Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2019.23424

141 (2019) 220–228
February

Copper adsorption by different extracts of shrimp chitin

Robson Andreazza[a,*], Kelly Kathleen Almeida Heylmann[b],
Tito Roberto Sant'anna Cadaval Junior[c], Maurizio Silveira Quadro[a], Simone Pieniz[a],
Flavio Anastacio de Oliveira Camargo[d], Thays França Afonso[a], Carolina Faccio Demarco[a]

[a]*Department of Environmental Science, Federal University of Pelotas, 989 Benjamin Constant St., Pelotas, RS 96010-020, Brazil, Tel. +55(53)999511538, email: robsonandreazza@yahoo.com.br (R. Andreazza), Tel. +55(53)32336967, email: mausq@hotmail.com (M.S. Quadro), Tel. +55(53)32336967, email: nutrisimone@yahoo.com.br (S. Pieniz), Tel. +55(53)991577339, email: thaysafonso@hotmail.com (T.F. Afonso), Tel. +55(53)32336967, email: carol_demarco@hotmail.com (C.F. Demarco)*
[b]*Department of Environmental Engineering, Federal University of Paraná, 405 Dr. Faivre St., Curitiba, PR 80060-140, Brazil,*
[c]*Department of Environmental Science, Federal University of Rio Grande, s/n km 08 Itália Ave., Rio Grande, RS 96203-000, Brazil, Tel. +55(53)32336967, email: titoeq@gmail.com (T.R.S. Cadaval Junior)*
[d]*Department of Soil Science, Federal University of Rio Grande do Sul, 7712 Bento Gonçalves Ave., Porto Alegre, RS 91541-000, Brazil, Tel. +55(51)33087466, email: fcamargo@ufrgs.br (F.A.O. Camargo)*

Received 10 April 2018; Accepted 3 November 2018

ABSTRACT

Shrimp fishing for commercial purposes has been done for centuries generating income for many families. Shrimp produces a high amount of wastes, with 50% of the total weigh wasted and these, if not disposed properly, can cause many environmental problems. In addition, copper contaminated areas, such as rural, metropolitan areas and mining areas have been studied as important problematic sites. The aim of this study was to evaluate the ability of copper ions adsorption using different chitin extracts from shrimp culture residues. Tests were designed with four different extracts obtained by simple boiling and milling, demineralization, deproteinization and deacetylation. After the contact time with extracts solution, samples were collected to detect levels of copper in solution. The possible interactions extracts-ion were investigated by thermal degradation analyse, X-ray diffraction, infrared spectroscopy, scanning electron microscopy and dispersive energy X-ray spectroscopy. In this study, the extracts showed a removal of 52.66 mg g^{-1}, 23.05 mg g^{-1}, 19.31 mg g^{-1} and 67.81 mg g^{-1}, respectively. Extract with deacetylation showed the highest efficiency of copper adsorption (Extract 4 – chitosan).

Keywords Copper; Chitin; Chitosan; Deacetylation; Adsorption

1. Introduction

There is now a concern about the correct disposal of fishery waste, especially exoskeletons of crustaceans, such as shrimp. Shrimp fishing for commercial purposes has been done for centuries, and it wastes represents 50% of its total weight, with high levels of organic matter and nutrients. When improperly disposed, wastes attracts rats, cockroaches and insects, causing problems for human health and environment [1]. An alternative to mitigate the adverse effects of shrimp waste in the environment is the production of a high added-value product, such as chitosan, through chitin. This allows this residue to be inserted again into the fishery production system.

Interests in studying chitosan and chitin increases due to its properties such as biodegradability, biocompatibility, hydrophilicity, as well as easy modification ability and high

---

*Corresponding author.

potential in removing metallic ions. Both the amine and the hydroxyl group can serve as active sites for metal ions, working as metal chelating agents and adsorbents of metal anions [2–4]. Therefore, the use of chitin is an alternative in the removal of heavy metals, because of its bonding capacity with metallic ions and subsequent reuse, as well as its possible biodegradability after its final use [2,5,6].

Contamination of natural waters by heavy metals presents a serious problem in several countries. Heavy metals can be released into aquatic systems by anthropogenic sources, through urban and industrial effluents, agricultural activities, mining tailings areas, among others. The removal of heavy metals present in industrial effluents is one of the practices aiming conservation of water resources, thus reducing potential pollution and contamination of water bodies [2]. One of the metals that is commonly present in industrial effluents is copper, a heavy metal used in industry and agriculture, and its improper disposal contaminates the soil, water and plants [7,8]. Once in the aqueous solution, the metal is solubilized, with the possibility of cancer incidence in human through its ingestion, and can cause dysfunctions in the nervous system, threatening the health and life of animals and human [9]. Thus, the application of remediation techniques aiming the removal of heavy metals is essential to maintain environment quality [10].

In relation to the removal of metallic ions, adsorption is an alternative method, due to its easy operation and high efficiency compared to conventional methods that are costly or technically difficult [1,11,12]. In this context, the aim of this work was to evaluate the ability of four chitin extracts in the adsorption of copper ions. The extracts–ions interactions were investigated using thermogravimetric analysis (TGA), X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and dispersive energy X-ray spectroscopy (EDS).

2. Materials and methods

2.1. Raw material

The raw material used for the different extracts of chitin was obtained from shrimp waste (*Penaeus brasiliensis*), kindly provided by the fishing community named Z3 in the city of Pelotas, RS, Brazil.

2.1.1. Process of adsorbents production

The four different extracts were prepared to adsorb the Cu(II) ions in aqueous solution. Each batch contained about 500 g of shrimp and the wastes were washed manually and boiled in water (at 100°C, for 3 h). After boiling, the exoskeletons were dried (at 80°C, for 24 h), milled and mechanically sifted (2 mm particles). This procedure was used for the first extract [13].

After this procedure, demineralization (Extract 2) was carried out by adding 1 L of HCl (1 M) to the dried milled material (140 g). The demineralized extract was filtered and washed with water until neutrality, followed by further drying at approximately 80°C for 24 h. The mixture was stirred for 3 h. This material was then filtered and washed with water until neutrality. After this procedure, the material was dried in oven for 24 h at 80°C. Finally, the deproteinated material (Extract 3) was led to the latter process.

The chitosan production process was conducted from the deacetylation of chitin with 45o Be NaOH solution (42.3%). This reaction occurs in a reactor with agitation and heating. The reactor temperature was maintained at 130°C for 2 h. After this period, it was performed a wash with water, removing the excess of reagent which is checked by pH measurement. After deacetylation, the chitosan has been solubilized in 1% acetic acid. The solution was centrifuged in order to remove the undissolved material, and to obtain a solution with lower impurities content. The chitosan was precipitated in alkaline solutions, with the pH 12.5. The separation was performed by centrifugation. Drying was performed in a tray dryer to obtain commercial moisture. The chitosan purification process is based in these previous steps of solubilisation in acetic acid and centrifugation; and then precipitated and separated by centrifugation again with further drying the chitosan [14].

After obtaining the different extracts, the adsorption efficiency of heavy metals was tested aiming the application in remediation of contaminated areas.

The materials were prepared to act as an adsorbent to remove the Cu(II) ions in aqueous solution. In this work, four new adsorbents were developed: boiling compound (Extract 1), compound with boiling and demineralization (Extract 2), compound with boiling, demineralization and deproteinization (Extract 3) and compound demineralization with all previous treatment (Extract 4).

2.2. Adsorption capacity test

For the adsorption capacity test, it was used 500 mL of Cu(II) solution (100 mg L^{-1}). One gram of each extract was added and incubated for 24 h with 150 rpm rotation. After this time, the solution was filtered to remove the extracts. The remaining Cu(II) ions was detected in the solution. Detection of copper levels were done using ICP-OAS at the Laboratory of Soil Analysis of the School of Agronomy in Federal University of Rio Grande do Sul (UFRGS). The extracts were dried and stored for Scanning Electron Microscopy and Energy Dispersive System (SEM/EDS) analysis, along with thermogravimetric analysis (TGA), X-ray diffraction analysis (XRD) e Fourier-transform infrared (FT-IR).

2.3. Adsorption kinetics

The copper solution was prepared using copper-salt (99% purity, Merck, Germany). The copper solution was used with an initial concentration of 100 mg L^{-1}. It was added 2.0 g of the adsorbent to the copper containing solution. This solution was kept under constant stirring at 160 rpm for 6 h. Designed in triplicates, adsorption capacities in time "t" were determined according to Eq. (1):

$$q_t = \frac{V\left(C_o - C_t\right)}{m} \tag{1}$$

In order to adjust the experimental data, kinetic models of pseudo-first-order, pseudo-second-order and Elovich were used. Eqs. (2), (3) and (4) express the models, respectively [15].

$$q_t = q_1\left(1 - \exp\left(-k_1 t\right)\right) \quad (2)$$

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_2^{\,2}}\right) + \left(\frac{t}{q_2}\right)} \quad (3)$$

$$q_t = \frac{1}{a} In\left(1 + abt\right) \quad (4)$$

The kinetic parameters were estimated with non-linear regression adjustments in experimental data. The Quasi-Newton estimation method was used. Estatística 7.0 software (Statsoft, USA) was used and the quality of the adjustments were measured according to the coefficient of determination (R^2) and mean relative error (MRE) [16].

2.4. Analysis of SEM/EDS and copper levels

The scanning electron microscopy (SEM) technique was used to observe the morphology, and the distribution of the elements through the micro structure (JEOL, JSM-5800, Japan).

2.5. Materials characterization by TGA, XRD e FT-IR

The dynamic degradation studies (TGA) for the samples were carried out in air atmosphere in a thermo balance (Shimadzu, TA60, Japan). The samples were heated from 25°C to 500°C, at heating rate of 10°C min^{-1}.

The X-ray diffraction (XRD) patterns were obtained using a diffractometer (Brunker D–8, Germany), provided with a diffracted beam monochromator and Ni filtered *CuK* α radiation (λ = 1.5406 Å). The voltage was of 40 kV and the intensity of 40 mA. The 2ɵ angle was scanned between 10° and 60°, and the counting time was of 1.0 s at each angle step (0.02°).

The functional groups were identified by FT–IR (Prestige, 21210045, Japan) using diffuse reflectance in KBr pellets.

2.5. Factorial plan

The experimental design was carried out by the entirely randomized with four different treatments and each evaluation of the pH, adsorption, temperature and kinetics were carried out 5 times (5 replications). The MEV/EDS, FTIR, TGA, and XRD analysis were characterized in one composed sample.

3. Results and discussion

3.1. Adsorption test

All extracts showed copper adsorption capacity (Table 1). Among them, extract with deacetylation process (Extract 4) and extract with simple boiling and milling (Extract 1) showed higher copper adsorption capacity, with levels of 67.81 mg $g^{-1}$and 52.66 mg g^{-1}, respectively. The lowest copper adsorption was 19.31 mg g^{-1} (Extract 3) and 23.05 mg g^{-1} (Extract 2).

Table 1
Copper adsorption by different chitin extracts in 24 h of incubation.

Extract	Treatment	pH	Ads. (mg g^{-1})	Temp. (°C)
1	Boiling and milling	6.31	52.66	21.56
2	Demineralization	6.19	23.05	21.23
3	Deproteinization	6.24	19.31	21.21
4	Deacetylation	6.18	67.81	23.04

The higher adsorption of copper by the deacetylated chitin extract (Extract 4) could be justified because chitosan, a cationic polysaccharide produced from the chitin deacetylation, is produced from hydrolysis under high temperatures. The chitosan then presents pairs of free nitrogen electrons in the amine groups being responsible for the adsorption of the cationic metals [17,18].

According to an experiment conducted by [19], chitosan showed the highest biosorption index for the copper ion, while chitin showed highest biosorption index for iron (Fe), demonstrating that the deacetylation process is necessary for the removal of copper ions. Recent studies by [20] show that the absorption of copper (II) using nano chitosan particles reached the maximum capacity of 21.5 mg g^{-1} ($C_e < 1000$ mg/L) in 4 h, which suggests a reactive activity of intense electron transfer representing a high performance in the chemical adsorption of heavy metals.

In this context, it is also possible to observe that the extracts with demineralization and deproteinization (Extracts 2 and 3) showed lower efficiency in the copper ion adsorption than the simple boiling and milling extract (Extract 1). This result may be related to the amount of protein present in Extract 1 capable of retaining part of the metal present in the solution. The degree of deacetylation is related to the fraction of amino groups in the polymer chain. Chitosan becomes soluble in acid solutions when the degree of deacetylation of chitin is greater than 70%, thus chitosan behaves as a cationic polyelectrolyte, which configures a higher rate of adsorption of metals, as shown in Table 1 for Extract 4 [21,22,23].

3.2. Adsorption kinetics

Fig. 1 shows the adsorption capacity of copper as a function of time at a 120 rpm rotation, related to the temperature during the adsorption of copper. It is possible to observe that the highest adsorption index occurred in chitosan (Extract 4). Extract 3 obtained the lowest copper adsorption value in solution over the course of 6 h, being 9.27 mg L^{-1}. It is important to note that Extract 2 and 3 did not showed satisfactory results for removal of copper in solution as can be seen below.

There are correlation between the availability of sites and the adsorption kinetics, thus, the number of available sites decreases gradually with decreasing adsorption kinetics [21]. In this context, Extract 4 (Fig. 2) with higher removal levels of copper in solution presented ideal kinetic behaviour, with its adsorption increasing gradually over time. Another important fact to consider is the low thermal variation during the process.

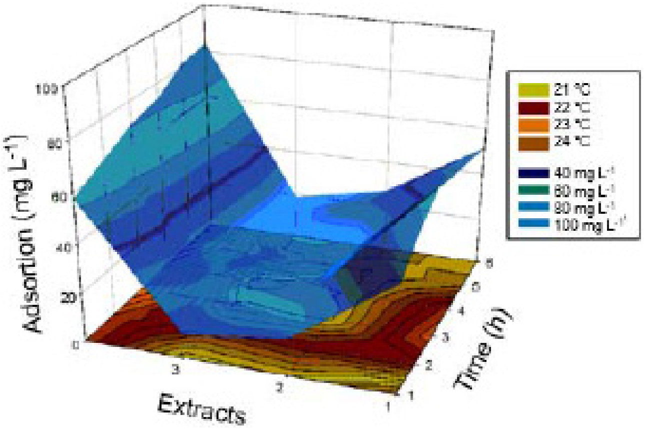

Fig. 1. Adsorbent and thermal behaviour of the different extracts of chitin.

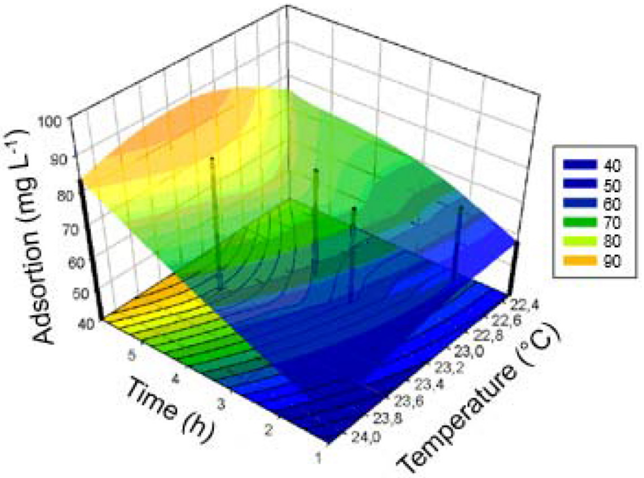

Fig. 2. Adsorbent and thermal behaviours of Extract 4 with in copper solution.

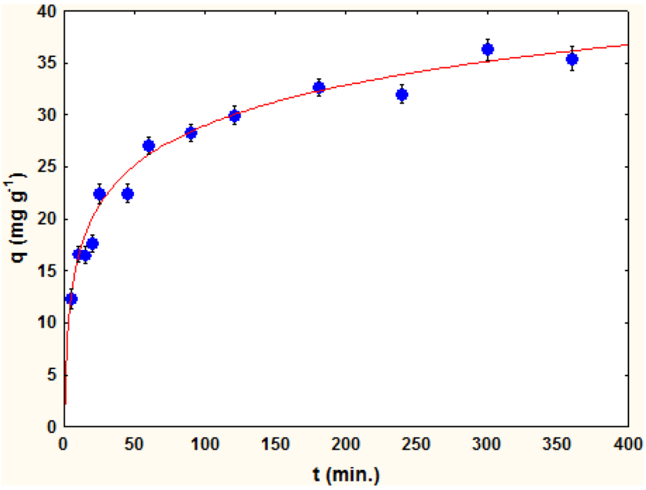

Fig. 3. Experimental equilibrium data for adsorption of copper by shrimp extracts.

Table 2
Adjustment parameters of the kinetic models for adsorption of copper by shrimp. extracts.

Pseudo-first-order			
q_1 (mg g^{-1})	k_1 (min^{-1})	R^2	ARE (%)
31.63	0.05	0.80	11.83
Pseudo-second-order			
q_2 (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	ARE (%)
34.83	2993.20	0.89	8.59
Elovich			
α (g mg^{-1})	β (mg g^{-1} min^{-1})	R^2	ARE (%)
0.18	9.72	0.94	4.45

The chitin extraction processes and their transformation into chitosan should not be done simplified, since it requires the consumption of reagents and heating sources, resulting in a final value added product. In this way, the production of chitosan with reduced costs represents a great opportunity, since its properties of adsorbing of heavy metals and possible application in techniques for remediating degraded areas [24].

Fig. 3 shows the adsorption capacity of copper as a function of time at a stirring rate of 160 rpm as well as the adjustment of the most suitable model.

The adsorption capacity after 360 min was approximately 35 mg g^{-1}. The experimental data of Fig. 3 were adjusted to the pseudo-first-order, pseudo-second-order and Elovich models (Table 2). The kinetic analysis showed that the Elovich model was the most suitable to represent the kinetic experimental data (R^2 > 0, 90 and MRE < 5.00).

However, the pseudo-second-order model (R^2 > 0.96) applied for Cu(II) absorption was used by [21], the K_2 values ranged from 1.881 × 10^{-4} to 4.029 × 10^{-4} showing insufficiencies in the adsorption process. Otherwise, K_1 ranged from 0.015 to 0.020, concluding that Cu(II) could diffuse into the pores before being adsorbed, and that intra particle diffusion may not be controlling the rate of the reactions, thus, the external absorption and the equilibrium absorption have equal importance in the adsorption processes. According to [20] the adsorption of metals is higher in materials with high specific surface area (chitosan) and achieve the equilibrium faster, which was noticed in their studies with chitosan, pseudo-second-order obtained R^2 > R^1 for adsorption of Cu(II) through the coordination bond. [25] showed Cu(II) adsorption values of 71.36 mg g^{-1} (C_e < 200 mg L^{-1}) in 12 h.

3.3. SEM/EDS

Scanning electron microscopy (SEM/EDS) of the different chitin extracts was carried out to compare the possible changes in the surface of the biopolymers. Extract 1 (Fig. 4) shows that there was a high adsorption after 24 h of incubation in Cu solution (100 mg L^{-1}). The images of the shrimp shell with simple boiling and milling as in Extract 1, show that chitin (Figs. 4a and 4c) already have an irregular porous structure and can adsorb copper, as shown in the EDS analysis in Fig. 4d.

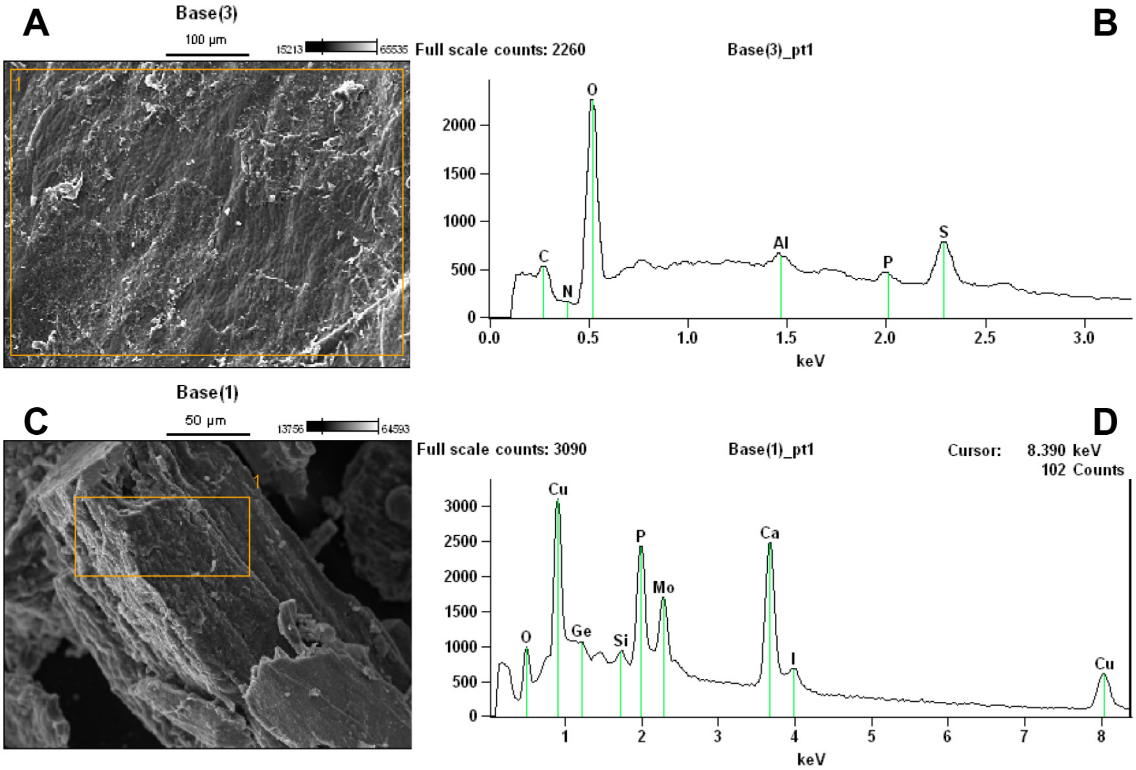

Fig. 4. Scanning Electron Microscopy and Energy Dispersive System (SEM/EDS) from Extract 1 (a) SEM before adsorption; (b) EDS before adsorption; (c) SEM after 24 h; (d) EDS after 24 h.

It was observed that Cu, P, Mo and Cain Extract 1 showed a positive correlation of the Spike type in adsorption after 24 h (Fig. 4d). The fact may be justified by the competition of the molecules by the same active sites in the matrix that should be filled by copper ions, since the occurrence of complexes can retain more than one type of chemical element in the active site [2].

Extract 2, after demineralization (Fig. 5) shows a heterogeneous, fibrous and irregular structure. Changes in the surface of the material were observed, where the rounded white spots (Fig. 5a) after demineralization were replaced by rounded holes (micro pores) (Fig. 5c) resulting from removal of $CaCO_3$ by the acid treatment. This fact is evidenced by the absence of Ca in the EDS in Fig. 5d, where Cu(II) was adsorbed. This absence of Ca was also detected in other studies related with the production of chitosan from shrimp shells [26]. Therefore, it was observed that the capacity to adsorb copper in the Extract 2 after 24 h through demineralization is lower, comparing with Extract 1 from Fig. 4d.

In Extract 3 (Fig. 6), the shrimp waste was boiled and milled, followed by demineralization and deproteinization. After this last treatment, a more uniform, non-fibrous structure was obtained with regular pores and few imperfections (Figs. 6a and 6c), compared to previous treatments.

It was noticed that there were rounded white spots ($CaCo_3$) (Figs. 6a and 6c) after deproteinization, and that micropores (Fig. 6a) were filled by both Cu(II) and Si and S. The Ca element appearing in the EDS (Fig. 6b), is not present in the EDS of (Fig. 6d). Thus, the deproteinization treatment (Fig. 6) also removed the copper contained in the solution (Fig. 6d) after 24 h, but was not as effective comparing with Extracts 1 and 2.

The last extract tested in this study (Extract 4), chitosan with the final purification, demonstrated that the deacetylation promoted a differentiated physical structure. The EDS (Figs. 7b and 7d) showed absence of Ca in the extracts that were demineralized, comparing with the other extracts (Fig. 7). In addition, a difference between chitosan before (more fibrous structure with presence of irregular pores) and after incubation with copper (Figs. 7a and 7c) is noticed.

It is possible to observe that the metal concentrations increased (Fig. 7d) after incubation with the copper solution. Extract 4 has the highest Cu(II) adsorption among all extracts (Fig. 7d), and this treatment may be the most effective way to remove copper, according to the spectrum (EDS) observed below. Studies carried out by [26] and [20] demonstrate the higher absorptive capacity of metals in chitosan materials take place after the deacetylation process.

The different extracts of chitin presented good performance in the adsorption of copper in solution, the same performance was found by [2], [17] and [21], in adsorption treatment of heavy metals, especially Cu(II), on chitosan surface.

However, it is important to emphasize that there are many variables that interfere in the adsorption process, for example, the surface area or size of the adsorbent particle, concentration of the metal ions to be adsorbed, dosage of the adsorbent and temperature, pH of the medium, among other factors [21,27].

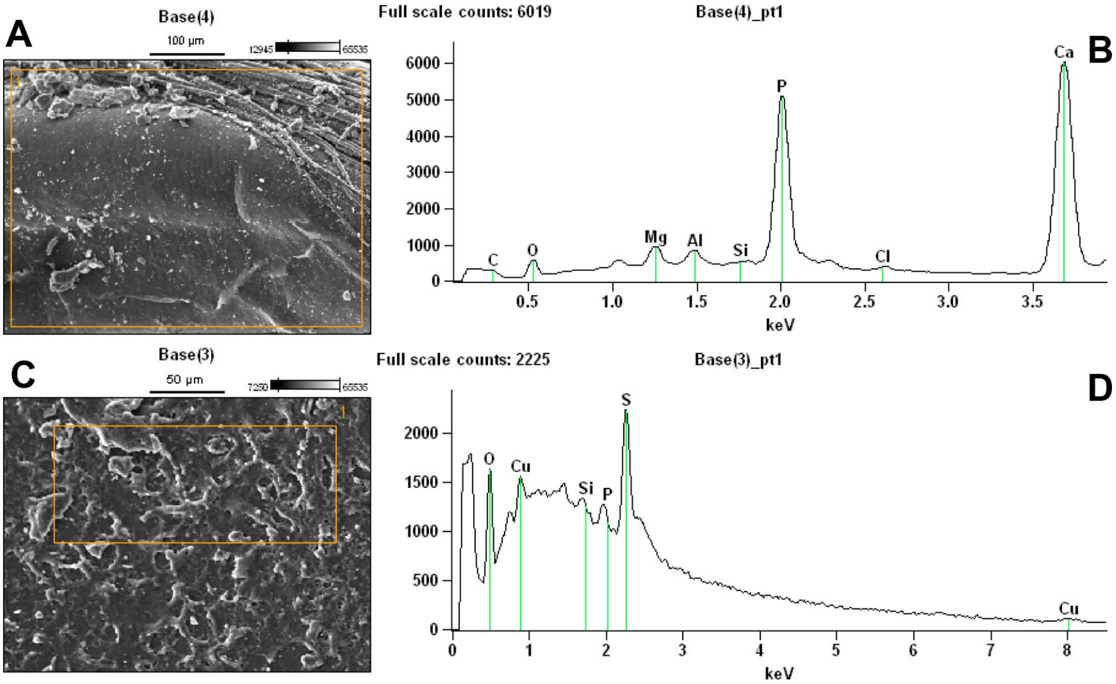

Fig. 5. Scanning Electron Microscopy and Energy Dispersive System (SEM/EDS) from Extract 2 (a) SEM before adsorption; (b) EDS before adsorption; (c) SEM after 24 h; (d) EDS after 24 h.

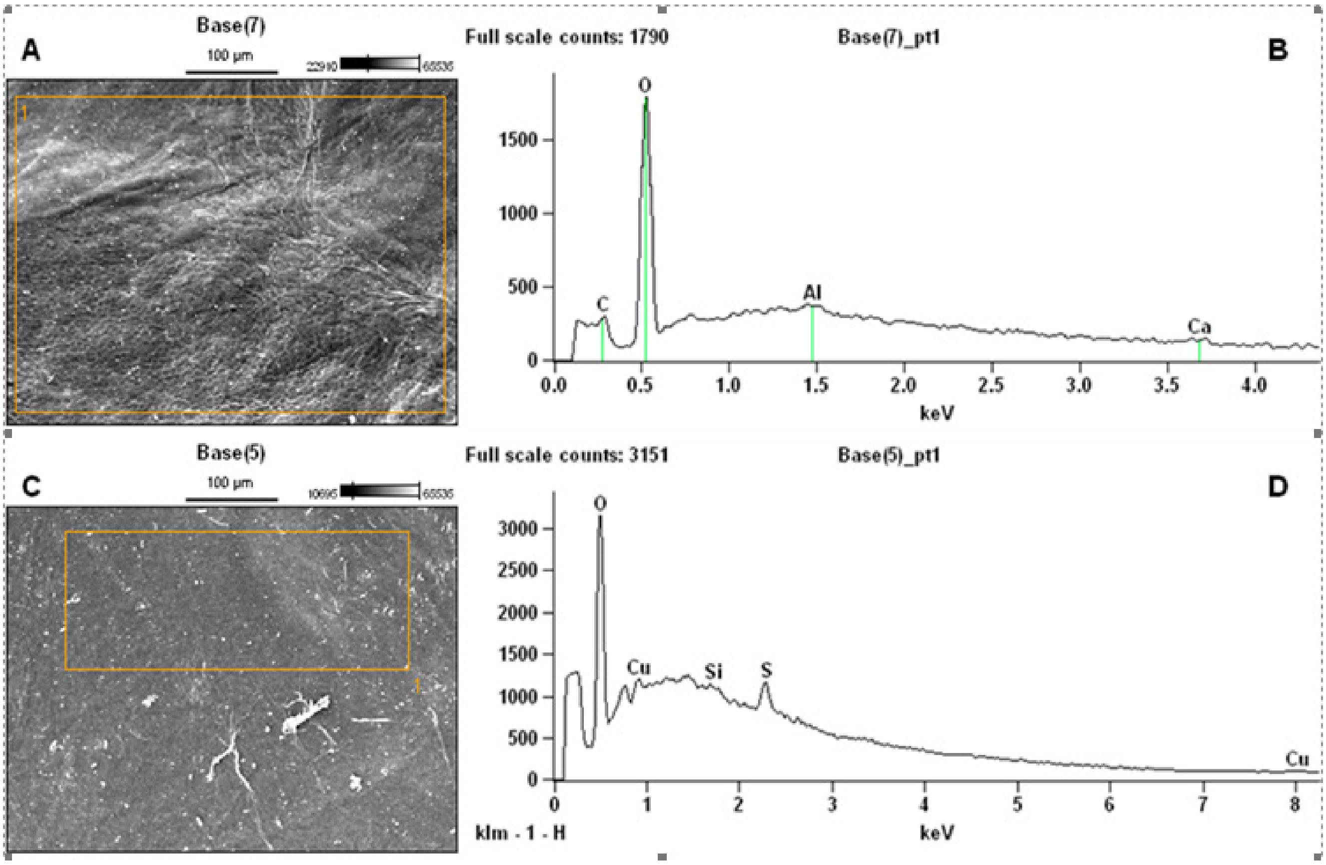

Fig. 6. Scanning Electron Microscopy and Energy Dispersive System (SEM/EDS) from Extract 3 (a) SEM before adsorption; (b) EDS before adsorption; (c) SEM after 24 h; (d) EDS after 24 h.

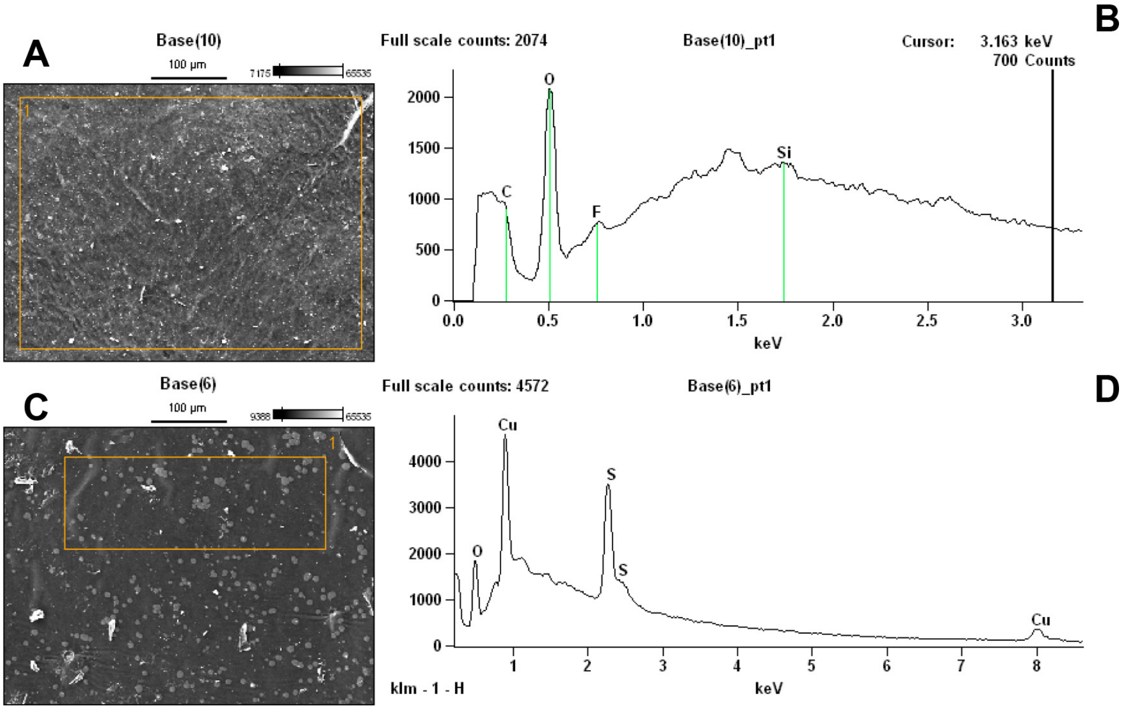

Fig. 7. Scanning Electron Microscopy and Energy Dispersive System (SEM/EDS) from Extract 4 (a) SEM before adsorption; (b) EDS before adsorption; (c) SEM after 24 h; (d) EDS after 24 h.

3.4. Materials characterization by TGA, XRD e FT-IR

Fig. 8 shows the TGA curves, for the extracts. In all the TGA curves there were three characteristic temperature intervals of weight loss. The first weight losses occurred until 226°C with 18% weight loss, which corresponds to the evaporation of physically adsorbed and strongly bonded water to the films. The second weight losses were caused by depolymerization/decomposition of polymer chains through deacetylation and cleavage of glycosidic linkages.

Kaya et al. [28] characterizing chitosan isolated from different sources (the insect *M. melolontha* and the crustacean species *O. asellus*) in the TGA analysis detected the mass losses in two steps. The first step for both species was described as being related with the water evaporation from the structure. However, the range of temperature observed for these results were between 0 and 150°C and the percentual of mass losses were quite lower, being 4 and 5%, for *M. melolontha* and *O. asellus*, respectively. The authors attributed the second step of mass losses to the deterioration of chitin molecules.

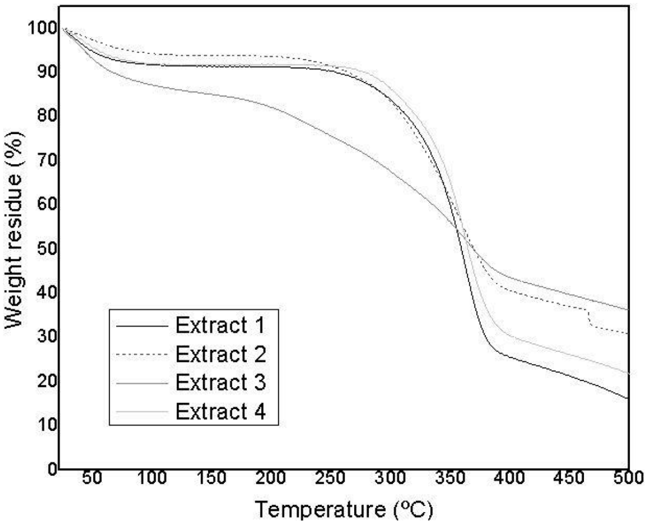

Fig. 8. TGA curves, of different extracts.

Moussout et al. [29] showing the TGA results of chitin and chitosan extracted from shrimp shells also detected three intervals of weight loss, being the first also related with the evaporation of hydrogen bonded water to the materials and corresponding to 10–15% of mass loss. The second interval found by the authors and by Borowska et al. [30] corroborates with the results found in this study, with the mass losses in this stage correlated with breaking polysaccharide chains.

Fig. 9 shows the XRD patterns of the extracts, achieved in the field 5° < 2θ < 60°. The two main peaks, located at d = 6.90 Å and at d = 4.41 Å, are in agreement with the literature. The first peak is assigned to N-acetyl-D-glucosamine sequences and the second peak to the sequences N-glucosamine in the polymer chain.

The results of XRD analysis corroborates with Moussout et al. [29] regarding the detection of N-acetyl-D-glucosamine sequences in the first peak of XRD analysis and with Zia et al. [31] that reports chitin as being a crystalline polymer of N-acetyl-d-glucosamine (GlcNAc) monomers with its structure well known by previous studies.

Kaya et al. [32] studying the structures of chitin obtained from three common wasp species (*Vespa crabro*, *Vespa orientalis* and *Vespula germanica*) detected the XRD peaks very similar with some other chitin samples from organisms pre-

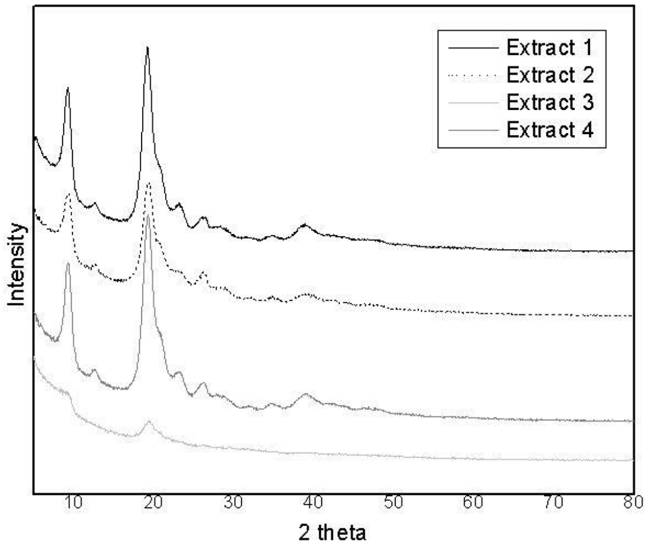

Fig. 9 XRD patterns of different extracts.

viously reported, i.e. *Holotrichia parallela, Euphausia superba* and the results were also similar with those found in this study, having two sharp (around 9° and 19°) and 4-week peaks (around 13°, 21°, 23°, and 26°).

Kaya et al. [33] in another study characterizing chitosan obtained from scorpion also observed two peaks around 10 and 20º and described them as being typical for chitosan, thus indicating that the chitosan was successfully obtained from scorpion.

In Fig. 10 was observed at 3350 and 3150 cm^{-1} the chitin and chitosan characteristic stretches of N–H and O–H. The C–N stretching of amides was identified at 1550 cm^{-1}. The angular deformations of C–O–H and H–C–H appeared at 1450 cm^{-1}. At 1075 cm^{-1}, the C–N stretching related to the amino groups was identified.

Zhang et al. [34] studying the determination of the degree of deacetylation of chitin and chitosan from shrimp detected the FTIR spectra exhibiting broad peaks around 3450 cm^{-1} assigned to OH stretching, corroborating thus the results found in this study. In addition, Moussout et al. [29] characterizing the chitin and chitosan extracted from shrimp shells detected a broad band centred at the infrared spectra at 3250 and 3500 cm^{-1} corresponding to stretching vibrations of the O–H and N–H groups.

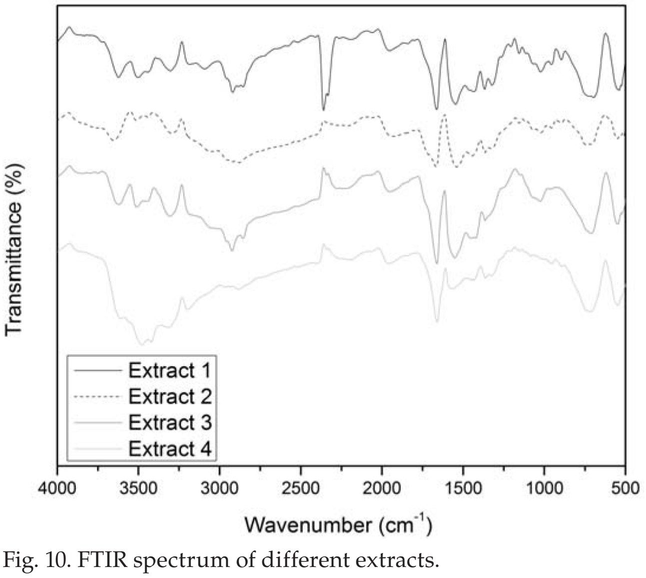

Fig. 10. FTIR spectrum of different extracts.

The study of Kaya et al. [32] regarding the *V. crabro*, *V. orientalis*, and *V. germanica* chitin also detected the O–H stretching at the three different species at respectively, 3437 cm^{-1}, 3434 cm^{-1} and 3440 cm^{-1}. In another study, Kaya et al. [33] evaluating the low molecular weight scorpion (Mesobuthus gibbosus) chitosan also identified the C-N stretching of amides at 1550 cm^{-1}.

4. Conclusion

Among the different treatments analysed, the chitosan (Extract 4) showed the highest efficiency in copper adsorption. With the development of studies related to the properties found in shrimp wastes (shrimp shells), it can be concluded that this technology could be useful for the treatment of effluents containing copper and other metals, and that the deacetylation process is essential in improving removal efficiency. In this way, it is possible to reduce the amount of metals released into the water bodies and to reduce the amount of improperly disposed waste.

Acknowledgement

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance code 001, by the CNPq (National Council for Scientific and Technological Development) and FAPERGS (Research Support Foundation of the State of Rio Grande do Sul).

Funding Sources

This project was funded by the National Council for Scientific and Technological Development (CNPq) and Research Support Foundation of the State of Rio Grande do Sul (FAPERGS).

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

[1] F.M. Souza, R.M.S. Ferreira, R.C. Barbosa, Utilização da casca de camarão para produção de quitina, Scire, 7 (2015) 1–11.
[2] T.S. Frantz, N. Silveira, M.S. Quadro, R. Andreazza, A.A. Barcelos, T.R.S. Cadaval, L.A.A. Pinto, Cu(II) adsorption from copper mine water by chitosan films and the matrix effects, Environ. Sci. Pollut. Res., 24 (2017) 5908–5917.
[3] S. Yalçınkaya, C. Demetgül, M. Timur, N. Çolak, Electrochemical synthesis and characterization of polypyrrole/chitosan composite on platinum electrode: Its electrochemical and thermal behaviors, Carbohydr. Polym., 79 (2010) 908–913.

[4] R. Schmuhl, M.H. Krieg, K. Keizer, Adsorption of Cu(II) and Cr(VI) ions by chitosan: kinetics and equilibrium studies, Water SA, 27 (2001) 1–7.

[5] M. Barikani, E. Oliaei, H. Seddiqi, H. Honarkar, Preparation and application of chitin and its derivatives: A review, Iran Polym. J., 23 (2014) 307–326.

[6] R.A. Muzzarelli, Biomedical exploitation of chitin and chitosan via in imidazolium ionic liquids and supercritical drying, Mar Drugs, 9 (2011) 1510–1533.

[7] R. Andreazza, F.A.O. Camargo, Z.I. Antoniolli, M.S. Quadro, A.A. Barcellos Biorremediação de áreas contaminadas com cobre, Revista de Ciências Agrárias (Lisboa), 36 (2013) 127–136.

[8] R. Andreazza, L. Bortolon, S. Pieniz, F.M. Bento, F.A. Camargo, Evaluation of two brazilian indigenous plants for phytostabilization and phytoremediation of copper-contaminated soils, Braz. J. Biol., 75 (2015) 868–877.

[9] N.H. AbRazak, S.M. Praveena, A.Z. Aris, Z. Hashim, Drinking water studies: a review on heavy metal, application of biomarker and health risk assessment (a special focus in Malaysia), J. Epidemiol. Glob. Health, 5 (2015) 297–310.

[10] S. Dhananasekaran, R. Palanivel, S. Pappu, Adsorption of methylene blue, bromophenol blue and coomassie brilliant blue by α-chitin nanoparticles, J. Adv. Res., 7 (2016) 113–124.

[11] S. Noor, M. Waseem, U. Rashid, M. Anis-Ur-Rehman, W. Rehman, K. Mahmood Fabrication of NiO coated SiO_2 and SiO_2 coated NiO for the removal of Pb^{2+} ions, Chin Chem. Lett., 25 (2014) 819–822.

[12] W.S.W. Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: a review, Carbohydr Polym., 83 (2011) 1446–1456.

[13] R.F. Weska, J.M. Moura, L.M. Batista, J. Rizzi, L.A.A. Pinto, Optimization of deacetylation in the production of chitosan from shrimp wastes: use of response surface methodology, J. Food Eng., 80 (2007) 749–753.

[14] C. Moura, P. Muszinski, C. Schmidt, J. Almeida, L. Pinto, Quitina equitosana produzidas a partir de resíduos de camarão e siri: avaliação do processo em escala piloto. Vetor, Rio Grande, 16 (2006) 37–45.

[15] H. Qiu, L. Lv, B. Pan, Q. Zhang, W. Zhang, Q. Zhang, Critical review in adsorption kinetic models, J. Zhejiang Uni. Sci., 10 (2009) 716–724.

[16] M.I. El-Khaiary, G.F. Malash, Common data analysis errors in batch adsorption studies, Hydrometallurgy, 105 (2011) 314–320.

[17] M. Xiao, J. Hu, Cellulose/chitosan composites prepared in ethylene diamine/potassium thiocyanate for adsorption of heavy metal ions, Cellul., 24 (2017) 545–2557.

[18] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purif. Technol., 38 (2004) 43–74.

[19] L.O. Franco, R.C.C Maia, A.L.F Porto, A.S. Messias, K. Fukushima, G.M.C. Campos-Takaki, Heavy metals biosorption by chitin and chitosan isolated from *Cunninghamella elegans* (IFM 46109), Braz. J. Microbiol., 35 (2004) 243–247.

[20] Y. Zhu, Z. Bai, H.L. Wang, Micro fluidic synthesis of thiourea modified chitosan micro sphere of high specific surface area for heavy metal wastewater treatment, Chin. Chem. Lett., 28 (2017) 633–641.

[21] Y.C. Lin, H.P. Wang, F. Gohar, M.H. Ullah, X. Zhang, D.F. Xie, J. Huang, J.X. Yang, Preparation and copper ions adsorption properties of thiosemicarbazide chitosan from squid pens, Int. J. Biol. Macromol., 95 (2017) 476–483.

[22] K. Kurita, Controlled functionalization of polysaccharide chitin, Prog. Polym. Sci., 26 (2001) 1921–1971.

[23] P.L. Dung, M. Milas, M. Rinaudo, J. Desbrières, Water soluble derivatives obtained by controlled chemical modifications of chitosan Carboydr. Polym., 24 (1994) 209–2014.

[24] P. Tamiasso-Martinhon, J.M.T. Souza, M.C.S. Silvia, F.L.P. Pessoa, C. Sousa, Water treatment: chitosan associated with electrochemical methods. IOP Conf Ser, Mater Sci. Eng., 191 (2017) 1–6.

[25] Y. Ren, M. Zhang, D. Zhao, Synthesis and properties of magnetic Cu(II) ion imprinted composite adsorbent for selective removal of copper, Desalination, 228 (2008) 135–149.

[26] R.S.C.M.Q, Antonino, B.L, Fook, V.O. Lima, R.F. Rached, E. Lima, R.S. Lima, C.P. Covas, M.L. Fook, Preparation and characterization of chitosan obtained from shells of shrimp (Litopenaeus vannamei Boone), Mar Drugs, 15 (2017) 141–153.

[27] B. Kannamba, K.L. Reddy, B.V. Apparao, Removal of Cu(II) from aqueous solutions using chemically modified chitosan, J. Hazard. Mater., 175 (2010) 939–948.

[28] M. Kaya, V. Baublys, E. Can, I. Satkauskiene, B. Bitim, V. Tubelyte, T. Baran, Comparison of physicochemical properties of chitins isolated from an insect (*Melolontha melolontha*) and a crustacean species (*Oniscus asellus*), Zoomorphology, 133 (2014) 285–293.

[29] H. Moussout, H. Ahlafi, M. Aazza, M. Bourakhouadar. Kinetics and mechanism of the thermal degradation of biopolymers chitin and chitosan using thermogravimetric analysis, Polym. Degrad. Stab., 130 (2016) 1–9.

[30] M.Z. Borowska, D. Chełminiak, H. Kaczmarek, Thermal stability of magnetic nanoparticles coated by blends of modified chitosan and poly(quaternary ammonium) salt, J. Therm. Anal. Calorim., 119 (2015) 499–506.

[31] K.M. Zia, I.A. Bhatti, M. Barikani, M. Zuber, M.A. Sheikh. XRD studies of chitin-based polyurethane elastomers, Int. J. Biol. Macromol., 43 (2008) 136–141.

[32] M. Kaya, N. Bagrıacık, O. Seyyar, T. Baran, Comparison of chitin structures derived from three common wasp species (Vespa crabro Linnaeus, 1758, Vespa orientalis Linnaeus, 1771 and Vespula germanica (Fabricius, 1793)), Arch Insect Biochem. Physiol., 0 (2015) 1–14.

[33] M. Kaya, M.A. Ozusaglam, S. Erdogan, Comparison of antimicrobial activities of newly obtained low molecular weight scorpion chitosan and medium molecular weight commercial chitosan, J. Biosci. Bioeng., 121 (2016) 678–684.

[34] Y. Zhang, C. Xue, Y. Xue, R. Gao, X. Zhang, Determination of the degree of deacetylation of chitin and chitosan by X-ray powder diffraction, Carbohydr. Res., 340 (2005) 1914–1917.