) and, afterward, their performances were evaluated on coagulation/flocculation processes in surface water treatment. The biomaterials had the same functional groups and composition (C, N and O), but the chitin, protein and ash contents were very different. The surfaces morphologies of the

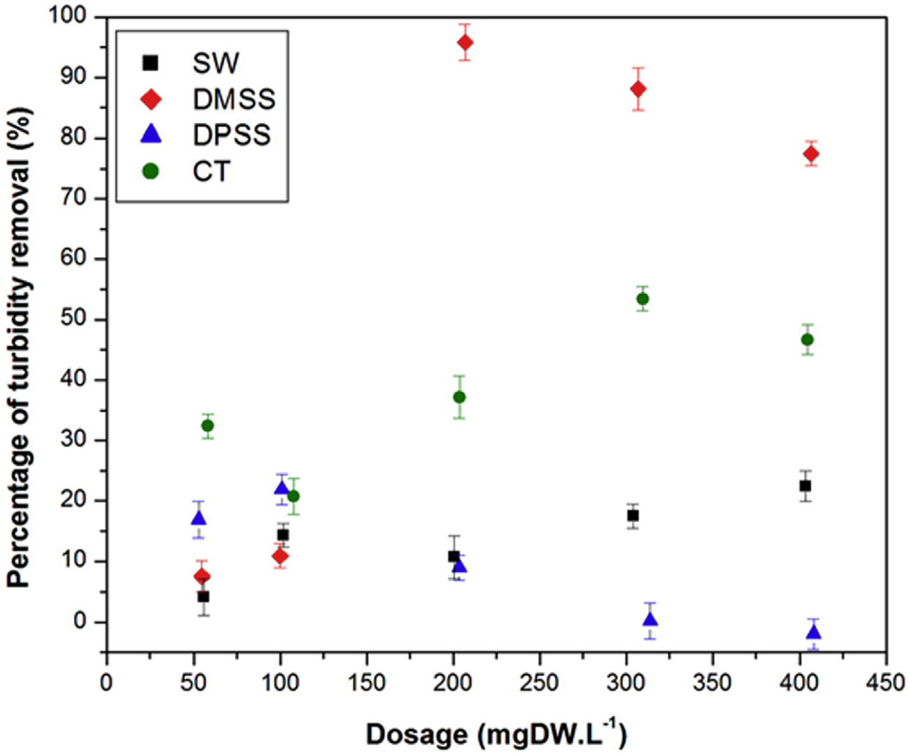

Fig. 8. Removal percentage of turbidity using biocoagulants in different dosages.

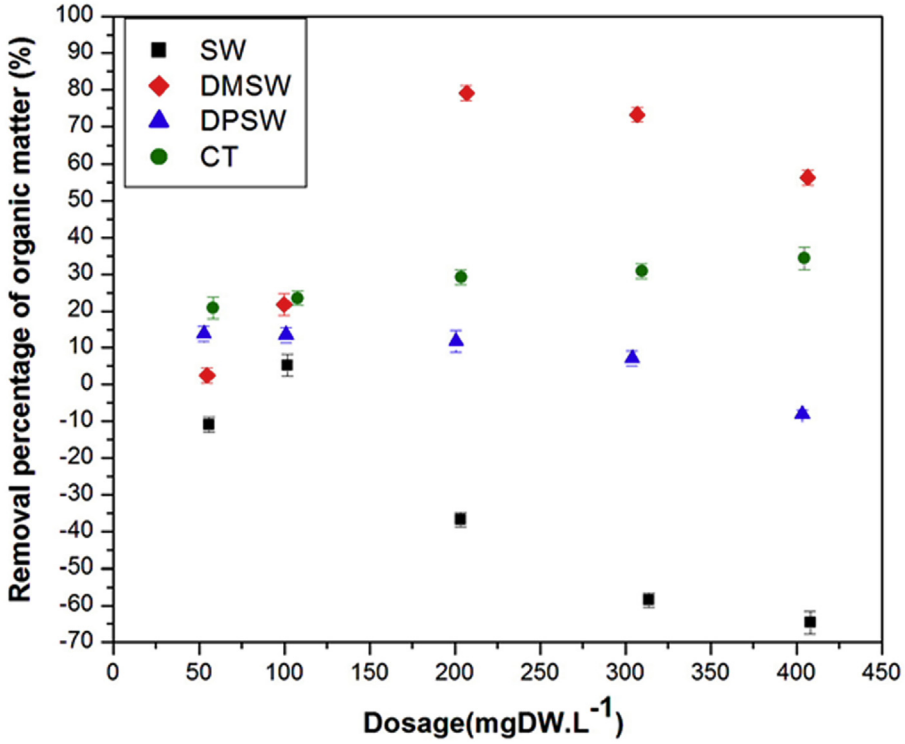

Fig. 9. Removal percentage of organic matter using the biocoagulants in different dosages.

biomaterials and the biocoagulants powders were very similar to each other, with roughness through their structures. The crystallinity was increased from SW<DMSW<DPSW<CT. The experimental assays indicated that the coagulation/flocculation processes with the biocoagulants effectively reduced the turbidity and organic matter in the water, with exception of the SW. The best dosages were 100 mg_{DW} L^{-1} for DPSW, 300 mg_{DW} L^{-1} for CT was and 200 mg_{DW} L^{-1} for DMSW. The SW was the only one that was not efficient because its residual material increased after the treatment. This is the first attempt to produce biocoagulants from direct solubilization of different systems composed of shrimp waste. Based on results, the biocoagulants produced from shrimp waste can be considered a potential and green alternative to be used in surface water treatment, especially the biocoagulant from demineralized shrimp waste.

Author contribution section

Tuanny Frantz: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Visualization. Bruna Farias: Methodology, Resources, Data Curation. Victor Leite: Methodology. Felipe Kessler: Methodology. Tito Cadaval Jr: Validation, Formal analysis, Resources, Data Curation, Supervision. Luiz A. A. Pinto: Conceptualization, Validation, Formal analysis, Resources, Data Curation, Writing - Review & Editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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