Adsorption of methylene blue dye by different methods of obtaining shrimp residue chitin

Adsorção de corante azul de metileno por diferentes métodos de obtenção de quitina de resíduo de camarão

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ABSTRACT

The textile industry, very important for the world economy, generates an effluent containing dyes, and which, when discarded in water bodies without proper treatment, can cause impacts to human health and the environment. One of these widely used dyes is methylene blue, whose characteristics are high solubility in water and its toxic potential, and which effects range from eye irritations, nausea, vomiting and even mental confusion. Among the potential adsorbents of this dye is chitin, which is a biopolymer extracted from the shrimp exoskeleton. Aiming at the development of a low-cost adsorbent material with potential use in the textile effluent treatment industry, the ability to remove methylene blue dye by shrimp residue chitin, obtained by eleven different methodologies, was verified. The three most efficient treatments reached approximately 75% of dye removal, proving the high adsorption power of shrimp residue. In addition to providing technological development of materials, the research brings socio-economic benefits to the fishermen's colony with the use of shrimp residue for the adsorption of other waste from the textile industry, contributing to the sustainability of both activities and reducing the environmental impact.

Keywords: biopolymer; dye removal; fishing waste; textile waste.

RESUMO

A indústria têxtil, muito importante para a economia mundial, gera um efluente que contém corantes e, quando descartado em corpos hídricos sem o tratamento adequado, pode causar impactos na saúde humana e no meio ambiente. Um desses corantes amplamente utilizado é o azul de metileno, cujas características são a alta solubilidade em água e seu potencial tóxico, causando desde irritações nos olhos, náuseas e vômitos até confusão mental. Entre os potenciais adsorventes desse corante está a quitina, que é um biopolímero extraído do exoesqueleto do camarão. Objetivando o desenvolvimento de um material adsorvente de baixo custo com potencial uso na indústria de tratamento de efluentes têxteis, verificou-se a capacidade de remoção de corante azul de metileno por quitina de resíduo de camarão, obtida por onze diferentes metodologias. Os três tratamentos mais eficientes alcançaram aproximadamente 75% de remoção do corante, comprovando o alto poder de adsorção do resíduo de camarão. Além de proporcionar desenvolvimento tecnológico de materiais, a pesquisa traz benefícios socioeconômicos para a colônia de pescadores com a utilização de resíduo de camarão para a adsorção de outro resíduo proveniente da indústria têxtil, contribuindo para a sustentabilidade de ambas as atividades e reduzindo o impacto ambiental.

Palavras-chave: biopolímero; remoção de corante; resíduo pesqueiro; resíduo têxtil.

Introduction

The pollution of water bodies is a worrying environmental impact, considering that it brings more comprehensive damage to the environment, due to difficulties in controlling and monitoring, and provides indirect impacts to the soil, atmosphere, economy, public health and ecosystems in general (Barbosa, 2014). The sources of water pollution come from inadequate land occupation, deforestation and untreated dumping of sanitary and industrial effluents in water bodies (Sánchez, 2013). Among the effluents released in the springs is the effluent of the textile industry.

Brazil, the second largest textile chain in the West and the fourth largest knitwear producer in the world, produced approximately 2.04 million tons of pieces only in 2019 (ABIT, 2021). In the production process of the textile industry, dyes are generally used, which are recalcitrant, highly toxic molecules, even in low quantities (Ferreira et al., 2007). During the washing of textile parts, approximately one third of reactive dyes are left in wastewater, which, when released into water bodies, without proper treatment, can impact human health and the environment (Oliveira et al., 2018).

One of these dyes widely used in the textile, cellulose and cosmetic industries is methylene blue (MB), whose characteristics are the high solubility in water and its toxic potential, causing eye irritations, nausea, vomiting and even mental confusion (Wang et al., 2011; Bedin et al., 2018). Therefore, it is of paramount importance to remove this dye from industrial effluents (Sabar et al., 2020).

For the removal of MB from effluents, physical-chemical processes of effluent treatment are used, such as coagulation, or removal with activated charcoal, whose cost is high (Oliveira et al., 2018). The treatment of textile effluents requires efficient practices, through the use of alternative adsorbent materials, seeking efficiency and cost-effectiveness (Queiroz et al., 2019).

According to Bailey et al. (1999, p. 2469), the adsorbent must have "little processing, be of an abundant nature, or a by-product or material of waste from another industry." Potential adsorbents are numerous organic residues, such as sugarcane residues (Jorge et al., 2015), ryegrass straw (Silva et al., 2018), fly ash (Cunico et al., 2015), green coconut (Oliveira et al., 2018), pine and bamboo sawdust (Müller et al., 2019). Many research on adsorption of dyes from crustacean residues (Dotto et al., 2011; 2015; Labidi et al., 2019; Mabel et al., 2019) refer to the use of chitin.

Chitin is a biopolymer extracted from the shrimp exoskeleton and, after the deacetylation process, turns into chitosan, which is also widely studied as an adsorbent of dyes (Bajaj et al., 2015). Chitin, the second most available natural biopolymer after cellulose (Ahmed et al., 2020), received due attention only after the beginning of the 21st century, when studies revealed the biological importance of its characteristics and by-products (Wan et al., 2021). Chitin and Chitosan are structurally related, renewable and low-cost biopolymers, which are gaining importance as sustainable alternatives for various applications (Kostag and Seoud, 2021; Kumaran et al., 2021; Ribeiro et al., 2018).

There are also studies aimed at using chitin or chitosan to remove elements such as copper (Frantz et al., 2017; Adeeyo et al., 2019), aluminum (Lobo-Recio et al., 2013), gold (Zhao et al., 2019; Chang, 2021) and arsenic (Shan et al., 2020). Studies that make changes in the chemical and physical characteristics of chitin or chitosan indicate optimized results with variations in pH, use of clay, combination of chitin with chitosan, preparation of chitosan films, for example (Wang et al., 2011; Auta and Hameed, 2014; Honório et al., 2014; Frantz et al., 2017).

The process of obtaining chitin and chitosan require energy consumption and reagents, which imply actions to be performed with criteria. Due to these characteristics, the extraction of these products has complexity and added value (Assis and Brito, 2008). On the other hand, chitin and chitosan come from large amounts of waste from the fishing industry. Considering that fish processing can generate 40 to 70% of waste (Dragnes et al., 2009), its use for the development of products with added value can be an alternative for the sustainability of artisanal fishing, generating the interest of fishermen and fish farmers in the residue. Thus, the aim of this study was to verify the ability of blue methylene dye removal by shrimp residue chitin, obtained by different methodologies, for use in the textile effluent treatment industry.

Methodology

Eleven adsorption treatments were performed, based on the adsorption methodologies used by several authors (Longhinotti et al., 1996; Assis and Brito, 2008; Auta and Hameed, 2014; Wang et al., 2011). The adsorbate used was methylene blue in solution with an initial concentration of 20 mg L^{-1} and molar mass of 319.85 g mol^{-1}. As adsorbent, samples of 1g of chitin were used. Shrimp residues were collected in the Fishermen's Colony, located in the city of Pelotas, RS, in the south of Brazil, and then frozen. The samples underwent defrosting, washing with water under room temperature and manual separation. The following reagents were used: hydrochloric acid (HCl), for the elimination of minerals present, sodium hydroxide (NaOH), to reduce the protein nitrogen content, and sodium hypochlorite (NaClO), for the removal of pigments and minimization of the odor of shrimp residues in processing.

The steps for obtaining chitin are pre-treatment (PT), demineralization (DM), deproteinization (DP), deodorization (DD) and drying (DR). Chitin was obtained using 11 different methodologies, as shown in Chart 1.

In order to evaluate the quality of the chitin obtained, the scanning electron microscopy (SEM) analysis was performed in the SEM JSM - 6610LV equipment, of the T6 treatment, where the sample was metallized with gold and 15 kV voltage acceleration and magnification ranges of 30, 5,000 and 10,000 times.

The 11 treatments were submitted to adsorption capacity analysis at: 0, 5, 10, 20, 40, 60, 120, 180 and 240 minutes of incubation at 160 RPM and neutral pH. The aliquots, as soon as removed, were centrifuged for removal of the adsorbent from the solution in order to

Chart 1 – Stages of the 11 treatments of chitin.

STEPS	SHARE	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11
PT	Autoclave	127 a 130°C/3h	NA	127 a 130°C / 3h						NA		
	Drying	50°C/24h	NA	50°C/24h						NA		
	Crunch	Blender	NA	Blender								
DM	Conc. HCl	2.5%										
	Equipment	Bath Mary	NA	Jar Test								
	Temperature	50°C	Room temperature									
	Agitation/time	Manual (10 em 10 min/2h)		120 RPM/1h				160 RPM/3h		160 RPM/1h	160 RPM/2h	160 RPM/3h
	Washing	Until neutrality										
	Drying	50°C/24h	NA						50°C/24h			
	Crunch	NA						Bld.		NA		
DP	Conc. NaOH	5%		15%				5%		15%		
	Equipment	Bath Mary	Jar Test									
	Temperature	50°C	Room temperature									
	Agitation/time	Manual (10 em 10 min/2h)		120 RPM/1h				160 RPM/3h		160 RPM/1h	160 RPM/2h	160 RPM/3h
	Washing	Until neutrality										
	Drying	50°C/24h	NA	50°C/24h		NA		50°C/24h				
	Crunch	NA						Bld.		NA		
DD	Conc. NaClO	0.36%	NA	0.4%	1.2%	2.0%	0.5%	1%				
	Equipment	NA	NA	Jar Test								
	Temperature	Room temperature	NA	Room temperature								
	Agitation/time	Manual (10 em 10 min/3h)	NA	120 RPM/1h				160 RPM/3h		160 RPM/1h	160 RPM/2h	160 RPM/3h
	Washing	Until neutrality	NA	Until neutrality								
DR	Drying	50°C/24h										
	Crunch	NA	Bld.	NA								

PT: pre-treatment; DM: demineralization; DP: deproteinization; DD: deodorization; DR: drying; RPM: revolutions per minute; Conc.: Concentration of; NA: Not applicable; Bld.: blender.

avoid interference during reading in the spectrophotometer. The reading was performed at a wavelength of 660 nm.

The adsorption results were analyzed by regression and Equation 1 to determine adsorption capacity (q) in mg g^{-1}, using the initial concentrations (Ic), the final concentration (Fc), both in mg L^{-1}, the adsorbent mass (m) in g and the volume of the solution in L. Regression analysis and graphs were made through the Sigmaplot 10.0 and Excel programs. The percentage of removal (%R) was determined using Equation 2.

$$q(mg/g) = \frac{(Ic - Fc)}{m} \times V \tag{1}$$

$$\%R = \frac{(Ic - Fc) \times 10C}{Ci} \tag{2}$$

With the results of adsorption capacity obtained, statistical analysis was performed by ANOVA variance, through the f-test, having as variables the 11 treatments of chitin and incubation time of 0 and 240 min. Thus, one can compare the distribution of sample groups independently and summarize a linear regression model by decomposition of the sum of squares for each source of variation using the Fisher-Snedecor F-test. Multiple comparison analysis was performed by the Tukey test with 5% probability of error. The procedures from Vieira (2006) were followed.

Results

Regression of adsorption treatments

The regression results of the adsorption treatments are presented in Figures 1 to 4, and all curves were significant. Although the T1 meth-

odology is more conservative regarding its execution and the T2 is simpler, both demonstrated evident variations to be obtained, according to Figure 1.

It is observed that in the regression analysis of T1 and T2 there is a projection of reduction in concentration between 150 and 240 minutes, but there are no measurements in this interval to confirm this
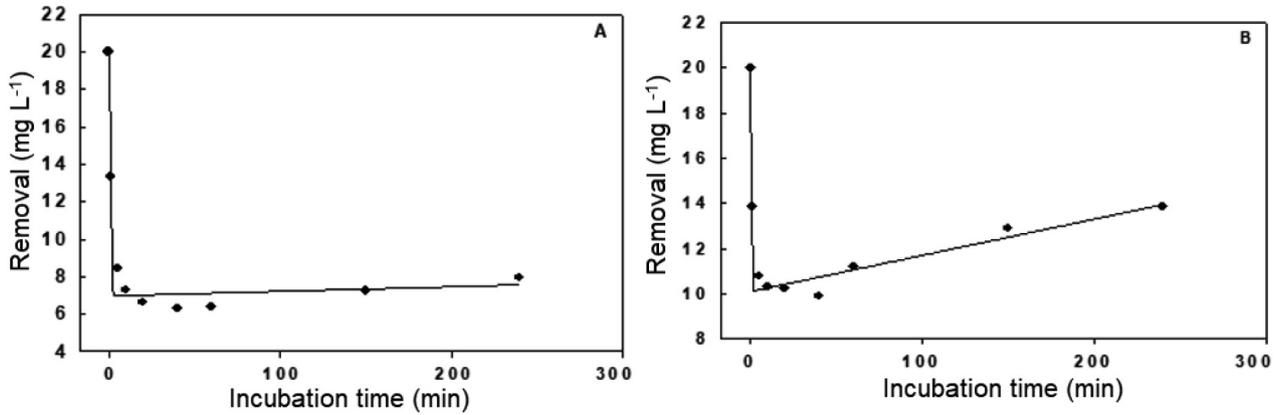

Figure 1 – Regression analysis for adsorption treatments with chitins obtained by the T1 (A) and T2 (B) methodologies.
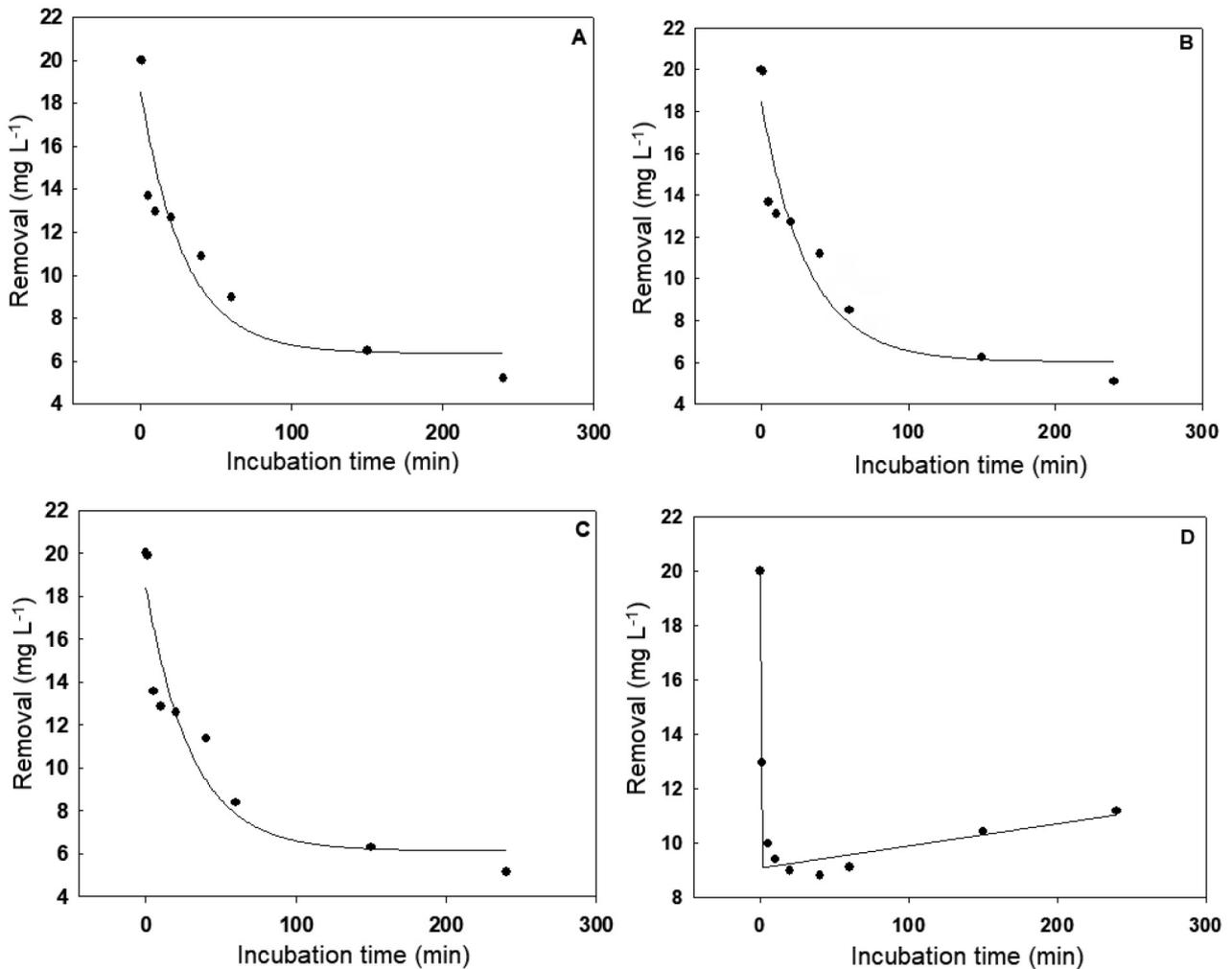

Figure 2 – Regression analysis for adsorption treatments with chitins obtained by methodologies T3 (A), T4 (B), T5 (C) and T6 (D).
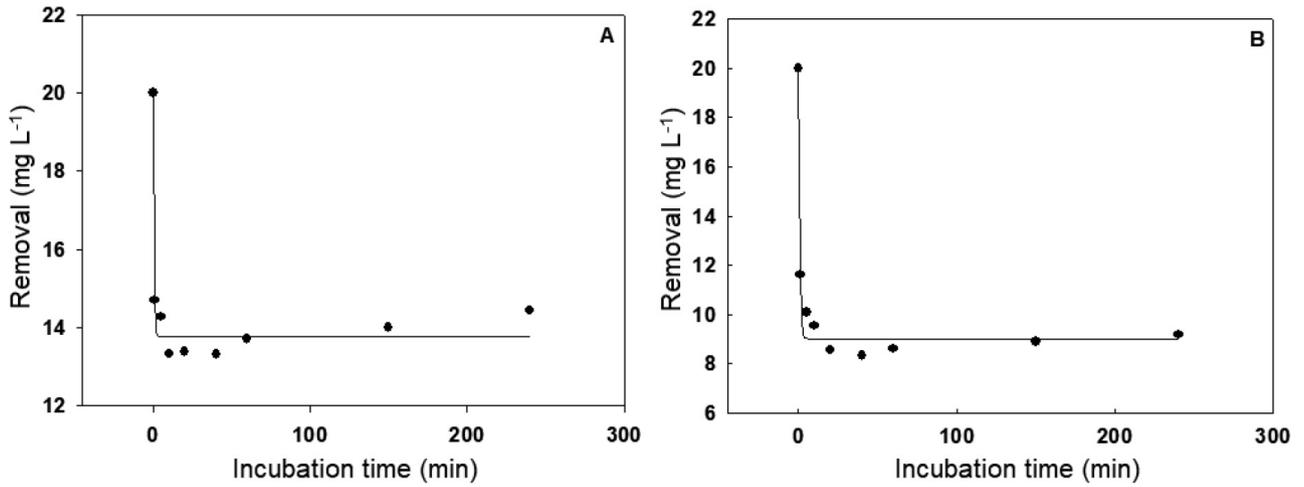
Figure 3 – Regression analysis for adsorption treatments with chitins obtained by methodologies (A) T7 and (B) T8.
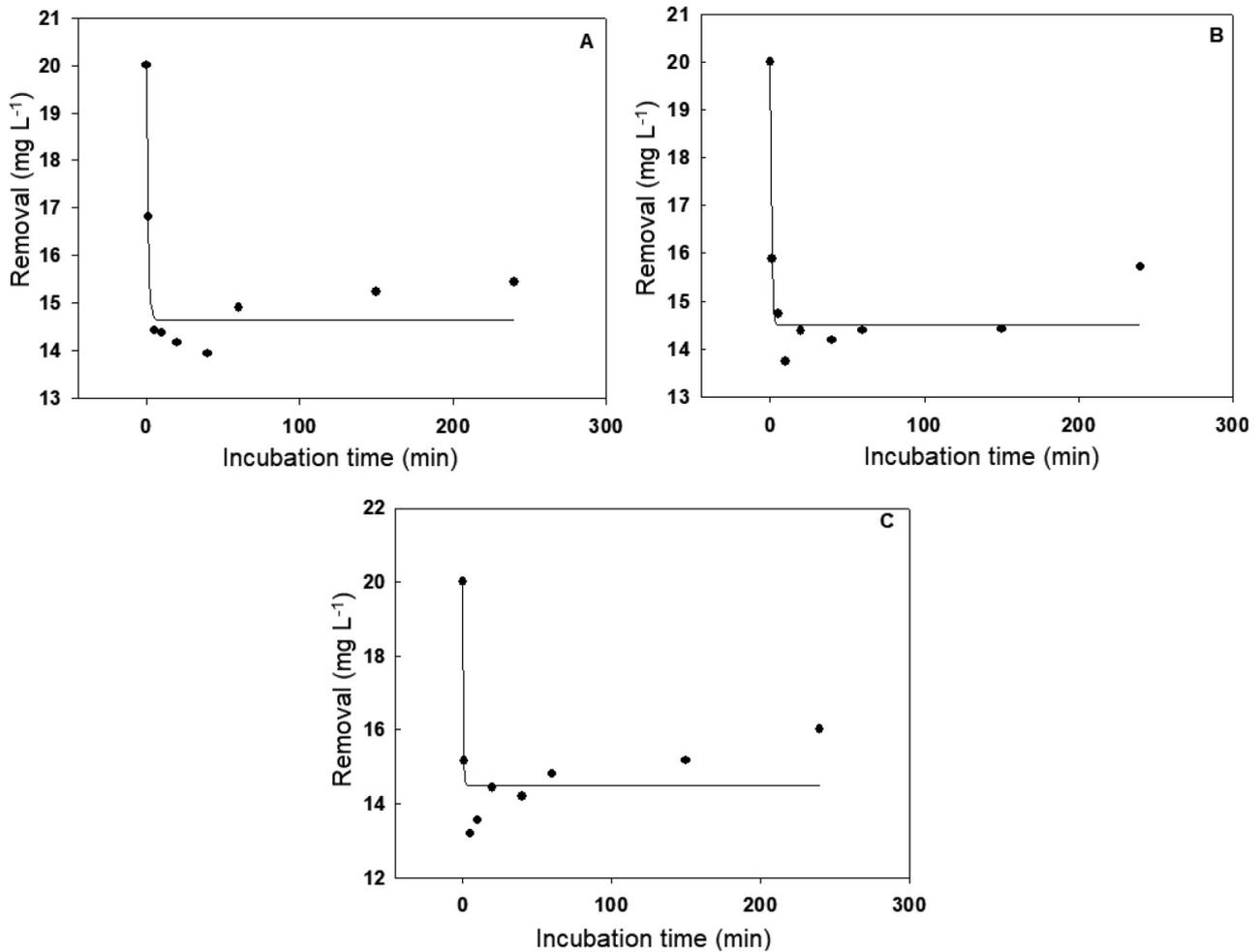

Figure 4 – Regression analysis for adsorption treatments with chitins obtained by the methodologies (A) T9, (B) T10 and (C) T11.

trend. Both in T1 and T2, regression confirmed that at 40 minutes of incubation there was maximum adsorption, that is, when chitin adsorbates the highest amount of MB. This action was confirmed by the following measurements that indicate the decrease in the amount of MB adsorbed. This moment is called the beginning of the desorption.

Figure 2 presents the regression results for T3, T4, T5 and T6, which are characterized by small alterations among them. However, T6 has more significant differences from the deproteinization stage.

The trend curve presents a slight desorption for T3, T4 and T5 between 60 and 100 minutes, however, these 3 treatments had as a marked characteristic the absence of desorption over the 240 minutes of incubation. T6 showed more pronounced curves between the actual adsorption results and the trend line, but showed the beginning of the desorption at 40 min both in the projection and in the analysis in the spectrophotometer.

Figure 3 shows the regression results for T7 and T8, which have as difference the milling in the DM and DP stages. The T7 presents greater accentuation in the curve between 150 and 240 min as compared to

the T8. And, in both treatments, the trend line shows the beginning of desorption at 40 min.

The adsorption results of T9, T10 and T11 are presented in Figure 4 and were characterized by the alteration of an action in the stages of DM, DP and DD. It was observed that the curve between the times of 150 and 240 minutes is more accentuated in T9. And, like all previous treatments, except T3, T4 and T5, the trend line shows the beginning of the desorption that occurred at 40 minutes. However, for these three treatments (T9, T10 and T11), the line presents a more tenuous slope.

Scanning electron microscope

A SEM analysis was performed, presented in Figure 5 of chitin T6, with one of the lowest production cost methodologies, in the magnification range of 30 times (A), 5,000 times (B) and 10,000 times (C).

From the SEM analysis, it was observed that chitin presented particles with sizes ranging from 250 µm to 750 µm, approximately, and the average was around 400 µm. In general, the observed particles presented flattened and floccular shape, and there were also particles of
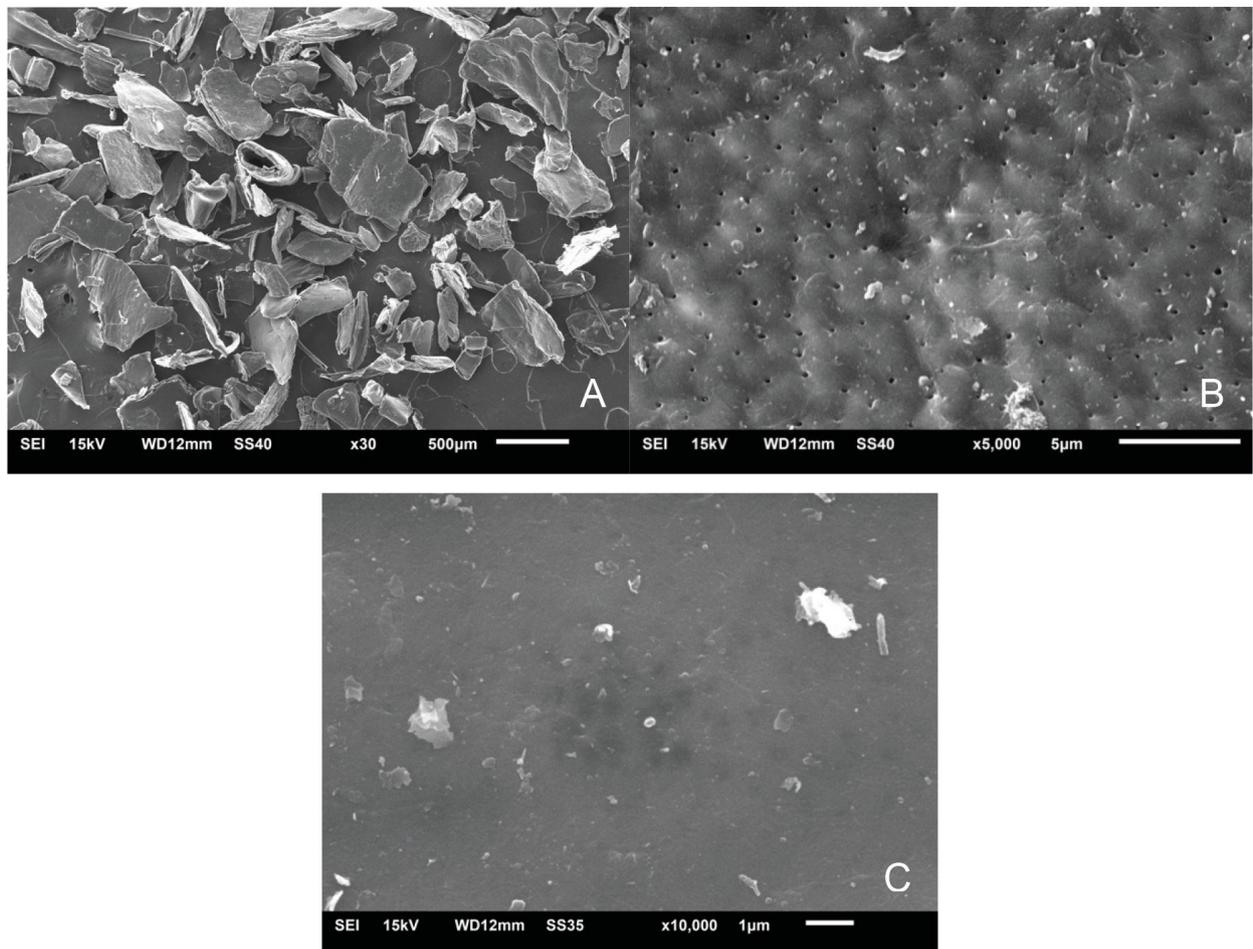

Figure 5 – Scanning electron microscopy of the chitin sample obtained in magnification range (A) 30 x, (B) 5,000 x, and (C) 10,000 x.

more rounded and polygonal shape, in a smaller amount. There was also a large presence of regular and linear faces in the particles, with a low degree of superficial imperfections. And, specifically with the approximation of 5000 times (B), it can be noted that the surface is mostly smooth, but presents a high concentration of pores with very small dimensions, less than 1 nm. This demonstrates that there is still a need for greater treatments to promote chitosan, and that the structures are closer to the chitin format.

Methylene blue adsorption

For the analysis of the results of MB adsorption with different chitins, the percentage of removal was verified at 40 min and at the end of each treatment, i.e., at 240 min of incubation. Finally, the adsorption capacity (q) was verified at 0 and 240 min. The results showed that T3, T4 and T5 obtained the best removal percentages, with 74%, 75% and 74% efficiency in the removal of the dye at the end of incubation, respectively (Figure 6). In addition, treatments T1, T6 and T8 achieved adsorption percentages higher than 50%.

After 240 minutes of incubation, there was a reduction of 58% of the dye with treatment T1 (Figure 6). Treatment T2 demonstrated a removal capacity of 31%. The treatments T3, T4 and T5 did not present desorption until the end of the incubation period. Thus, at the end, the adsorption capacity was verified, which was 2.95 mg g^{-1} for T3, 2.98 mg g^{-1} for T4 and 2.96 mg g^{-1} for T5 (Table 1). Thus, it was observed that there was no significant difference between T3, T4 and T5 regarding the removal percentage.

The maximum adsorption capacity of T7 was 1.33 mg g^{-1}, representing a removal percentage of 34%, and reaching 28% in the to-tal incubation time (Table 1 and Figure 6). For T8, the adsorption capacity in 40 minutes of incubation was 2.33 mg g^{-1}, presenting a removal percentage of 58% at this time and a percentage of 54% at 240 min. The treatments T9, T10 and T11 present, in 40 minutes, the maximum adsorption capacity of 1.21 mg g^{-1}, 1.25 mg g^{-1} and 1.35 mg g^{-1}, respectively. Thus, T9 and T11 presented the same removal percentages of 29%, and T10 had 30% at the beginning of the desorption, but, at 240 minutes, the results were 23% for T9, 21% for T10 and 20% for T11.

Looking exclusively at the statistical analysis presented in Table 1, it is observed that the adsorption capacity data, in 0 and 240 minutes, vary between the different treatments, since the distinct letters in each treatment indicate a differentiation between them, through the analysis by the Tukey test with a probability of error of 5%.

At 0 minutes, the adsorption capacity showed fewer definitions between the variations of the treatments performed, because they present more than one variation, except for T3, T4, T5, T8 and T9. At 240 min, the variations were more defined. Analyzing the results according to the criterion adopted for the regression analysis, similarity, or difference between the methodologies to obtain chitin, it is observed that T1 and T2 differed significantly from each other, as well as T3, T4 and T5 in relation to T6. The statistical similarity occurred between T9, T10 and T11, between T3, T4 and T5, and also when comparing T7 with T2. The coefficient of variation (CV) related to the 11 results represented the variation of the results in relation to the mean, being higher at 0 minutes (22.85%), and lower at 240 minutes (2.92%).

It is observed, therefore, that the results of the regression analysis (Table 1) are close to those of adsorption capacity (q) and adsorption
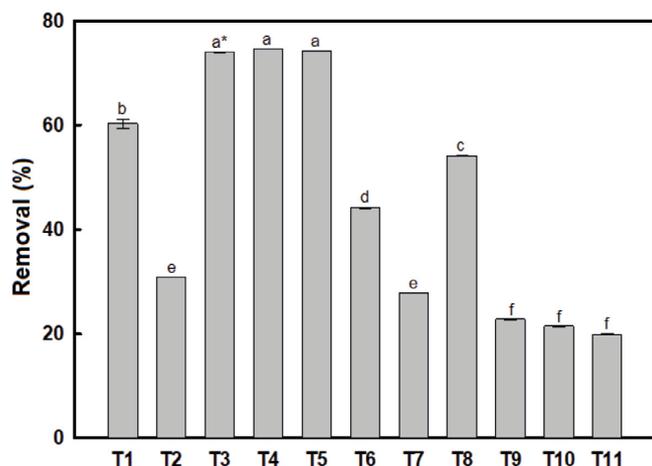
Figure 6 – Percentage of removal of the MB dye from the adsorption tests with chitins obtained from the treatments after 240 minutes of incubation at 160 RPM*.
*Distinct letters represent statistically different treatments by Tukey test with the probability of error of 5%.

Table 1 – Adsorption capacity (mg g^{-1}) of each treatment at 0 minutes and at the end of incubation, at 240 minutes, with the respective statistical analysis*.

Treatment	q in 0 minutes	q in 240 minutes
T1	1.3336 ABC	2.41233 B
T2	1.2330 ABCD	1.23530 E
T3	0.0111 E	2.95840 A
T4	0.0250 E	2.98593 A
T5	0.161 E	2.96763 A
T6	1.4121 AB	1.76647 D
T7	1.0599 BCD	1.11167 E
T8	1.6780 A	2.16447 C
T9	0.6934 D	0.91163 F
T10	0.8238 CD	0.85810 F
T11	0.9698 BCD	0.79700 F
CV	22.85	2.92

*The averages followed by the same letter differ from each other by the Tukey test with a probability of error of 5%; CV: coefficient of variation; CV %: 2.92 at 240 minutes.

percentage (%R), because, for these analyses (q and %R), the best treatments were T3, T4, T5, followed by T1, T8 and T6, and the worst were T9, T10 and T11. The differences between the adsorption capacity in each treatment and the expressiveness of the CV are justified by the methodological variations of chitin. Among the best results of dye adsorption, the methodologies differed only in the concentration of NaClO, which was 0.4%, 1.2% and 2.0% for T3, T4 and T5, respectively. The most efficient methodology was T4, using 1.2% NaClO and adsorption of 75% of dye.

Discussion

The treatments that presented the best results for adsorption were, respectively, those that used chitins of T4, T3 and T5, with results close to 75% and with results higher than 55% in T1, T6 and T8 (Figure 6). These results prove the statement of Ahmed et al. (2020) that chitin, as well as chitosan, has a good adsorption capacity.

The values found in this research were higher than those obtained by: Labidi et al. (2019), with an MB removal between 50% and 60%, through the use of chitosan and chitin; by Dotto et al. (2011) with a 50% removal of textile dyes with chitosan; and Cunico et al. (2015) with a 50% removal from modified fly ash.

However, some studies have achieved higher efficiencies in MB removal, such as: Dotto et al. (2015), with a 85% removal of the dye with shrimp residue; Ahmad and Ansari (2021), who achieved results above 88% in neutral pH, with the use of hybrid clay with modified nanocompost of chitosan; Ma et al. (2016), which reached up to 90% of MB removal by using foam composed of graphene oxide/chitin; Mabel et al. (2019), with an efficiency of 90% of adsorption with crustacean chitin; Lima et al. (2006), with a 97% MB removal with the use of activated carbon; Jorge et al. (2015), which also removed 97% of the initial concentration of MB, but with the use of sugarcane bagasse; Silva et al. (2018), with a removal efficiency of 99% of MB with the use of activated charcoal of ryegrass straw.

Jawad et al. (2020) obtained 90% MB removal efficiency, differing in the methodology applied to the research in time and rotation parameters, from 180 minutes at 110 RPM. The authors verified the highest adsorption capacity of the dye with 31.3 mg g^{-1} in pH 9 solution. Future studies seeking the best efficiency of the adsorbent obtained could be performed, therefore, analyzing pH values distinct from the neutron used, different rotations per minute and different temperatures.

The treatment of textile effluents usually goes through a combination of physical, chemical and/or biological processes. Depending on the process applied, its efficiency and the pollutants present in the effluent, there may be the formation of unwanted by-products, such as halides, metals, acids, aldehydes and sludge generation (Holkar et al., 2016; Khan et al., 2019).

The use of biopolymers produced from shrimp exoskeleton could be evaluated for adsorption of other pollutants, such as heavy metals. Yazidi et al. (2020) and Ma et al. (2016) verified that in addition to MB dye, chitin and chitosan can simultaneously adsorb heavy metals such as molybdenum, lead, cobalt and nickel, elements commonly present in industrial effluents, which demonstrates other potentials for residue application.

For Kostag and Seoud (2021), there should be a search for application of green chemistry, with the use of environmentally benign chemicals, which allow the recycling of solvents. The present study contributes to a relationship of industrial symbiosis, in which there is the return of residues from the fish process as raw material for the process of treatment of another residue, in this case the waste from the textile industry.

Conclusion

Pure chitin obtained from shrimp residues has a high power of adsorption of methylene blue dye, and the research points to an important potential for the use of waste on a commercial scale, in a relationship of industrial symbiosis. In this context, the fishing waste ceases to be an environmental problem and becomes a solution for the treatment of textile effluents, with prospects of economic, social and environmental benefits, enabling employment generation, valorization of the fishing activity and waste management optimization.

This research opens space for studies on the expansion of the adsorption capacity through physical and chemical changes in the adsorbent and combinations of adsorbents. With the methodological differences observed in chitin treatments and their adsorption capacities, an opportunity is observed to improve the processes of obtaining the material.

In addition to providing technological development of materials, the research brings perspectives of socioeconomic benefits to the fishing community, with the use of shrimp residue for the adsorption of other waste from the textile industry, contributing to the sustainability of both activities and reducing the environmental impact.

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