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Ultrasound-assisted treatment of chitin: evaluation of physicochemical characteristics and dye removal potential

Abstract: Chitin was ultrasonically treated to improve its dye adsorption characteristics. The effects of ultrasound cycle and amplitude on the chitin Sauter diameter (D_{Sauter}), deacetylation degree (DD), crystallinity index (CI) and specific surface area (S_{BET}) were evaluated. The untreated and treated chitin samples were applied to remove Methylene Blue (MB) and Ponceau 4R (P4R) dyes from aqueous solutions. Chitin D_{Sauter} decreased from 625 to 250 μm after the ultrasonic treatment. Chitin DD was not influenced by the ultrasound treatment, remaining in the range of 42.3–45.8%. For all ultrasonic conditions, the chitin CI values decreased from 86.3% (untreated chitin) to 70.0%. The specific surface area (S_{BET}) increased from 2.2 to 38.5 $m^2 g^{-1}$. After ultrasonic treatment, the dye removal percentage increased from 53.2 to 74.3% for MB and from 3.3 to 20.2% for P4R, at initial dye concentration of 50 mg l^{-1}. Treated chitin can be used seven times maintaining the same performance. The ultrasound-assisted treatment is an alternative to improve the chitin dye adsorption characteristics.

Keywords: amplitude; crystallinity index; cycle; Methylene Blue; Ponceau 4R.

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1 Introduction

Chitin is a copolymer of N-acetyl glucosamine (GlcNAc) and glucosamine (GlcNH$_2$) with β-D-(1→4) glycoside linkages. It is the second most abundant natural polysaccharide, and is synthesized by a number of living organisms. Chitin is the major structural component in the exoskeleton of arthropods and cell walls of fungi and yeast. The main commercial sources of chitin are crab and shrimp shells, which are abundantly supplied as waste products of the seafood industry (1, 2). As reviewed by Harish et al. (2), chitin is used in a wide range of applications, such as, food nutrition, materials science, medical applications, environmental remediation and others. Among these, stand out the use of chitin for dyes removal from aqueous media by adsorption (3–7).

Adsorption is an alternative and low-cost unit operation used for dyes removal from aqueous solutions (8–11). Once chitin is a low-cost, renewable and eco-friendly biopolymer, it was used in the adsorption field for the removal several dyes, such as, Tartrazine (4), Reactive Yellow 2, Reactive Black 5 (3) and Malachite Green (6). Furthermore, chitin is abundant and can be obtained from waste materials (12). In spite of this, chitin is not still used at large scale, due to some drawbacks, including high crystallinity, low specific surface area and porosity, which prejudice its adsorption potential (3, 4). In this way, it is desirable the search for techniques which can modify the chitin physicochemical characteristics in order to improve its adsorption potential.

An alternative to modify the chitin characteristics is the ultrasound-assisted treatment (13). Ultrasound represents mechanical waves with frequencies above 18 kHz, where acoustic cavitation can occur. Due to high sound intensities, the tensile stress of the liquid is exceeded and little gas bubbles are formed. The bubbles collapse provokes extreme thermodynamic conditions, which can modify the physicochemical characteristics of chitin (14).

In this work, the ultrasound-assisted treatment was applied for chitin, aiming to improve its adsorption

potential for Methylene Blue (MB) and Ponceau 4R (P4R). At first, chitin was obtained from shrimp wastes and submitted to the ultrasonic treatment. In this step, the effects of ultrasound cycle (0.50–1.00) and amplitude (20–100%) on the chitin physicochemical characteristics, like, Sauter diameter (D_{Sauter}), deacetylation degree (DD), crystallinity index (CI) and specific surface area (S_{BET}) were evaluated. Thereafter, chitin (untreated and treated in all ultrasonic conditions) was applied for the removal MB and P4R dyes from aqueous solutions by adsorption.

2 Experimental

2.1 Chitin obtainment

The shrimp (*Penaeus brasiliensis*) wastes were obtained from a fishery industry located in southern Brazil and stored in freezer (-18°C) until its use. Chitin was obtained from shrimp wastes by the following steps (15): demineralization (7 kg of shrimp wastes and 14 l of HCl solution 2.5 g l^{-1} in stirred tank during 2 h at room temperature), deproteinization (21 l of NaOH solution 5.0 g l^{-1} in stirred tank during 2 h at room temperature) and deodorization (35 l of NaClO solution 0.4 g l^{-1} under agitation during 3 h). After each above step, washing was done with water to remove the remaining solutions. Finally, chitin was dried (16), ground (Wiley Mill Standard Model 03, Thomas Scientific, Swedesboro, USA) and sieved until the discrete particle size ranging from 425 to 850 μm.

2.2 Ultrasound-assisted treatment of chitin

Chitin samples (5.00 g) were mixed with 300 ml of deionized water. The mixture (water/chitin) was treated in an ultrasonic processor (UP400S, Hielscher, Teltow, Germany) of 400 W equiped with a titanium sonotrode during 1 h at 24 kHz. The ultrasound-assisted treatment of chitin was performed under different ultrasound cycles (0.50, 0.75 and 1.00) (for example, considering 1 min of treatment, when the cycle is 0.50, the suspension remained under ultrasound during 0.50 min) and amplitudes (20, 60 and 100%) without temperature control. After the ultrasonic treatment, the chitin slurry was separated by filtration, oven dried (40°C, 24 h) and stored for further characterization and use. These conditions were determined by preliminary tests. All experiments were performed in replicate (n=3)

2.3 Determination of chitin characteristics

Chitin, before and after the ultrasonic treatments, was characterized according to the moisture content, ashes content (17), Sauter diameter (D_{Sauter}), deacetylation degree (DD), crystallinity index (CI), specific surface area (S_{BET}) and scanning electron microscopy (SEM).

The chitin grain-size analysis was carried out in a standardized mesh screen. The average diameter was calculated by (18):

$$D_{Sauter} = \frac{1}{\sum \frac{\Delta X_i}{D_{mi}}} \qquad [1]$$

where, D_{Sauter} is the average diameter of Sauter (μm), D_{mi} is the arithmetic average diameter between two screens (μm) and X_i is weight fraction of particle size D_{mi} (%).

The identification of the chitin characteristic functional groups was performed by Fourier transform infrared spectroscopy (FTIR) (Shimadzu, Prestige 21, Kyoto, Japan), using the technique of diffuse reflectance in potassium bromide (19). From the absorbance of amide I band ($A_{C=O}$) at 1655 cm^{-1} and hydroxyl groups (A_{-OH}) at 3450 cm^{-1}, the deacetylation degree (DD, %) was determined by (20):

$$DD = 100 - [75.2(A_{C=O}/A_{-OH})] \qquad [2]$$

The amorphous/crystalline structure of chitin was assessed by X-ray powder diffractometry (XRD). Chitin samples were analyzed in a diffractometer (Rigaku, Miniflex 300, Tokyo, Japan) equipped with Ni–filtered Cu K<alpha> radiation (λ=1.54051 Å), with 2θ=5–60°. The diffractometer was operated with 1° diverging and receiving slits at 30 kV and 10 mA. The crystallinity index (CI) was calculated from the normalized diffractograms after mathematical treatment of the peaks, corresponding to its deconvolution and application of the Lorentzian function. The intensities of the peaks at 110 lattices (I_{110}, at 2θ≈20° corresponding to maximum intensity) and at 2θ≈16° (amorphous diffraction, I_{am}) were used to calculate CI, as follows (21):

$$CI = \frac{I_{110} - I_{am}}{I_{110}} 100 \qquad [3]$$

The specific surface area (S_{BET}) was determined in a adsorption analyzer (Micromeritcs, ASAP 2020, Norcross, USA) at 77 K. Samples were pre-treated at 473 K for 24 h under a nitrogen atmosphere in order to eliminate the moisture adsorbed on the solid sample surface. The samples were then submitted to 298 K in

vacuum, reaching the residual pressure of 10^{-4} Pa. The multi-point BET method was used to estimate the specific surface area (S_{BET}) (22).

Scanning electron microscopy (SEM) was carried out to verify the possible structural, morphological and textural changes, which were caused by ultrasound-assisted treatment. The images were obtained at 15 kV with magnification of 300× (Jeol, JSM-6060, Tokyo, Japan) (23).

2.4 Evaluation of dye removal potential

The dye removal potential of chitin (untreated and treated in all ultrasonic conditions) was evaluated using batch adsorption experiments with MB and P4R dyes. The cationic dye, MB (color index 52015, molar weight of 319.8 g mol^{-1}, λ_{max}=664 nm) and the anionic dye P4R (color index 16255, molar weight of 604.5 g mol^{-1}, λ_{max}=505 nm) were purchased from Plury Chemical Ltd. (Diadema, Brazil). All other reagents utilized were of analytical grade (Vetec, Duque de Caxias, Brazil). Deionized water was used to prepare all solutions.

The batch adsorption experiments were performed in a thermostated agitator (Marconi, MA 093, Piracicaba, Brazil) as follows: 250 mg of chitin (untreated and treated in all ultrasonic conditions) were added in Erlenmeyer flasks containing 50 ml of solution with initial dye concentration of 50 mg l^{-1}. The flasks were stirred at 200 rpm for 120 min at 303 K [these experimental conditions were determined by preliminary tests and the literature (3–7)]. The initial pH of dye solutions was not adjusted, being 7.00 for MB and 6.00 for P4R. After the experiments, the solid phase was separated by filtration (Whatmann no 40) (the amount of dye retained in the filter was considered for the calculations) and the remaining dye concentration in the liquid phase was measured by a spectrophotometer (Shimadzu, UV1800, Kyoto, Japan) at 664 nm for MB and 505 nm for P4R. The experiments were performed in replicate (n=3) and blanks were realized. The dye removal percentage (R, %) and adsorption capacity (q, mg g^{-1}) were determined as follows:

$$R=\frac{(C_0\text{-}C_f)}{C_0}100 \qquad [4]$$

$$q=\frac{V(C_0\text{-}C_f)}{m} \qquad [5]$$

where, C_0 is the initial dye concentration in liquid phase (mg l^{-1}), C_f is the final dye concentration in liquid phase (mg l^{-1}), m is the chitin amount (g) and V is the volume of solution (L).

3 Results and discussion

3.1 Physicochemical characteristics of chitin

In this study, chitin was ultrasonically treated to improve its dye adsorption characteristics. It is know that the dye adsorption potential of chitin/chitosan is dependent of its physicochemical characteristics, such as, moisture content, ashes content (24), Sauter diameter (25) deacetylation degree (26), crystallinity index (27) and specific surface area (24). In this way, the effects of ultrasound cycle (0.50, 0.75 and 1.00) and amplitude (20, 60 and 100%) on the above mentioned characteristics were evaluated.

The chitin moisture content before and after all ultrasonic treatments was 6.0±1.2% (wet basis). The ashes content decreased from 4.8±1.0% (untreated chitin) to 0.5±0.1% (ultrasonic treated chitin). This can be occurred because chitin was exposed to high frequency mechanical waves during the ultrasound-assisted treatment. These waves can have caused the leaching of inorganic salts and minerals, decreasing the chitin ashes content. For comparison, the commercial α-chitin has moisture content of 5.8% (wet basis) and ashes content of 2.4% (28). These results revealed that the ultrasonic treatment provides a highly pure chitin.

Figure 1 shows the influence of ultrasonic treatments on the chitin Sauter diameter. It can be seen in Figure 1 that chitin D_{Sauter} decreased from 625 to 250 μm after the ultrasonic treatment and this decrease was independent of the ultrasonic condition (cycle or amplitude). This result is important from the dyes adsorption viewpoint, since, lower D_{Sauter} values provide higher free surface area and
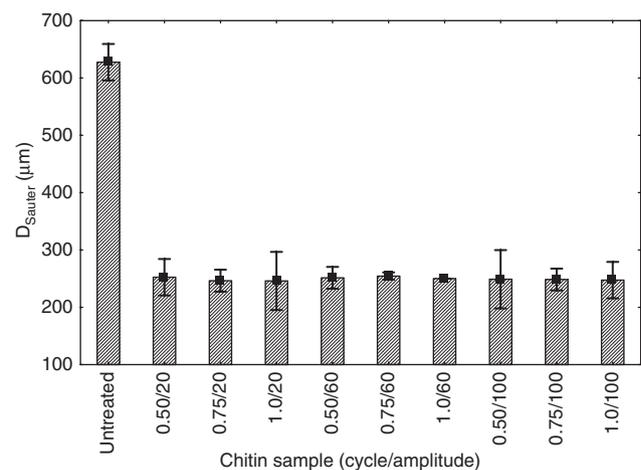
Figure 1: Influence of ultrasonic treatment on the chitin Sauter diameter (D_{Sauter}).

make the adsorption sites more accessible. This phenomenon can be explained according to the "hot spot" theory, i.e. cavities are formed on the liquid, and the implosion of these cavities releases liquid jets at high velocities, fragmenting the chitin particles (29, 30). Jambrak et al. (31) verified that a significant particle size decrease occurred during the ultrasound treatment of whey proteins.

FTIR was used to identify the chitin characteristic functional groups and to estimate the deacetylation degree (DD), before and after the ultrasound-assisted treatment. Figure 2 shows the FTIR vibrational spectrums of (A) untreated chitin and (B) ultrasonic treated chitin (cycle 1.0 and amplitude 60%) (the spectrums after ultrasonic treatment were similar for all conditions of cycle and amplitude). For untreated chitin (Figure 2A), the OH stretching vibration can be observed in a broad band centered at 3450 cm^{-1}. The NH stretching vibrations can be verified at 3250 and 3100 cm^{-1}. The C-H stretching band around 2850 cm^{-1} was observed. The bands of 1650 and 1550 cm^{-1} can be assigned to the amide I (vibration of carbonyl C=O stretching of amide) and amide II (N-H deformation of amide II), respectively. The CH$_X$ deformation can be noted at 1450 cm^{-1}. The bands in the region 1250–950 cm^{-1} can be attributed to the C-O and C-O-C bonds (20). After the ultrasonic treatment (Figure 2B), some bands were slightly modified. This indicated that modifications and rearrangements on the chitin polymeric chains can be occurred during the ultrasound assisted treatment. Chitin DD was not influenced by the ultrasound treatment, remaining in the range of 42.3–45.8%.

The CI reduction can be visualized in Figure 3A and B. In Figure 3A (untreated chitin), the diffraction planes at (020) (2θ≈9–10°) and (110) (2θ≈20°) of the shrimp type

Figure 3: XRD diffractograms of untreated chitin (A) and ultrasonic treated chitin (B) and (C), influence of ultrasonic treatment on the chitin crystallinity index (CI).

of α-form orthorhombic crystal structure can be visualized. However, for ultrasonic treated chitin (cycle 1.0 and amplitude 60%) (Figure 3B), the diffraction planes were less intense, confirming that chitin was decrystallized. Figure 3C shows the influence of ultrasonic treatment on the chitin crystallinity index (CI). It was found from Figure 3C that, for all ultrasonic conditions, the chitin CI values decreased from 86.3% (untreated chitin) to 70.0%. This CI reduction is probably related to a rearrangement of chitin chains during the ultrasonic treatment. Also, the CI reduction can be attributed to the leaching out of chitin inorganic compounds. Similar trend was verified by Villa-Lerma et al. (32) when used ultrasonication as pretreatment for chitin oligosaccharide production by chitinases. They found, for native chitin, CI of 88.13%, and after the ultrasound treatment, CI decreased to 85.50%. Regarding to the dyes adsorption, low crystalline chitin is preferred, since the accessibility to the internal sites is facilitated (24).
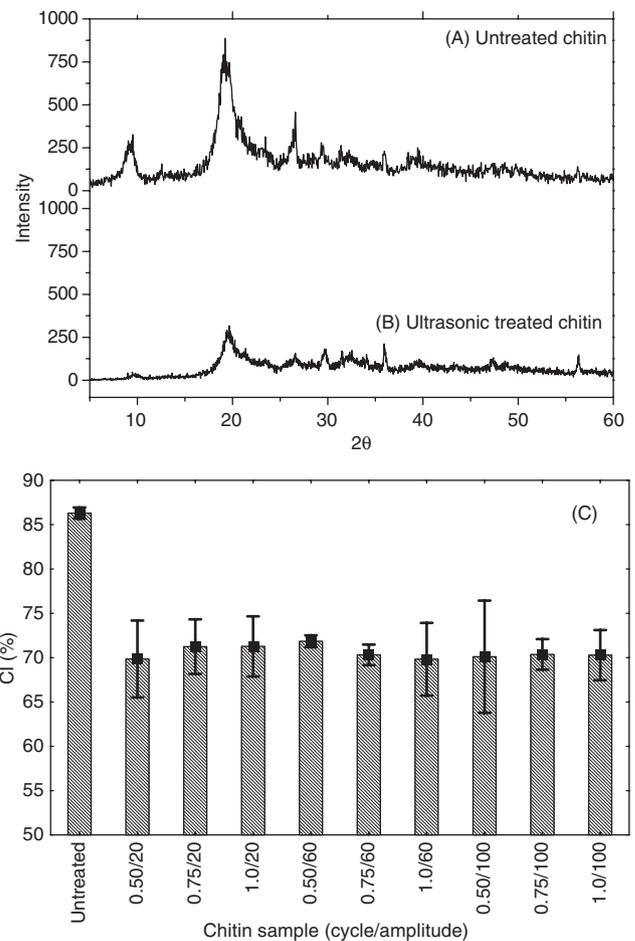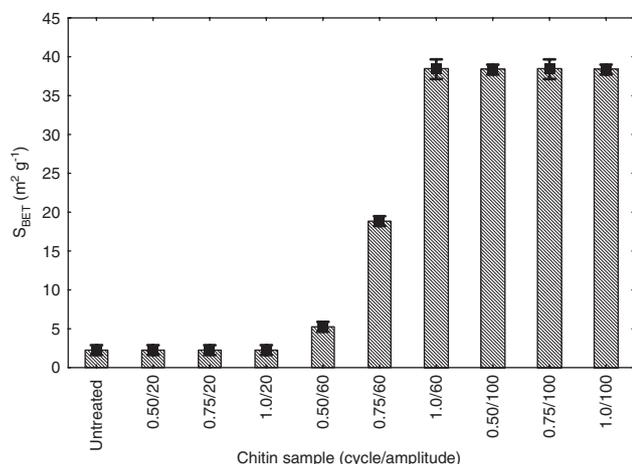

Figure 2: FTIR vibrational spectrums of (A) untreated chitin and (B) ultrasonic treated chitin.

Figure 4: Influence of ultrasonic treatment on the chitin specific surface area (S_{BET}).

Figure 5: SEM images of (A) untreated chitin and (B) ultrasonic treated chitin.

The influence of ultrasonic treatment on the chitin specific surface area (S_{BET}) is presented in Figure 4. It was found that, at lower amplitudes (20%), the specific surface area was not influenced by the ultrasonic treatment. However, at 60% of amplitude, the S_{BET} values, increased until 38.5 $m^2 g^1$. A further increase to 100% of amplitude presented no influence in the S_{BET} values. Thus, the use of ultrasound cycle of 1.0 and amplitude of 60% is sufficient to increase 17.5 times the chitin specific surface area. This behavior can be also attributed to the "hot spot" theory (above mentioned) (29, 30). The increase in S values is essential for dyes adsorption purposes, since facilitates the access of the large dye molecules to the adsorption sites (4, 22 , 24).

The possible structural, morphological and textural changes caused by the ultrasound-assisted treatment on the chitin surface were assessed by scanning electron microscopy (SEM). SEM images of untreated chitin and ultrasonic treated chitin (cycle 1.0 and amplitude 60%) are show in Figure 5A and B, respectively. As can be seen in Figure 5A, chitin has a smooth, rigid and non porous surface. However, after the ultrasound-assisted treatment (Figure 5B), a rough surface with cavities and protuberances was observed. These cavities and protuberances are desirable for adsorption purposes, since improves the transfer of the dye solution to the inner and lower pores of the adsorbent.

In summary, it was verified that the ultrasound assisted treatment provides a highly pure and fine chitin, without changes in deacetylation degree, with lower crystallinity and higher specific surface area. Some important modifications on chitin surface were also observed after the ultrasound assisted treatment, such as, formation of cavities and protuberances. These
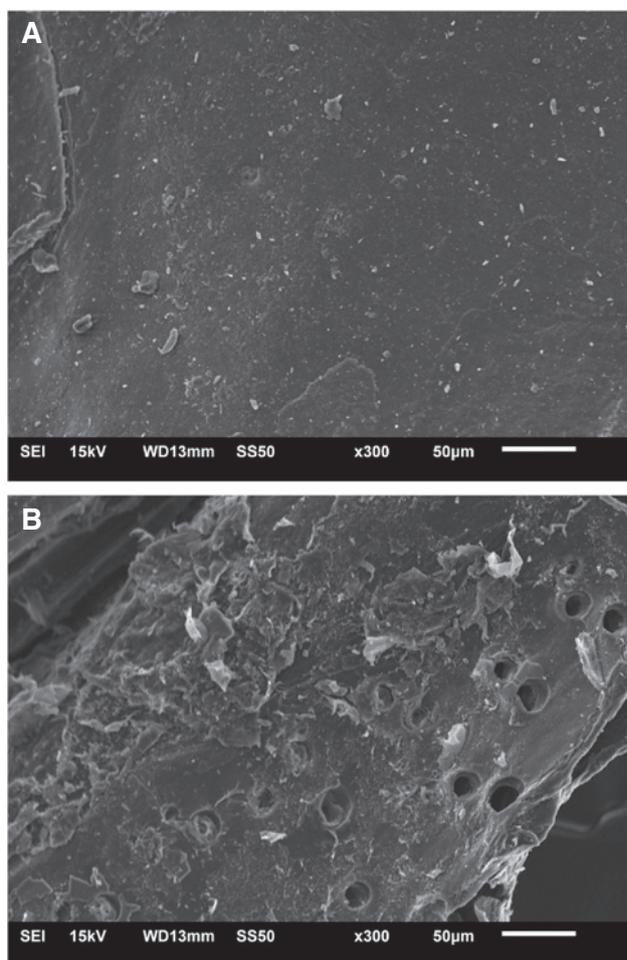
structural modifications can be favorable for the adsorption processes.

3.2 Dye removal potential of chitin

The dye removal potential of chitin (untreated and treated in all ultrasonic conditions) was evaluated for MB (cationic dye) and P4R (anionic dye) dyes. The results, in terms of dye removal percentage (R, %) and adsorption capacity (q, mg g^1) are shown in Figure 6.

In general lines, it can be seen in Figure 6 that the ultrasonic treated chitins were more efficient to remove MB and P4R than untreated chitin. For MB (Figure 6A), the R values increased from 53.2 (untreated chitin) to 74.3% (ultrasonic treated chitin at cycle of 1.0 and amplitude of 60%). In the same way, the q values increased from 5.3 to 7.4 mg g^1 (Figure 6B). For P4R (Figure 6C), the R values increased from 3.3 (untreated chitin) to 20.2%
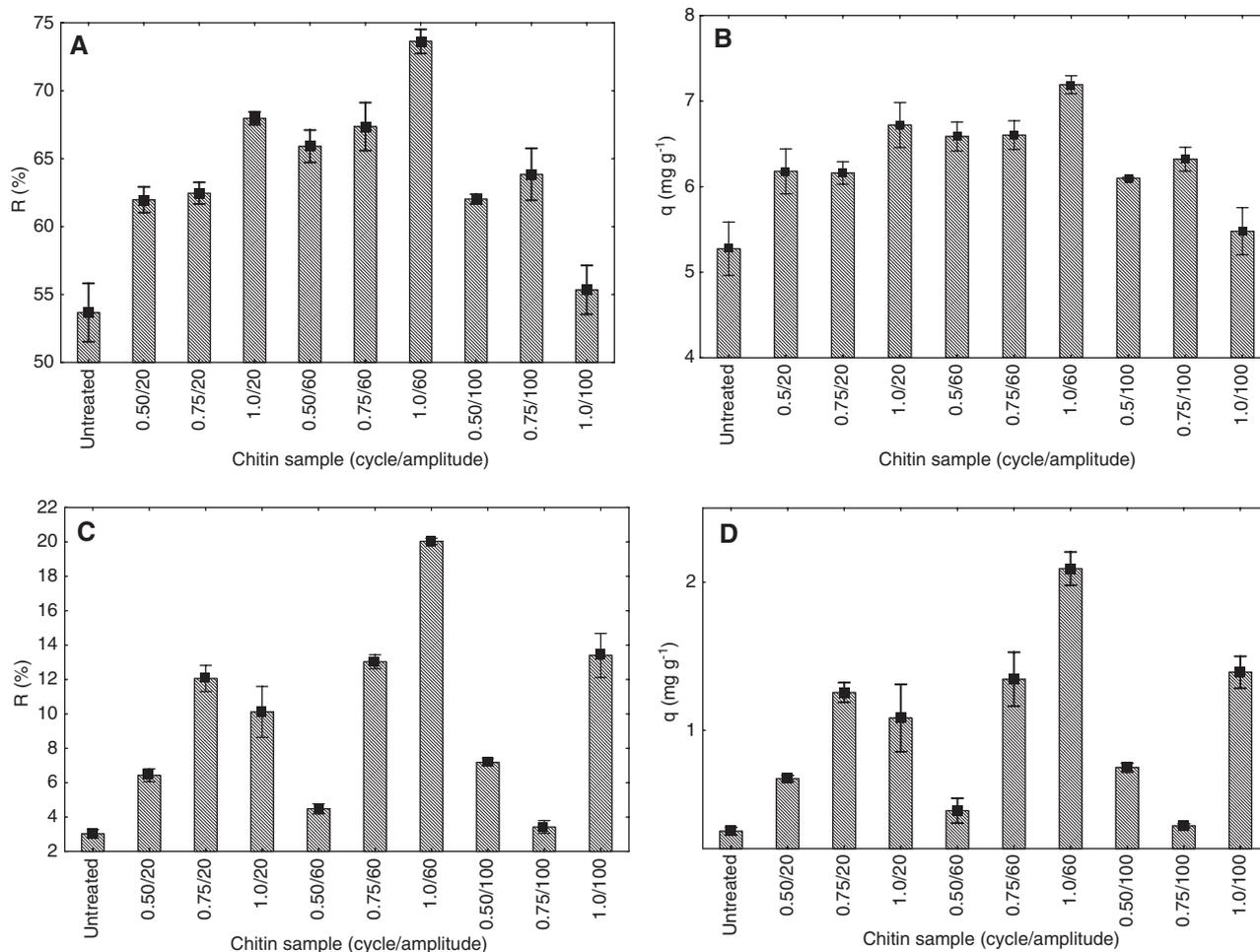
Figure 6: Potential of untreated and ultrasonic treated chitin for the adsorption of MB [(A) Dye removal percentage, (B) adsorption capacity] and P4R [(C) Dye removal percentage and (D) adsorption capacity].

(ultrasonic treated chitin at cycle of 1.0 and amplitude of 60%). In the same way, the q values increased from 0.3 to 2.0 mg g^{-1} (Figure 6D). This behavior can be attributed to the better adsorbent characteristics of ultrasonic treated chitin, such as, higher purity and specific surface area; and lower crystallinity index and Sauter diameter (20–23). Similar trend was found by Küncek and Şener (30) in the adsorption of Methylene Blue (MB) onto sonicated sepiolite. They verified that the adsorption capacity of sepiolite for MB increased from 79.37 to 128.21 mg g^{-1} after the sonication.

Comparing Figure 6A and C, it can be seen that chitin is more efficient for the removal MB than P4R. This occurred because the point of zero charge of chitin is 5.4 (experimentally measured). So, chitin is positively charged at pH values lower than 5.4 and negatively charged at pH values higher than 5.4. Since the experiments were made at pH>6.00, electrostatic attraction occurred between MB (cationic dye) and chitin, increasing the R and q values.

On the contrary, electrostatic repulsion occurred between P4R (anionic dye) and chitin, decreasing the R and q values. In this work, the maximum values for the chitin adsorption capacity (q) were 7.4 mg g^{-1} and 2.0 mg g^{-1} for MB and P4R, respectively. These values can be compared with the following systems in the literature: chitin-Methylene blue (2.60 mg g^{-1}) and chitin-yellow croconate (7.69 mg g^{-1}) (33); chitin-indigo carmine (5.78 mg g^{-1}) (34) and chitin-Ponceau S (3.3 mg g^{-1}) (5). Furthermore, a detailed comparison between the (q) values is presented in Table 1.

3.3 Desorption and reuse

According to the literature (24), desorption and reuse studies are fundamental to verify the possible industrial application of the adsorbents. Desorption experiments were performed for MB and P4R dyes. For MB dye (cationic), the testes were performed using HCl at different

Table 1: Comparison between untreated chitin and ultrasonic treated chitin with other adsorbents used for dyes adsorption.

Adsorbent	Dye	pH	T (K)	q_{max} (mg g^{-1})[a]	References
Untreated chitin	Methylene Blue	7.0	303	5.3	This work
Untreated chitin	Ponceau 4R	6.0	303	0.3	This work
Ultrasonic treated chitin	Methylene Blue	7.0	303	7.4	This work
Ultrasonic treated chitin	Ponceau 4R	6.0	303	2.0	This work
Chitin	Reactive Yellow 2	6.0	293	39	(3)
Chitin	Reactive Black 5	8.0	333	65	(3)
Chitin	Tartrazine	3.0	298	30	(4)
Chitin	Ponceau S	3.5	303	3.3	(5)
Chitin hydrogel	Malachite Green	7.0	303	33.6	(6)
Chitin	Methylene Blue	8.5	298	2.60	(33)
Chitin	Yellow Croconate	3.5	298	7.69	(33)
Chitin	Indigo Carmine	–	298	5.78	(34)
Chitin nanoparticles	Methylene Blue	6.0	298	6.90	(35)
Chitin nanoparticles	Bromophenol Blue	6.0	298	22.72	(35)
Chitin nanoparticles	Brilliant Blue	10.0	298	8.55	(35)
Chitin	Orange G	4.0	298	16.40	(36)
Chitin	Orange IV	4.0	298	1.64	(36)
Chitin	Remazol Black	4.0	298	92	(37)
Chitin	Neutral Red	5.0	298	17	(37)

[a]Maximum adsorption capacity.

concentrations (from 0.1 to 1.0 mol l^{-1}) and, for P4R dye (anionic), the testes were performed using NaOH at different concentrations (from 0.1 to 1.0 mol l^{-1}). The fixed conditions were 250 mg of dye loaded chitin (raw and ultrasonic treated in the more adequate condition), 50 ml of solution, 200 rpm, 120 min and 303 K. The results revealed that for raw and modified chitins, the MB desorption was complete using 0.3 mol l^{-1} HCl. For P4R, desorption was complete using 0.5 mol l^{-1} NaOH. For both dyes, using raw and treated chitins, ten adsorption-desorption cycles were performed. The most promising results were found for treated chitin with MB, where, the adsorbent could be used seven times maintaining the same performance.

4 Conclusion

An ultrasound-assisted treatment was applied for chitin in order to improve its adsorption potential. Some chitin physicochemical characteristics were evaluated before and after the ultrasound treatment and, the samples were applied for the removal MB and P4R dyes from aqueous solutions. After the ultrasonic treatment, chitin Sauter diameter decreased from 625 to 250 μm, while the specific surface area increased from 2.2 to 38.5 m^2 g^{-1}. The deacetylation degree was not influenced by the ultrasound treatment. The crystallinity index decreased from 86.3% to 70.0% after the ultrasonic treatment. Ultrasonic treated chitin was more efficient than untreated chitin for the removal MB and P4R from aqueous

solutions, being the maximum dye removal percentages of 74.3% for MB and 20.2% for P4R. The ultrasound-assisted treatment is an alternative way to improve the chitin dye adsorption characteristics. These results revealed a new perspective regarding physical modifications of biopolymers for dye removal.

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