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Pectin and SDS as auxiliary flocculants for complementary treatment of textile wastewater by electrocoagulation

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Abstract−Textile wastewaters currently remain as one of the major sources of environmental pollution. In addition to the presence of several recalcitrant species, the volume of the effluent to be treated is usually quite high, due to the excessive consumption of water in this kind of processing. To avoid all the negative impacts associated with the discharge of these untreated effluents, effective remediation techniques should be applied. Although there are currently several methods available, due to complexity and volume of the wastewater, combined technologies can provide better efficiency, lower cost and less time consumption. In this work, electrocoagulation (EC) combined with the conventional flocculation process was studied for the removal of methylene blue dye (MB) in aqueous medium. Under specific EC conditions (4 pairs of electrodes, 2.5 cm spacing, electrolysis time of 203 min, $pH_{initial}$ 4, 32 V, 1.5 A) it was possible to remove 63% of the dye. Combining EC with conventional flocculation, a notable reduction in electrolysis-required time (203 to 60 min), dye (99.8%), color (100%) and turbidity (99.2%) was observed.

Keywords: Pectin, SDS, Electroflotation, Electrocoagulation, Methylene Blue

INTRODUCTION

The textile industries have a prominent and recognized importance in the global economy, providing millions of direct and indirect employments. Currently, Brazil alone has 25,200 formalized companies referring to this productive sector, generating 1.5 and 8 million of direct and indirect employees, respectively [1,2].

However, in opposition to economic development, this important sector also accumulates high amounts of water use and waste generation with environmental and societal negative impacts. In fact, the textile industry is one of the many that utilizes large volumes of water in the manufacturing process. In Brazil alone, about 2.3 million liters of water are used every second by industries, and it is projected that this demand will be 400% higher by 2050 [3]. This large volume of water ends up as wastewater, therefore needing appropriate treatment for reuse or for its final discharge. Unfortunately, textile wastewaters are characterized by the presence of recalcitrant, high toxicity and low biodegradability species, resistance to aerobic digestion, and stability to light, heat, and oxidizing agents [4-8]. The chosen methodology must take into account not only the diversity of dyes existing (and there are more than 100,000 commercially available dyes), but also the presence of salts, acids, heavy metals, suspended particles, pigments and organ-chlorine-based pesticides in the same effluent, which increases its complexity and the treatment requirements [7,9].

To achieve an efficient and economic treatment, many methodologies have been developed, which are categorized, regarding their nature, into physical (e.g., physisorption, sedimentation, flotation, flocculation, coagulation, ultrafiltration, photoionization, and incineration), chemical (neutralization, reduction, oxidation, electrolysis, chemisorption, ion-exchange, wet-air oxidation) or biological (microbiological decomposition, aerobic and anaerobic degradation) [5-7,10].

According to Sghaier et al. [5] and Singh and Arora [10] despite the physical and chemical methods showing encouraging trends, they are not efficient for all textile wastewater types. The physical methods, for instance, remove undissolved chemicals and particulate matter present in wastewater and are more effective for such

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situations. Adsorption has been effective for a considerable number of synthetic dyes [8,11,12]. However, due to the large volume of effluent to be treated, costs become prohibitive. In addition, this technology is pH dependent, operates at slow speed, and the reuse of adsorbents is not always possible [5,10].

Chemical treatments, on the other hand, usually use excess of chemicals, which requires a high cost and may result in secondary pollution [5,9,10]. Overcoming this condition, electrocoagulation uses few reagents, producing *in situ* the cation coagulant without adding counter-ions [9,13]. By uniform metal anodic dissolution, individual ions (usually Al or Fe) leave the electrode surface for the bulk of the solution and, depending on pH, generate aquo-type species, hydroxides, or metal polyhydroxides, which neutralize the charges of the contaminants, favoring the formation of flocs. Hydrogen molecules formed at the cathode evolve from the solution and assist in flotation and removal of the particulate [13-20].

Widely applied to various classes of effluents (wastewater from industries, oil refineries, galvanizing processes, laundries, etc.), EC is a well-regarded, practical and efficient technique that not only produces low amount of sludge, but also requires low capital investment [21,22]. At present, with the greater penetration of solar energy, EC technology is becoming increasingly attractive from an economic point of view and emerges as a sustainable technology [9,22,23].

However, EC technology also presents some difficulties that can compromise the efficiency of the removal process and increase operating costs. Among them, passivation and non-uniform electrode consumption, requirement for high effluent conductivity, and hydroxide solubilization deserve special attention [13,14,16,17]. In addition, the effectiveness of the electrocoagulation process is dependent on the dyestuff type, and for most textile wastewater, although significant, it usually reaches the limits of 87% [9,18-22]. Nevertheless, due to the abovementioned advantages, EC should not be discarded for this type of effluent but should be combined with other techniques or unit operations to increase the process' efficiency.

Presently, a combination of technologies treatment is gaining acceptability for removal of dyes from textile wastewaters [7,10,24,25]. GilPavas et al. [24], for example, treated a wastewater from a jeans manufacturing plant using EC coupled with activated carbon adsorption. Under optimized conditions, they achieved the following percentage removal: color 96%, COD 72%, and TOC 61%. Sun et al. [25] mineralized methylene blue very efficiently (>97%) by plasma oxidation process combined with microbial fuel cell treatment. Barhoumi et al. [26] and Hansson et al. [27] also successfully applied coupled techniques (EC/activated carbon adsorption) for the treatment of other matrices, copper removal from used water and wastewaters from wood-based industry, respectively. We strongly recommend Sing and Arora1's critical review [10] for other cases involving the textile wastewater treatments.

From this perspective, the effluent discharged from an EC station could be subjected to a simple clarification process (e.g., flocculation), which would improve its physicochemical characteristics. In this case, special attention should be paid to the choice of flocculating agent, which may damage the environment [28]. Polyacrylamide, for instance, is a flocculant whose degradation can form harmful substances, such as a carcinogenic monomer, and, when in cationic form, causes choking in fish by blocking their gills [29]. Surfactants, which promote the formation of self-assembled molecular clusters (micelles), may represent a good option once their flocculating potential and toxicity are determined [30-34]. Sodium dodecyl sulfate (SDS) is a surfactant that stands out because of its biodegradability, and has already been applied in the remediation of soils polluted by heavy metals and organic contaminants [35]: in the removal of crude oil loaded in the soil [36], in the modification of the alumina surface for adsorption of herbicides [37], and in the removal of dyes [32,38].

There is a class of natural flocculants that not only are biodegradable and non-toxic, but also may present returns and efficiencies comparable to synthetic flocculants, such as pectin [28,39]. This family of oligosaccharides and plant anionic polysaccharides, varying on the species, can constitute up to 35% of the primary cell walls [40-42]. The pectic substances have a diverse chemical structure, containing d-Galacturonic acid with α (1→4) bonds as the main constituent, as illustrated in Fig. 1(a). The three main biopolymers are homogalacturonan (≈65% of pectin), rhamnogalacturonan I and II [43].

Pectin is easily found in most fruits, in different percentages of composition. Citrus peels such as lemon, orange, passion fruit, and apple pomace are the main sources for the commercial extraction of pectin. Despite the several sources and percentages of secondary structures, their physicochemical properties are very similar to each other [42,44].

Pectic substances are currently mainly applied in food, pharmaceutical, and cosmetic industries. Its characteristics allow it to promote texture in food and ensure the stabilization of emulsions for a range of liquid drugs [45]. There are also reports of a varied range of applications, namely: anticancer effects through probiotic activi-

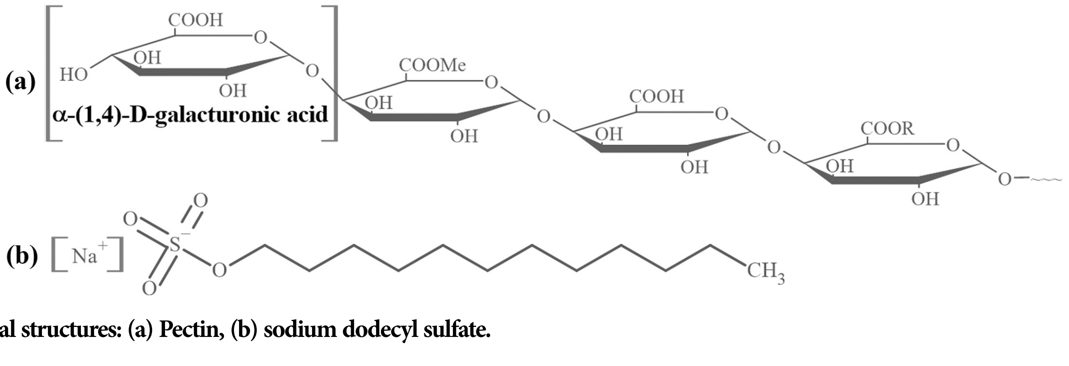

Fig. 1. Chemical structures: (a) Pectin, (b) sodium dodecyl sulfate.

ties [46], means of transportation for chemotherapeutic drugs [47], removal of metals [48,49], flocculating agent in wastewater treatment [50], and, in gel form, removal of dyes [51].

Thus, the aim of this study was to propose a simple and fast methodology as complementary treatment to EC of a synthetic textile wastewater (methylene blue solution). Using mild EC conditions, experimental planning [52], and SDS and pectin (commercial, extracted from orange and passion fruit) as flocculating agents, *in situ* and *ex situ* conditions were investigated.

MATERIALS AND METHODS

1. Reagents and Solutions

All chemicals used were of analytical grade and used as received without any further purification: sodium hydroxide (PA, ISOFAR-BRA), potassium chloride (PA, ISOFAR-BRA), potassium bromide (PA, ISOFAR-BRA), aluminum chloride hexahydrate (PA, ISOFAR-BRA), phosphoric acid (PA, ISOFAR-BRA), etanoic acid (PA, ISOFAR-BRA), Boric acid (PA, ISOFAR-BRA), potassium biphthalate (PA, ISOFAR-BRA), phenolphthalein (PA, ISOFAR-BRA), commercial citrus pectin (ISOFAR-BRA), methylene blue-MB (PA, ISOFAR-BRA), hydrochloric acid (ENSURE®, MERK-BRA), ethanol (EMPARTA® ACS, MERK-BRA), sulfuric acid (EMPARTA® ACS, MERK-BRA), sodium dodecyl sulfate-SDS (PURO, SYNTH-Brazil), and standard color solution APHA platinum-cobalt (PA, QUIMLAB-BRA). Aluminum electrodes were made from a 1.0 mm thick blade with an active electrode surface of 41.40 cm^2. All solutions were prepared with distilled water only.

The process efficiency was measured in terms of color and turbidity. A Quimis pHmeter (model Q400AS) with combined glass electrode and temperature correction was used for pH control. The evaluation of the turbidity removal was made with an ITT Corporation turbidimeter, model B 1000, and the reminiscent color and the MB concentration were evaluated by Uv-Vis spectroscopy. All electronic spectra were recorded on a Kasuaki Uv-Vis spectrophotometer, model IL-592S-BI.

Vibrational absorption spectra in the region of 4,000-400 cm^{-1} were obtained using a Fourier transform spectrophotometer (Shimadzu IR-Prestige-21 model), KBr pellet, 2.0 cm^{-1} resolution, and 40 scans.

A lab scale electrocoagulation cell was made of acrylic glass and designed with the following internal dimensions: 30.0×15.0×25.0 cm. For fitting and controlling the electrodes' spacing, the cell cover was made containing 22 slits with 1 cm spacing between them.

2. Extraction of Pectins from Passion Fruit and Orange Peels

The extraction of fruit pectins occurred based on the method described by Canteri et al. [53]. The fruits were sanitized, and the epicarp, endocarp, and seeds were removed and placed in an autoclave for 10 min, at 10^2 kPa and 120 °C. They were then segmented into smaller pieces, dried in a greenhouse at 50 °C until there was no more mass variation. The dry biomass was crushed in a cutting mill (wiley SL-31) to obtain the flour used for the pectin extraction.

Samples containing 5 g of flour were added to 250 mL of water under constant stirring at 90 °C, at pH 2 (HCl) for 60 min. The extract was filtered into a thin cotton fabric and the material retained in the filter was discarded. To the filtered, containing pectins, the same volume of ethanol was added and laid to rest for 1 hour, thus obtaining coagulated pectins. These were filtered and washed with an alcohol acid solution (0.5% HCl). Then, we washed them twice at neutral pH, with alcohol to remove mono and disaccharides, amino acids, organic acids, and salts, as well as enzymes, which can degrade polysaccharides. The excess alcohol was removed by a dialysis membrane for 24 hours. After that, they were frozen, taken to a lyophilizer (Enterprise II) for 72 hours, macerated, and sieved in 60 mesh size. The results (%R) were calculated from Eq. (1) [54]:

$$\%\,R=\frac{m_{pectin}}{m_{dried}}\times 100 \tag{1}$$

where m_{pectin} and m_{dried} correspond to the mass of pectin obtained and the dried mass, respectively.

3. Determination of the pKa of Pectins

Samples of 20 mL of a 500 mg L^{-1} pectin solution were titrated, by potentiometry, with NaOH 0.1 mol L^{-1} previously standardized with potassium biphthalate. The Gran method [55] was applied for determination of the equivalence points and pKa, according to Eq. (2):

$$[H^+]V_{NaOH}=K_aV_{eq}-K_aV_{NaOH} \tag{2}$$

$[H^+]$ is equal to 10^{-pH}, in each added NaOH volume (V_{NaOH}), K_a corresponds to the acid constant, and V_{eq} is the NaOH volume at the equivalence point.

4. Determination of the Pectin Degree of Esterification (DE)

The degree of esterification (D.E.) of pectins was evaluated from FTIR data. Peak areas (A) corresponding to COOR (≈1,747 cm^{-1}) and COO^- ((≈1,642 cm^{-1}) were obtained and DE calculation was performed using Eq. (3) [56]:

$$DE\%=\frac{A_{1747}}{(A_{1747}+A_{1642})}\times 100 \tag{3}$$

5. Pectins Flocculating Activity

5-1. Experimental Planning

Best pectin flocculation conditions were determined using a central composite rotational design (CCRD). The obtained results were assessed in the STATISTICA software version 9.0. The independent variables were pectin concentration, Al^{3+} concentration, and initial pH (Table 1). The response variable was flocculating activity. The CCRD presented 21 tests, 8 of them were factorial in two levels (+1 and −1), 6 axial points (α), and 7 central points. The concentration ranges chosen for the planning were based on results of [39]. Yokoi et al. [39] demonstrated that the flocculating activity of pectins is greatly influenced by the presence and quantity of cations (Al^{3+}, Fe^{3+}, 0.2 mmol L^{-1}), pH (3.0), pectin concentration

Table 1. Variables, levels and actual values used in the CCRD for the flocculating activity

Variable	Levels/Actual values				
	$-\alpha$	−1	0	+1	$+\alpha$
Pectin (mg L^{-1})	8	20	60	100	128
Al^{+3} (mmol L^{-1})	1	2	11	20	30
Initial pH	2.4	4.5	7.5	10.5	12.6

(15 mgL^{-1}), and temperature (30 °C). For the purposes of this work, the temperature was ambient (*ex situ* experiments=27±1 °C) and the other parameters varied according to the data presented in the Table 1.

In the validation of the model, we used the mathematical relationships of adjustment error and relative error according to Eqs. (4) and (5). These mathematical relationships measure the similarity between the experimental response and the response predicted in the model [57].

$$E_{adjustment} = Y - \hat{Y} \tag{4}$$

$$E_{relative} = \frac{E_{adjustment}}{Y} \times 100 \tag{5}$$

where Y corresponds to experimental value and $\hat{Y}$ to response expected by the model.

5-2. Flocculating Activity Tests

Pectin stock solutions (500 mg L^{-1}) and Al^{3+} (100 mmol L^{-1}) were mixed in test tubes. Dilutions were performed so that the species remained with concentrations established in the experimental design. Britton-Robinson buffer solution was used to adjust the pH. The mixtures were left under stirring and at rest for 1 hour, respectively. After sedimentation, the supernatant was carefully collected.

Pectin concentration was monitored according to the method developed by Albalasmeh et al. [58]. In a test tube containing 1 mL of pectin solution, 3 mL of concentrated sulfuric acid were added and stirred for 30 seconds. This caused an increase in the temperature of the mixture between 10 to 15 seconds. The solution was cooled in an ice bath for 2 min. Light absorption was performed in the UV/VIS (Kasuaki IL-592S-BI model) at 316 nm. The same procedure was performed for the supernatant solution after flocculating activity tests. Eq. (6) was used to calculate flocculating activity [41]:

$$\%\ \text{floc. activ.} = \frac{A_i - A_f}{A_i} \times 100 \tag{6}$$

A_i is absorbance of the initial solution after addition of concentrated sulfuric acid and A_f is absorbance of the supernatant solution after addition of concentrated sulfuric acid.

6. Methylene Blue Co-precipitation by Ionic Flocculation

6-1. Experimental Planning

The same procedure used to determine the flocculating activity of pectins was employed for determination of the best co-precipitation conditions of methylene blue, through CCRD, adjustment error, and relative error. The independent variables were methylene blue concentration (MB), Al^{3+} concentration, SDS concentration, and initial pH. The response variable was removal rate. The CCRD presented 31 tests, 16 of them were factorial at two levels (+1 and −1), 8 axial points (α), and 7 central points, as shown in Table 2.

Table 2. Variables, levels and actual values used in the CCRD for SDS co-precipitation

Variable	Levels/Actual values				
	$-\alpha$	-1	0	+1	$+\alpha$
MB (mmol L^{-1})	0.002	0.006	0.03	0.06	0.09
Al^{+3} (mmol L^{-1})	5	10	30	50	70
SDS (mmol L^{-1})	0.1	1.0	5.5	10.0	14.5
Initial pH	4.5	6.0	7.5	9.0	10.5

6-2. Methylene Blue Co-precipitation Tests by Ionic Flocculation

Stock solutions of MB, Al^{3+}, and SDS were mixed in test tubes so that final concentrations were the same as those established in the design. Britton-Robinson buffer solution was used to adjust pH. The mixtures were stirred and laid to rest for 1 hour. After sedimentation, the supernatant was carefully removed for analysis of removal rate, final pH, and turbidity (ITTB1000 turbidimeter). Concentrations of methylene blue were calculated by curves constructed in the UV/VIS at 665 nm, ionic medium, 0.01 mol L^{-1} KCl. Removal efficiency was calculated using Eq. (7):

$$\%\ \text{Removal} = \frac{C_i - C_f}{C_i} \times 100 \tag{7}$$

C_i and C_f correspond to initial and final dye concentrations, respectively, in mg L^{-1}.

7. Electrocoagulation Setup and Kinetic Procedure

The conditions of EC/EF in the removal of MB (5 mg L^{-1}) were: 4 pairs of aluminum electrodes in parallel, 2.5 cm spacing, initial pH 4, 32 V, and 1.5 A, in accordance with Góes et al. [18]. In these conditions, the kinetic study was performed with pectins and SDS, *in situ*, aiming to assess their complementary effects on the removal profile and thus establish comparisons with the optimized process conditions established by Góes et al. [18].

The concentrations of the pectins and SDS were determined after the optimization process through CCRD. Every 5 min, in a total of 90 min, an aliquot was removed from the electrochemical cell for analysis of removal, final pH, color, and turbidity. The obtained results were adjusted to the kinetic models of the first order and second order [59] according to Eqs. (8) and (9):

$$q_t = q_{eq}(1 - e^{-k_1 t}) \tag{8}$$

$$q_t = \frac{k_2 q_{eq}^2 t}{1 + q_{eq} k_2 t} \tag{9}$$

where q_{eq} (mg g^{-1}) is quantity adsorbed in equilibrium; q_t (mg g^{-1}) is quantity adsorbed in time t (min); k_1 (min^{-1}) is the speed constant of the first order and k_2 (g mg^{-1} min^{-1}) is the speed constant of second order.

8. ANOVA (Tukey test 95%)

The flocculants were also tested in complementary *ex situ* treatment, *i.e.*, after EC/EF, for 203 min under the same conditions previously described. Pectin and SDS concentrations were obtained after optimization through CCRD. Samples of the electroflocculated material with Al^{3+} were mixed in test tubes with solutions of the flocculants in 4.5, 7.5, and 10.5 buffers. The mixtures were stirred and laid to rest for 1 hour. After sedimentation, the supernatant was removed for analysis of removal rate, final pH, color, and turbidity. For the color, a curve was constructed in a concentration range between 25 and 500 mg L^{-1} from the APHA standard color solution at the UV/VIS at 440 nm.

The Tukey test ($p<0.05$) was used for the removal rate variable. By making two-by-two comparisons of the group averages [60], it

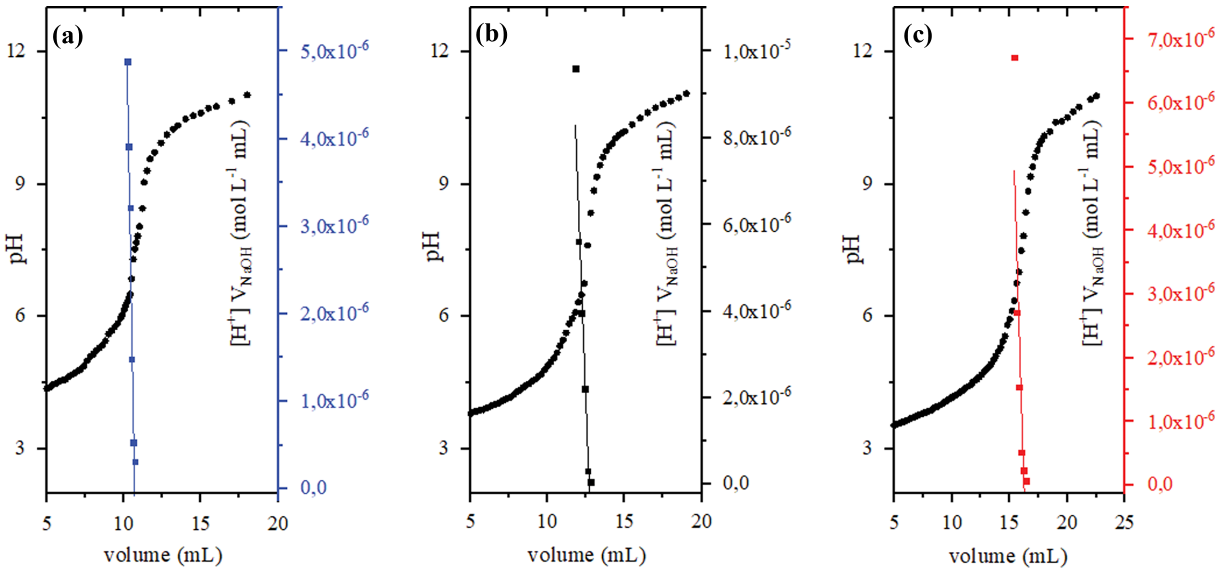

Fig. 2. Application of the Gran method in the calculation of the equivalence volume and pKa of pectins: (a) Commercial, (b) orange, and (c) passion fruit.

provides an honestly significant difference. To this end, 3 pectins and SDS combined in 3 pH values plus one control group totaled 13 groups, each with 5 replicates. The control group presented values after EC/EF without complementary treatment. The test was applied in groups with the same initial pH value, and with constant comparison with the control group.

RESULTS AND DISCUSSION

1. Extraction and Characterization of the Pectins

The results found in the extraction of pectins were 17% and 16% for orange and passion fruit, respectively. Similar values are available in the literature: 15.5% for orange [54] and 14.8% for passion fruit [61], indicating the efficiency of the adopted procedure.

The titration curve and the Gran plot (Fig. 2) allowed to determine titration's endpoint. Equivalence volumes were 10.7 mL (commercial pectin), 12.7 mL (orange pectin), and 16.2 mL (passion fruit pectin). Pectin is a weak acid with an equivalence point at pH>7. Gran equation (Eq. (2)) shows that when NaOH's volume is half the equivalence volume, the concentration of H^+ is equal to Ka (pH=pKa). The pKa is a key parameter for analysis of the charge as a function of pH, because when the system shows pH values above pKa ones, the pectin acquires negative charge density (deprotonated carboxyl groups), and the number of charges tends to increase with the increasing pH [62], making it necessary that at least one a logarithmic unit log is above the pKa to ensure that more than 50% of the carboxyl groups are free, thus providing enough negative charges for the formation of an ionic species [63]. The pKa's calculated were 4.46; 3.95; and 3.88, respectively, for commercial, orange, and passion fruit pectins. In this context, the biopolymers here in question are polyanions, and the pKa's are in accordance with those existing in the literature, where the range can vary from 2.8 to 4.5 [63,64].

Besides the pectin, the cell wall of vegetables presents cellulose microfibrils and hemicellulose. Higher vegetables may also contain glycoproteins, phenolic compounds, lignin, minerals, and enzymes [40]. This heterogeneity implies that the biomass here in question may show variations regarding the chemical structures, but the main component will always be pectins. Characteristic peaks of polysaccharides materials can be noted in Fig. 3. The broadband in the range of 3,700-3,000 cm^{-1} and another between 3,000-2,780 cm^{-1} were attributed, respectively, to the different stretching modes of the OH group and the symmetric and asymmetric stretches of the methyl and methylene groups [65] present in polysaccharides. Asymmetric stretches were also observed in 1,747 cm^{-1} and 1,645 cm^{-1} related to the esterified and free CO group, respectively [66]. At 1,346 cm^{-1}, the deformation corresponds to the OH in the plane [67], and at 1,240 cm^{-1} it corresponds to the stretching of the guaiacyl ring [68].

The highlighted regions in Fig. 3 represent the areas used for calculating the DE. The values were 37.4% (commercial), 82.6% (orange), and 94.6% (passion fruit). High methoxyl pectins (HMP) have DE>50%; if they present lower DE, they are classified as low methoxy pectins (LMP) [43]. When intended for trade, they are standardized products with sucrose, glucose, or lactose. Those extracted at pH 2.5 and 100 °C for 45 min have a degree of methoxylation bigger than 70% [69]. Thus, differences in DE reflect in changes that affect the properties of these polysaccharides.

2. Optimization of the Flocculating Activity and Co-precipitation by Ionic Flocculation

Bioflocculation results from the CCRD are presented in Table S1. Orange and passion fruit pectins stand out in front of commercial pectin, presenting a flocculating activity with higher values in almost all experiments carried out under the same conditions. On the right side of the Table S1 are the results of the CCRD for removal of the MB by co-precipitation. Adding SDS to Al^{3+} there was the formation of a white precipitate (Al-SDS) that caused the turbidity of the solution and was responsible for MB co-precipitation. The

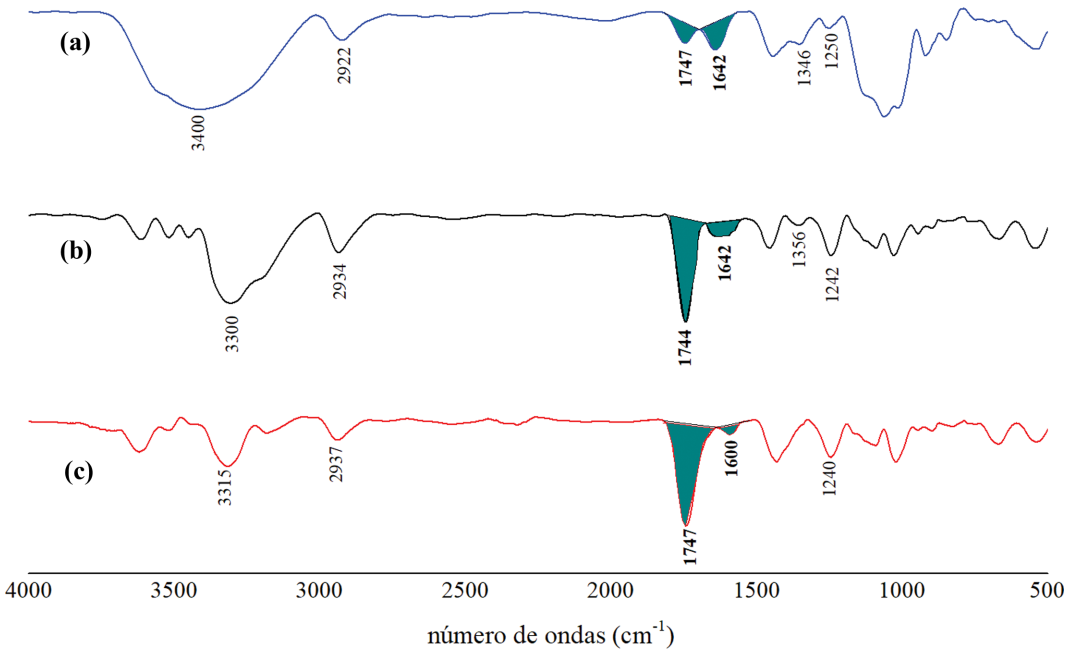

Fig. 3. Pectin FTIR spectrum, (a) commercial pectin, (b) orange pectin, and (c) passion fruit pectin.

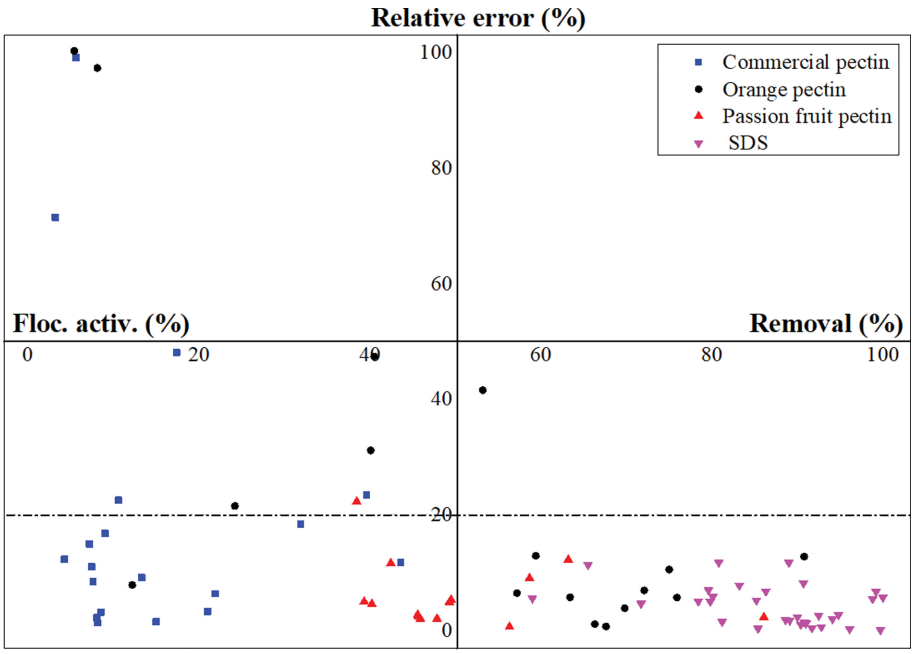

Fig. 4. Relative error for flocculating activity and co-precipitation removal.

system with SDS worked properly, with all removals between 65.3 and 99.8%. It is noteworthy that the hydrolysis of Al^{3+} is responsible for making the pH always acidic, with the possibility of correction with carbonate for its subsequent disposal in water bodies. Even though the turbidity increases in some cases, due to the SDS micelles formed [38], its values are within the limit established by Brazilian legislation (Table S1).

Variance (ANOVA) analysis showed a significant lack of adjustment ($p<0.05$) for the investigated responses (Table S2). Rodrigues and Iemma [57] state that adjustment is not a determining factor for the development of a predictive model, especially when it is related to the central points, thus reflecting a low value for the pure error.

Relative error (RE) of flocculating activity and co-precipitation is illustrated in Fig. 4. Commercial pectin showed divergence above 20% for relative error (Table S3), making it impossible to develop a predictive model for it [57]. Regarding orange and passion fruit pectins, the values of flocculating activity above 55% present a RE lower than 20%, corroborating with a smaller difference between the experimental and predicted values. As for the SDS, the values for removal rate are within a margin of error below 20% (Table S3). Thus, it was possible to determine the quadratic models from the coded regression coefficients (Table S4) for flocculating activity of orange and passion fruit pectin, and for the methylene blue removal rate by co-precipitation, with equations 10, 11 and 12 being the respective mathematical models.

$$\textbf{ativ. floc.}\ (\%)=66.9+16.1\text{pec}+12.2\text{pec}^2+9.9\text{Al}-8.1\text{Al}^2-4.1\text{pH}-17.3\text{pH}^2+19.9\text{pec Al}-5.53\text{pec pH}+5.78\text{Al pH} \quad (10)$$

$$\textbf{ativ. floc.}\ (\%)=46.6+1.46\text{pec}+6.53\text{Al}-7.18\text{Al}^2+7.36\text{pH}-7.74\text{pH}^2+31.3\text{pec Al}+1.86\text{pec pH}+4.46\text{Al pH} \quad (11)$$

$$\textbf{rem.}\ (\%)=92-1.15\text{MB}-1.03\text{MB}^2-2.45\text{Al}-1.22\text{Al}^2-3.66\text{pH}-2.44\text{pH}^2+5.5\text{SDS}-2.05\text{SDS}^2+1.69\text{MB Al}+1.94\text{MB pH}-3.37\text{MB SDS}+3.14\text{Al SDS}+3.07\text{pH SDS} \quad (12)$$

PEC, Al, MB, and SDS variables correspond, respectively, to the concentrations of pectin, aluminum, methylene blue, and SDS, in mmol L^{-1}, except pectin (mg L^{-1}). Positive coefficient signs indicate that the variables contribute to the desired response. Negative signs, on the other hand, show factors capable of decreasing the expected response [41].

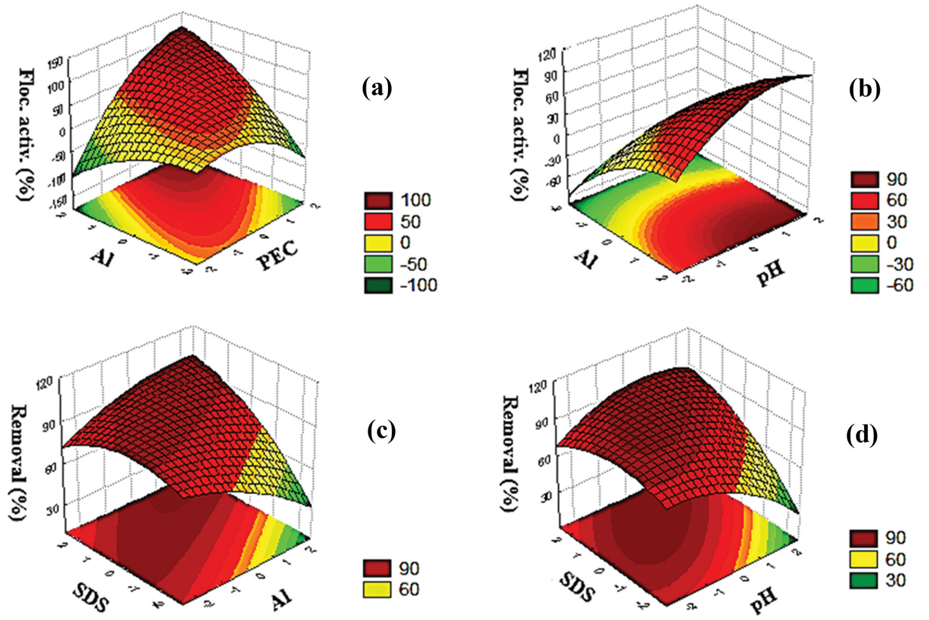

Fig. 5. Response surfaces for the variables: flocculating activity (%) and removal rate (%): (a) Aluminum - orange pectin (pH 7), (b) aluminum - initial pH for the passion fruit pectin (100 mg L^{-1}), (c) SDS - aluminum, and (d) SDS - initial pH.

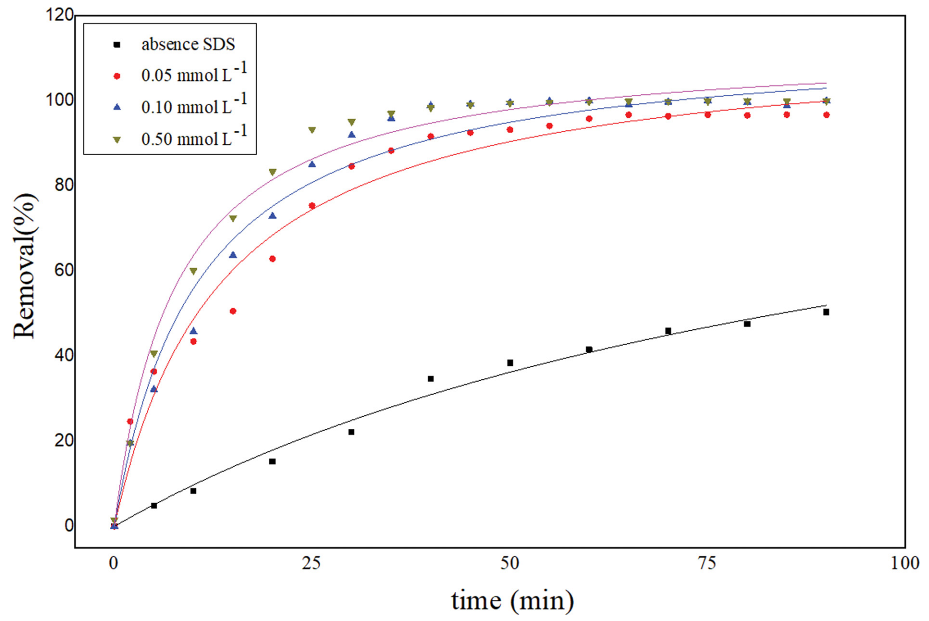

Fig. 6. Methylene blue removal kinetics by electroflotation in the presence of SDS.

Table 3. Results of adjustments for first- and second-order models for the removal of methylene blue by EC/EF in the presence of SDS

MB (mmol L^{-1})	SDS (mmol L^{-1})	$^{a}Re_{exp.}$ (%)	1st Order			2nd Order		
			k_1 (min^{-1})	$^{b}Re_{theo.}$ (%)	R^2 (%)	k_2 (% min)$^{-1}$	$Re_{theo.}$ (%)	R^2 (%)
0.014	0.05	96.7	7.6×10^{5}	75.1	33.4	6.4×10^{-4}	115	96.9
0.014	0.10	99.6	4.8×10^{3}	81.3	32.3	8.2×10^{-4}	115	97.4
0.140	0.50	100	5.4×10^{3}	86.5	38.6	1.1×10^{-3}	113	98.7

^{a}Experimental removal rate, ^{b}theoretical removal rate.

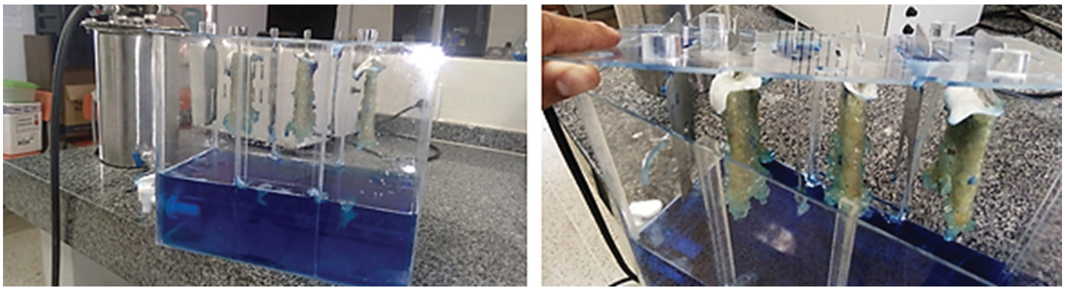

Fig. 7. End of the EC/F test with commercial pectin *in situ.*

Given the significant interactions, it was possible to obtain the response surfaces for the coded variables, as shown in Fig. 5. At pH close to 7, concentrations above 11 mmol L^{-1} aluminum (central point) require amounts greater than 60 mg L^{-1} pectin (Table 1), which allow 100% of the dissolved material to flocculate (Fig. 5(a)). Regarding SDS, for concentrations below the central point (5.5 mmol L^{-1}), 5 mmol L^{-1} aluminum (Table 2) is required to remove 90% of the dye at a pH close to neutrality (Fig. 5(c)).

3. Removal Kinetics

According to the response surface (Fig. 5(c)) low concentrations of SDS and Al^{3+} ions (produced in the anode) allow greater dye removal (>90%). The SDS minimum concentration was therefore established as of 0.05 mmol L^{-1} for kinetic studies (Table 2). Fig. 6 shows experimental data and nonlinear graphs for the first- and second-order models. The kinetic study allowed us to determine the removal rate, equilibrium time, and understand the removal efficiency. Kinetic constants and theoretical removal amounts ($Re_{theo.}$) of the dye are presented in Table 3.

Curve design showed that equilibrium time was around 60 min for systems with SDS. In SDS's absence, the plateau was not formed in 90 min, thus requiring longer times for balance to be reached. The effect of SDS concentration increased the removal by 3%, while the proportional increase of dye and SDS concentration improved by 4%, for the same conditions. The kinetic model with best adjustment was the second order. Since increased concentration of SDS and dye does not interfere with removal rate, kinetics is governed by the number of microbubbles and Al^{3+} formed by the electrodes in the flocculating system.

In the electrochemical system, flotation prevailed. Al-SDS flocs can aggregate the methylene blue cations and, with the action of microbubbles, undergo flotation predominantly to co-precipitation [38]. Thus, the use of SDS as an improvement agent in EC/EF processes is a viable alternative, because besides being biodegradable and removing 99% of the dye, it promotes a reduction in removal time, which saves energy. Additionally, turbidity (0.36-14.3 NTU), final pH (6.5-7.6), and color (no noticeable color) complied with Brazilian environmental standards.

Best conditions for pectin flocculation (100 mg L^{-1} pectin, pH above 4.5 and 20 mmol L^{-1} Al^{3+}) are presented on response surfaces 5a and 5b. *In situ* kinetic studies in the electrochemical system were carried out in the search for an efficient and low-cost bioflocculant, capable of removing cationic dyes. However, flocculation did not occur in the system. A pectin 'film' was formed on the surface of the anode, making it impossible to flocculate. Fig. 7 shows the electrode covered with the supposed biofilm that was produced. Therefore, the limitations of biomaterial in the treatment of effluents by electrochemical processes are evident.

4. ANOVA (Tukey test 95%)

In *ex situ* experiments, after EC/EF, pectin and SDS concentrations were the same as those used in *in situ* tests. It is important to note that the amount of aluminum dissolved in the solution by EC was not sufficient to flocculate pectins and SDS, requiring 11 mmol L^{-1} of Al^{3+} as additional aluminum.

Table 4 shows the results of the 12 analyzed groups. The mean values of the control group (13th) were: 63% (removal), 841 HU (color), 45 NTU (turbidity), and 6.14 (final pH). Pectins contributed to reducing color and turbidity, leaving, in some experimental conditions, values within the requirements established by the Brazilian Environmental National Council (CONAMA) [70]. Among them, the commercial one showed higher efficiency in the complementary treatment, having an increase of 14.1% in dye removal at pH 4.5. Results of the Tukey test (Table S5) allowed the plotting of Fig. 8. In it, it is possible to observe that there is no significant difference between the passion fruit pectin and the control group at all pH. The high degree of esterification (DE) of passion fruit pectin (94.6%) justifies low values of complementary removal, show-

Table 4. Results for significant comparisons of ANOVA (Tukey test), *ex situ*, for experiments after the electroflotation

							Commercial pectin							
**Comp. Re. (%)	*Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f
		pH_i 4.5					pH_i 7.5					pH_i 10.5		
+14.1	77.1^a	39.3	23	2.66	+12.0	75.0^b	22.1	17	3.03	+1.56	64.6^c	568	19	3.69
+11.7	74.7^a	77.7	22	2.64	+12.8	75.8^b	26.4	15	3.05	+2.65	65.7^c	651	24	3.83
+5.35	68.4^a	89.7	25	2.60	+4.28	67.3^b	41.9	20	3.07	0	63.0^c	566	17	3.70
+7.81	70.8^a	78.5	24	2.55	+9.19	72.2^b	34.5	16	3.09	+3.10	66.1^c	503	16	3.72
+11.5	74.5^a	59.8	28	2.72	+10.4	73.4^b	41.5	18	3.07	+4.42	67.4^c	505	22	3.65
							Orange pectin							
Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f
		pH_i 4.5					pH_i 7.5					pH_i 10.5		
+9.85	72.9^a	169	28	3.05	+11.0	74.0^b	53.2	25	3.20	+8.75	71.8	108	16	3.70
+9.61	72.6^a	208	27	2.57	+10.7	73.7^b	202	24	3.18	+10.7	73.7	159	16	3.73
+3.55	66.6^a	174	30	2.61	+4.55	67.6^b	79.2	24	3.21	+4.10	67.1	207	17	3.75
+6.03	69.0^a	222	28	2.6	+7.55	70.6^b	66.4	26	3.19	+5.83	68.8	204	17	3.72
+8.35	71.4^a	177	25	2.75	+10.6	73.6^b	43.2	24	3.20	+10.8	73.8	136	17	3.65
							Passion fruit pectin							
Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f
		pH_i 4.5					pH_i 7.5					pH_i 10.5		
+0.173	63.2	110	17	3.22	+2.55	65.6	23.4	20	3.45	+0.81	63.8^c	125	9.3	3.64
+1.908	64.9	99.0	16	3.10	+3.97	70.0	28.8	21	3.48	+2.27	65.3^c	130	9.4	3.80
0	63.0	99.4	20	3.20	0	63.0	77.3	28	3.50	0	63.0^c	147	9.0	3.75
0	63.0	101	22	3.30	0	63.0	69.1	23	3.60	0	63.0^c	142	9.8	3.70
+0.453	63.5	102	23	3.20	+0.49	63.5	79.6	30	3.65	0	63.0^c	149	10	3.59
							SDS							
Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f	Comp. Re. (%)	Total Re. (%)	Color (uH)	Turbidity (NTU)	pH_f
		pH_i 4.5					pH_i 7.5					pH_i 10.5		
+34.6	97.6	***	4.8	3.26	+34.7	97.7	***	5.2	3.07	+34.7	97.7	***	3.1	3.22
+36.0	99.0	***	6.4	3.41	+36.2	99.2	***	8.9	3.15	+36.8	99.8	***	4.8	3.35
+29.3	92.3	***	5.2	3.30	+29.4	92.4	***	6.8	3.03	+29.5	92.5	***	4.2	3.24
+31.7	94.7	***	4.6	3.28	+32.6	95.6	***	4.6	3.18	+32.5	95.5	***	4.0	3.50
+33.7	96.7	***	4.9	3.40	+33.8	96.8	***	5.6	3.22	+34.1	97.1	***	4.5	3.17

* Total removal, ** complementary removal, *** values below the detection limit of the analytical curve, ^{a,b,c} statistically equal values.

ing that deprotonated carboxyl groups are vital in the removal. Orange pectin shows no difference from commercial pectin at pH 4.5 and 7.5. At pH 10.5, commercial pectin did not perform well in the removal. The results of Table S1, for low flocculating activity, are in accordance with the lowest values of complementary removal, presented in Table 4. Therefore, the flocculating activity is a parameter that serves to predict possible removals under adjusted experimental conditions.

Unlike pectins, SDS had excellent efficiency in the complementary treatment with removals between 29.3 and 36.8%, and a total removal rate of 99.8%. Although solutions resulting from the treatment with SDS had virtually no color, it was impossible to calculate them, because the values were lower than the detection limit of the analytical curve.

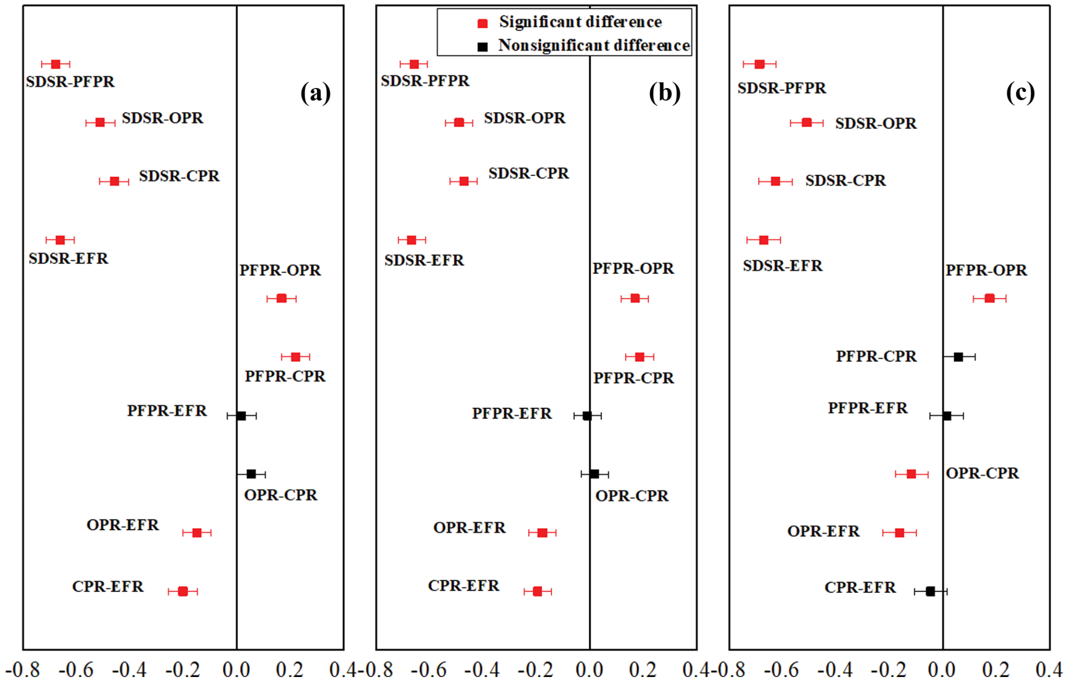

Fig. 8. Comparisons of means using the Tukey test for removals. (a) pH 4.5; (b) pH 7.5 and (c) pH 10.5. EFR - electroflotation removal, CPR - commercial pectin removal, OPR - orange pectin removal; PFPR - passion fruit pectin removal; SDS removal.

CONCLUSION

Results showed that pectins extracted from orange and passion fruit presented high degrees of esterification, thereby hindering the removal of methylene blue. Through the CCRD, it was possible to determine the favorable conditions of pectin flocculation and methylene blue co-precipitation by SDS ionic flocculation, and it was possible to describe predictive models. However, it was not possible to perform the complementary treatment of EC/EF using *in situ* pectins, because a film was formed on electrodes' surface. A low removal performance (14.1%) was observed in the complementary treatment using *ex situ* pectins.

The SDS acted efficiently in the electroflocculation system (*in situ*) and was able to complement the treatment, contributing to a removal of 99% and leaving the effluent under disposal conditions in water bodies. In the *ex situ* treatment, it was possible to remove 99.8% of the dye, leaving the effluent free of color and with low turbidity. This compound is biodegradable and is a viable alternative in the complementary treatment of EC/EF (*in situ* and *ex situ*) for effluents containing cationic dye.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Pectin and SDS as auxiliary flocculants for complementary treatment of textile wastewater by electrocoagulation

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Table S1. CCRD results for the flocculating activity and methylene blue co-precipitation

Variable Essay	Pectin /mg L^{-1}	Al^{3+} /mmol L^{-1}	Initial pH -	[a]Floc. Activ. commercial /%	Floc. Activ. orange /%	Floc. Activ. passion fruit /%
1	20	2.0	4.5	20.8	39.9	58.5
2	20	2.0	10.5	43.4	24.0	63.0
3	20	20	4.5	0.58	5.09	0
4	20	20	10.5	0.28	5.22	5.41
5	100	2.0	4.5	5.42	53.0	6.37
6	100	2.0	10.5	3.00	7.93	1.42
7	100	20	4.5	31.7	90.6	56.1
8	100	20	10.5	21.7	75.7	85.9
9	8.0	11	7.5	8.81	0.59	40.0
10	128	11	7.5	4.06	40.3	38.3
11	60	1.0	7.5	17.2	7.30	0
12	60	30	7.5	39.4	57.0	42.3
13	60	11	2.4	13.1	0	0
14	60	11	12.6	14.8	12.0	39.1
15 (C)	60	11	7.5	7.42	67.4	45.4
16 (C)	60	11	7.5	7.00	63.2	45.5
17 (C)	60	11	7.5	7.87	66.1	45.7
18 (C)	60	11	7.5	7.25	59.2	49.3
19 (C)	60	11	7.5	10.4	71.9	49.1
20 (C)	60	11	7.5	7.94	74.8	47.7
21 (C)	60	11	7.5	8.32	69.6	45.7

[c]Parameters for effluent release into water bodies			
Color	Turbidity	Dye	pH
75	100	Absent	5-9
(uH)	(NTU)	---	---

[a]Flocculating activity
[b]Methylene blue
[c]BRAZILIAN LEGISLATION 357/2005 [56].

Variable Essay	[b]MB /mmol L^{-1}	Al^{3+} /mmol L^{-1}	Initial pH -	SDS /mmol L^{-1}	Final pH -	Turbidity NTU	Removal /%
1	0.006	10	6.0	1.0	3.65	2.30	99.8
2	0.006	10	6.0	10	3.48	2.40	99.5
3	0.006	10	9.0	1.0	3.74	5.30	79.6
4	0.006	10	9.0	10	3.61	3.80	98.6
5	0.006	50	6.0	1.0	3.67	4.30	88.8
6	0.006	50	6.0	10	3.52	8.60	95.9
7	0.006	50	9.0	1.0	3.52	15.6	58.8
8	0.006	50	9.0	10	3.42	9.90	99.0
9	0.06	10	6.0	1.0	3.69	7.00	90.2
10	0.06	10	6.0	10	3.54	9.60	90.5
11	0.06	10	9.0	1.0	3.78	17.8	85.0
12	0.06	10	9.0	10	3.69	13.3	79.9
13	0.06	50	6.0	1.0	3.48	28.0	81.0
14	0.06	50	6.0	10	3.4	7.00	88.4
15	0.06	50	9.0	1.0	3.58	54.0	79.4
16	0.06	50	9.0	10	3.44	27.0	88.9
17	0.002	30	7.5	5.5	3.61	16.5	80.6
18	0.09	30	7.5	5.5	3.52	18.9	85.2
19	0.03	05	7.5	5.5	3.63	14.3	86.1
20	0.03	70	7.5	5.5	3.44	20.0	78.2
21	0.03	30	4.5	5.5	3.40	8.60	83.0
22	0.03	30	10.5	5.5	3.55	16.8	71.5
23	0.03	30	7.5	0.1	3.68	4.50	65.3
24	0.03	30	7.5	14.5	3.47	12.9	92.3
25 (C)	0.03	30	7.5	5.5	3.60	6.00	91.5
26 (C)	0.03	30	7.5	5.5	3.50	6.00	90.6
27 (C)	0.03	30	7.5	5.5	3.59	6.50	89.8
28 (C)	0.03	30	7.5	5.5	3.56	6.20	90.8
29 (C)	0.03	30	7.5	5.5	3.58	6.70	93.9
30 (C)	0.03	30	7.5	5.5	3.55	4.70	94.6
31 (C)	0.03	30	7.5	5.5	3.58	5.30	92.6

Table S2. Analysis of variance (ANOVA) for flocculating activity and methylene blue co-precipitation

Pectins flocculating activity

Factors	Commercial (R^2=0.893)			Orange (R^2=0.859)			Passion fruit (R^2=0.916)		
	SS[a]/10^2	MS[b]/10^2	P value	SS/10^2	MS/10^2	P value	SS/10^2	MS/10^2	P value
Pec[c] (L)	0.0923	0.0923	0.0371	35.4	35.4	0.0000[j]	0.292	0.292	0.0214
Pec (Q)	0.0833	0.0833	0.0444	22.4	22.4	0.0001	0.100	0.100	0.1195
Al[d] (L)	0.264	0.264	0.0041	13.4	13.4	0.0004	5.83	5.83	0.0000
Al (Q)	7.32	7.32	0.0000	9.78	9.78	0.0010	7.75	7.75	0.0000
pHi[e] (L)	0.119	0.119	0.0232	2.26	2.26	0.0289	7.40	7.40	0.0000
pHi (Q)	0.549	0.549	0.0006	45.0	45.0	0.0000	8.99	8.99	0.0000
Pec-Al (L)	14.67	14.67	0.0000	31.6	31.6	0.0000	78.3	78.3	0.0000
Pec-pHi (L)	1.51	1.51	0.0000	2.44	2.44	0.0250	0.28	0.28	0.0235
Al-pHi (L)	1.16	1.16	0.0001	2.67	2.67	0.0211	1.58	1.58	0.0004
Lack of fit	2.99	0.598	0.0001	24.1	4.82	0.0016	9.79	1.96	0.0000
Pure error	0.0778	0.0129		1.66	0.277		0.182	0.0304	
Total SS	28.8			183.3			119.4		

Methylene blue co-precipitation by ionic flocculation (R^2=0.762)

Factors	SS/10^2	MS/10^2	P value
MB[f] (L)	0.315	0.315	0.0201
MB (Q)	0.303	0.303	0.0218
Al (L)	1.44	1.44	0.0005
Al (Q)	0.423	0.423	0.0109
pHi (L)	3.22	3.22	0.0001
pHi (Q)	1.71	1.71	0.0003
SDS[g] (L)[h]	7.27	7.27	0.0000
SDS (Q)[i]	1.21	1.21	0.0009
MB-Al (L)	0.459	0.459	0.0091
MB-pHi (L)	0.605	0.605	0.0049
MB-SDS (L)	1.82	1.82	0.0003
Al-pHi (L)	0.0495	0.0495	0.2601
Al-SDS (L)	1.58	1.58	0.0004
pHi-SDS (L)	1.51	1.51	0.0005
Lack of fit	6.40	0.640	0.0008
Pure error	0.192	0.032	
Total SS	27.8		

[a]Sum square, [b]mean square, [c]pectin concentration, [d]aluminum concentration, [e]initial hydrogen ionic potential, [f]methylene blue concentration, [g]SDS concentration, [h]linear, [i]quadratic, [j]value lower than 10^{-4}.

Table S3. Relative error for pectin flocculating activity and methylene blue co-precipitation by SDS ionic flocculation

Commercial pectin			Orange pectin			Passion fruit pectin			SDS		
$Y_{exp.}$[a]	$\hat{Y}_{pred.}$[b]	RE[c] %	$Y_{exp.}$	$\hat{Y}_{pred.}$	RE %	$Y_{exp.}$	$\hat{Y}_{pred.}$	RE %	$Y_{exp.}$	$\hat{Y}_{pred.}$	RE %
43.4	38.3	11.8	90.6	78.9	12.8	85.9	83.9	2.37	99.8	94.0	5.79
39.4	30.1	23.5	75.7	71.3	5.77	63	55.3	12.3	99.5	99.3	0.163
31.7	37.5	18.4	74.8	66.9	10.6	58.5	53.1	9.12	99	92.3	6.8
21.7	23.1	6.43	71.9	66.9	6.99	56.1	56.5	0.694	98.6	93.2	5.53
20.8	20.1	3.39	69.6	66.9	3.92	49.3	46.6	5.38	95.9	96.2	0.348
17.2	25.5	48.1	67.4	66.9	0.780	49.1	46.6	4.96	94.6	92.0	2.78
14.8	15.0	1.55	66.1	66.9	1.17	47.7	46.6	2.11	93.9	92.0	2.05
13.1	11.9	9.22	63.2	66.9	5.81	45.7	46.6	2.05	92.6	92.0	0.679
10.4	8.05	22.6	59.2	66.9	13.0	45.7	46.6	2.09	92.3	95.0	2.67
8.81	7.33	16.8	57.0	60.7	6.51	45.5	46.6	2.52	91.5	92.0	0.515
8.32	8.05	3.21	53.0	30.9	41.6	45.4	46.6	2.79	90.8	92.0	1.29
7.94	8.05	1.42	40.3	59.4	47.4	42.3	37.3	11.7	90.6	92.0	1.51
7.87	8.05	2.32	39.9	27.5	31.2	40.0	41.9	4.65	90.5	83.0	8.25
7.42	8.05	8.52	24.0	18.8	21.6	39.1	37.1	5.05	90.2	91.2	1.09
7.25	8.05	11.1	12.0	11.0	7.93	38.3	46.8	22.3	89.8	92.0	2.42
7	8.05	15.0	7.93	0.22	97.3	6.37	−10.2	260	88.9	90.5	1.82
5.42	0.05	99.0	7.30	27.4	275	5.41	14.6	171	88.8	78.3	11.8
4.06	4.56	12.4	5.22	10.5	100	1.42	−0.678	148	88.4	86.7	1.92
3	0.857	71.4	5.09	−4.01	179	0	−5.26	-	86.1	92.0	6.85
0.58	3.41	489	0.59	5.27	793	0	12.4	-	85.2	85.6	0.425
0.28	6.34	2,164	0	24.7	-	0	15.3	-	85.0	80.5	5.29
-	-	-	-	-	-	-	-	-	83.0	89.5	7.87
-	-	-	-	-	-	-	-	-	81.0	82.3	1.58
-	-	-	-	-	-	-	-	-	80.6	90.1	11.8
-	-	-	-	-	-	-	-	-	79.9	84.6	5.91
-	-	-	-	-	-	-	-	-	79.6	75.6	5.08
-	-	-	-	-	-	-	-	-	79.4	73.8	7.03
-	-	-	-	-	-	-	-	-	78.2	82.2	5.13
-	-	-	-	-	-	-	-	-	71.5	74.9	4.73
-	-	-	-	-	-	-	-	-	65.3	72.7	11.4
-	-	-	-	-	-	-	-	-	58.8	62.1	5.61

[a]Experimental value, [b]Predicted value, [c]Relative error.

Table S4. Regression coefficients for flocculating activity and methylene blue co-precipitation

Pectins flocculating activity				
Factors	Orange (R^2=0.859)		Passion fruit (R^2=0.916)	
	Regression coefficients	P value	Regression coefficients	P value
Mean	66.9	0.0000[h]	46.6	0.0000
Pec[a] (L)	16.1	0.0000	1.46	0.0212
Pec (Q)	−12.2	0.0001	−0.817	0.1194
Al[b] (L)	9.91	0.0004	6.53	0.0000
Al (Q)	−8.07	0.0010	−7.18	0.0000
pHi[c] (L)	−4.07	0.0289	7.36	0.0000
pHi (Q)	−17.3	0.0000	−7.74	0.0000
Pec-Al (L)	19.9	0.0000	31.3	0.0000
Pec-pHi (L)	−5.53	0.0250	1.86	0.0235
Al-pHi (L)	5.78	0.0211	4.45	0.0004

Methylene blue co-precipitation by ionic flocculation (R^2=0.762)		
Factors	Regression coefficients	P value
Mean	92.0	0.0000
MB[d] (L)	−1.15	0.0201
MB (Q)	−1.03	0.0218
Al (L)	−2.45	0.0005
Al (Q)	−1.22	0.0109
pHi (L)	−3.66	0.0001
pHi (Q)	−2.44	0.0003
SDS[e] (L)[f]	5.50	0.0000
SDS (Q)[g]	−2.05	0.0009
MB-Al (L)	1.69	0.0091
MB-pHi (L)	1.94	0.0049
MB-SDS (L)	−3.37	0.0003
Al-pHi (L)	0.556	0.2601
Al-SDS (L)	3.14	0.0004
pHi-SDS (L)	3.07	0.0005

[a]Pectin concentration, [b]aluminum concentration, [c]initial hydrogen ionic potential, [d]methylene blue concentration, [e]SDS concentration, [f]linear, [g]quadratic, [h]value lower than 10^{-4}.

Table S5. ANOVA (Tukey test 95%) for significant comparisons, *ex situ*, for experiments after electroflotation

Tukey test - pH 4.5						
Source of variation	SS[a]	DF[b]	MS[c]	F_{ratio}	P_{value}	$F_{critical}$
Between groups	1.51	4	0.378	470	1.83×10^{-19}	2.87
Within groups	0.0161	20	0.000805			
Total	1.53	24				
Tukey test - pH 7.5						
Source of variation	SS	DF	MS	F_{ratio}	P_{value}	$F_{critical}$
Between groups	1.47	4	0.368	506	8.83×10^{-20}	2.87
Within groups	0.0145	20	0.000727			
Total	1.48	24				
Tukey test - pH 10.5						
Source of variation	SS	DF	MS	F_{ratio}	P_{value}	$F_{critical}$
Between groups	1.64	4	0.411	385	1.3×10^{-18}	2.87
Within groups	0.0213	20	0.00107			
Total	1.66	24				

[a]Sum square , [b]degrees of freedom, [c]mean square.