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Valorization of shrimp co-products "*Pandalus borealis*": Chitosan production and its use in adsorption of industrial dyes

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Abstract

The chitosan was extracted from shrimp "*Pandalus Borrealis*" co-products, by the classic and hydrothermo-chemical technique. The products obtained were characterized by infrared spectroscopy (FTIR). The results showed that the hydrothermo-chemical technique reduces the production time at least four times, and the chitosan has a higher deacetylation degree (60-85%) and yield (6-7% dry weight) than the classic process. The Chitosan has shown an adsorption capacity around 40 mg/g for removal the dye Reactive Red 23 for the following condition: initial dye concentration 150 mg/l; contact time 3 hours; pH = 3. This paper sets out a possibility or the use of waste from the sea food industry, so reducing their environmental impact.

Keywords: Chitosan, Hydrothermo-chemical, Adsorption, Textile dye, ReactiveRed23, Wastewater.

1. Introduction

The processing and shrimp peeling industry generates every year several tons of organic waste (co-products) [1] to landfill [2]. These wastes consist of heads, shells and shrimp tails begin to constitute an environmental problem for the original manufacturer companies, and hence with increased costs in their production [3]. In Morocco [4], and more particularly in the area of Tangier, are installed several factories that treat about 20 tons/year of imported shrimp from Canada, Denmark and the Netherlands, and as such responsible for generating more than 16000 tons of waste (75% are shelling) [5].

Companies in the areas of textile [6], paper [7], plastics and dyes [8] are also other sources with high environmental impact from its solid waste and effluents [9].

There are several techniques for the treatment of industrial effluents [10], [11], but the adsorption is one of the most used [12-15] taking into account the simplicity and costs. In this context, the chitosan presents itself as an economically viable alternative [15] to effluents treatment by the adsorption technique. It is a biodegradable glucosamine polymer [16] produced by deacetylation of chitin [17] from crustaceans shells [18]. Thus, this

possibility of the application of chitin solves the problems raised by the waste of the shellfish companies [19-20].
This article discusses the potentialities of the use of chitosan produced from chitin extracted of scandinavian shrimp waste, "*Pandalus borealis*", on adsorption of dyes.

2. Materials and methods

2.1. Apparatus:

A. Infra-red spectroscopy

The measurements were carried out using an infra-red spectrophotometer of type JASCO FT/IR-410 on potassium bromide pastilles KBr with 2% of chitosan. KBr was placed in an oven at 300°C for 24 h before mixing. Substances were mixed in agate mortar and pressed to pastille form. Pastilles were dried for 24 hours at 50°C in order to remove moisture. The spectrum obtained at summer recorded between 4000 cm^{-1} and 400 cm^{-1}.

B. UV spectrophotometer

The determination of the concentration of the dye Reactive Red23 (RR23) in solution was performed in the equipment UV Spectrophotometer JASCOV-360 for the wavelength of 511nm, value for which it has the largest absorbance, Fig. 1. The calibration curve, Fig. 2, was obtained from a "mother" dye solution of 50 mg/ l.

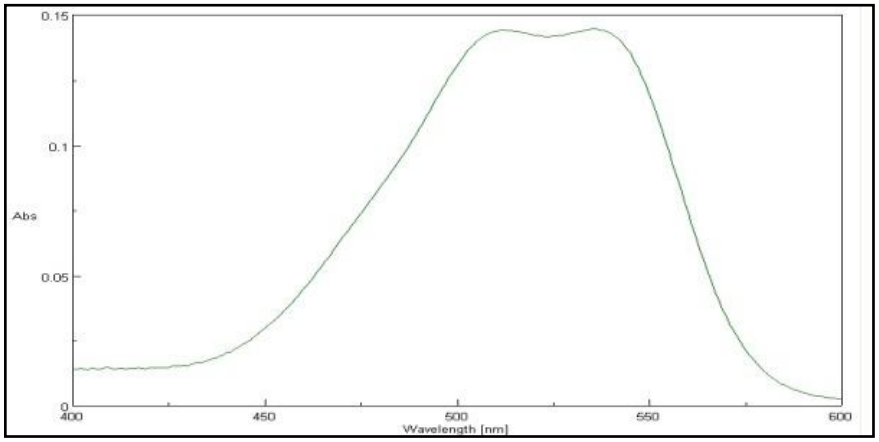

Figure1: Absorbance curve of RR23 dye.

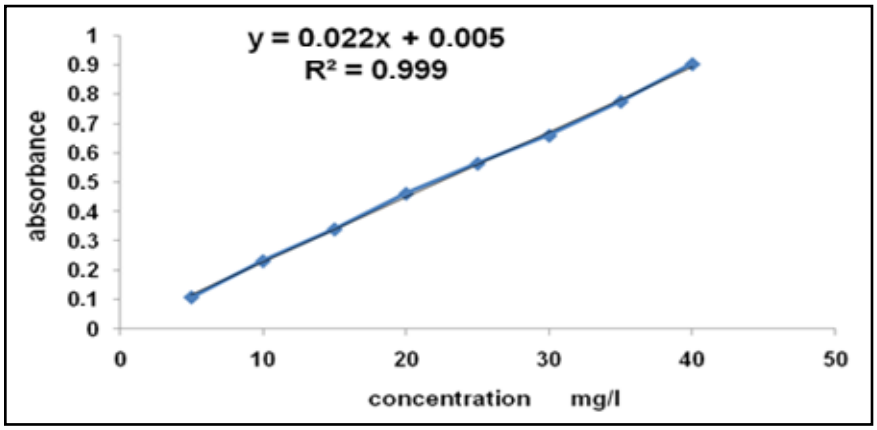

Figure2: Calibration curve of RR23 dye for λ_{max}= 511 nm.

2.2. Chitin extraction starting from the prawn carapaces and the production of chitosan

2.2.1. Pretreatment of co-products of prawns

Before use, the prawn scraps were first washed abundantly with water in order to eliminate the organic residues, and then dried at sun during 48 hours. Once dried it was reduced to powder and passed by a blender ensuring particles with a granulometry lower than 0.5mm.

2.2.2. *Classical method of extraction*

The classical method is that described by *Tolaimate and al*., 2003 [20] based on weak concentrations of reagents.

A. Demineralization

One weigh 10 g carapace dried and crushed were added to 100 ml of 0.55 M HCl at room temperature (23°C) beneath magnetic agitation during 45 min, followed by filtration in a sieve of 200 µm and washing with distilled water. This stage was repeated three times. Thereafter, washings were carried out until neutrality pH. Finally, the product was dried in oven at 80°C during one night, (equation 1):

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \quad (1)$$

B. Deproteination

Rough chitin obtained previously was soaked in 100 ml of 0.33 N NaOH using a 10% masse ratio (w:v) under magnetic agitation at a temperature of 80°C, during 45 min to dissolve proteins. This operation was repeated 3 times, then the mixture was filtered and washed several times with water distilled to eliminate the components from remaining NaOH. Around neutral pH, the substrate, deproteinized chitin, was washed more twice with methanol and dried with the free air.

C. Bleaching

Chitin obtained with the two previous treatments was treated with 35% H_2O_2 for several minutes.

D. Chitosan production by chitin deacetylation

Chitin was put in contact with 12.5 M NaOH at 80°C during 3 hours to remove the acetyl groups (equation 2). At the end, the product was filtered and washed several times with water distilled. Around neutral pH, the substrate was washed twice with methanol and dried in oven at 80°C:

$$R\text{-}NHCOCH_3 + OH^- \longrightarrow R\text{-}NH2 + CH_3COO^- \quad (2)$$

2.2.3. Hydrothermo-chemical method of extraction

The hydrothermo-chemical technique [21] to produce the chitosan was carried out in two steps:

1- Demineralization in acid medium; 2- Simultaneous deproteination and deacetylation in basic medium according with experimental conditions quoted in Table 1. The solid-liquid ratio was of 1:10 (dry weight of carapace: volume of diluted solution).

Table 1: Hydrothermo-chemical conditions for chitosan extraction.

Step	Temperature (°C)	Digestive Solution	Time (h)	DD(%)
Demineralization	50	2 M HCl	2.5	-
Deproteination and deacetylation	110	12.5 M NaOH	2.0	90

2.3. Analysis methods:

2.3.1. The deacetylation (DD) and acetylation degree (DA)

Chitosan is a copolymer of *N-acetylglucosamine* units and D-*glucosamine* units. The molar fraction (3) of *N-acetylglucosamine* units in the chain, defined as:

$$DD = 100\frac{n_{GlcN}}{n_{GlcN} + n_{GlcNAc}} \quad (3)$$

is called the degree of deacetylation (DD) (3), where, n_{GlcN}– average number of D-*glucosamine units*, n_{GlcNAc}- average number of N-*acetylglucosamine* units. In the FTIR spectroscopy, several procedures and equations are described in literature for calculation of degree of deacetylation. Calculation procedures are based on absorbance ratios of various spectral bands. In this work the amide I (1655 cm^{-1}) and hydroxyl (3450 cm^{-1}) bands were chosen. The acetylation (4) and deacetylation degree (5) was determined using the following formulas [22]:

$$DA\,[\%] = \frac{A_{1655}}{A_{3450}} \times 100/1.33 \quad (4)$$

$$DD\,[\%] = 100 - (\frac{A_{1655}}{A_{3450}} \times \frac{100}{1.33}) \quad (5)$$

2.3.2. Effect of chitosan amount and the deacetylation degree on adsorption

The study was carried out in erlenmeyers of 100 ml capacity, using 50 ml of RR23 with a concentration of 10 mg/l at 33ºC and agitation of 150 rpm during 90min, with chitosan amount ranging between 100 and 600 mg. The handling was performed for the chitosan with degrees of deacetylation of 64% and 83%. Adsorption is expressed in terms of percentages % of the RR23 dye eliminated by the chitosan (6) and calculated as follows:

$$\% = \frac{C_o - C_e}{C_o} \times 100 \quad (6)$$

C_0 = Initial concentration of RR23 (mg/l)

C_e = Final concentration of RR23 (mg/l)

2.3.3. Effect of pH on the adsorption

The pH of 150 ml of RR23 solutions was adjusted between 1 and 9 with concentrated HCl or NaOH. A chitosan amount of 200 mg was added to these solutions that were submitted to an agitation of 150 rpm during 90 min at 24ºC. The samples were filtered and analyzed by spectrophotometry UV.

2.3.4. Kinetics of chitosan adsorption

The kinetic study was carried out from 30 min up to 360 min at 26ºC on 50 ml solutions of RR23 (150 mg/l) with 200 mg of chitosan under agitation. After each trial the chitosan was filtered, and the solution analyzed.

The adsorption capacity was determinate by the following relation:

$$Q_e = \frac{(C0 - CE) \times v}{m} \quad (7)$$

Where: C0: initial concentration of RR23 in solution (mg/l).

CE: final concentration of RR23 in solution (mg/l).

m: mass of chitosan (g).

V: the volume of solution.

Q_e: adsorption capacity (mg/g).

2.3.5. Isothermal adsorption

Chitosan (200 mg) was introduced into 10 erlenmeyers containing 50 ml of RR23 solutions (10 to 200 mg/l).The suspensions under agitation were maintained in contact at 24°C for a contact time of 90min. At the

end, the solutions were filtered and analyzed to establish a relation between the adsorbate and the remaining solution. The results were analyzed according to the isotherm model of Langmuir (8).

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{b\,Qm} \qquad (8)$$

where Qe: amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g),
Ce: equilibrium concentration of the adsorbate (mg/l),
and Qm and b are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (l/mg).

3. Results and discussion

3.1. Chitin and chitosan extraction yields according the processing

Table 2 presents the results of the yield of extraction of chitin and the chitosan, respectively, 5% and 4.7%, from co-products of the prawns "*Pandalus borealis*" by the classical method. So, the chitosan yield in relation to chitin is of 94%.

Table 2: Chitin and chitosan extraction yields from shrimp co-products "*Pandalus borealis*" by the classical method.

Sample	dry Weight (g)	Mass of the chitin (g)	Mass of the chitosan in (g)	% Mass of the chitin from waste dryness prawns	% Mass of the chitosan from waste dryness prawns
ECH1-co-products	10	0.49	0.45	4.90	4.50
ECH2-co-products	10	0.51	0.48	5.10	4.80

The chitosan extraction yield by the hydrothermo-chemical method, Table 3, is 6.01% on average, i.e., about plus 1.36% in comparison with the classical method.

Table 3: Chitosan extraction yield from shrimp co-products "Pandalus borealis" by the hydrothermo-chemical method.

Sample	Dry Weight (g)	Mass of the chitosan (g)	% Mass of the chitosan from waste dryness prawns
ECH3-co-products	20	1.37	6.85
ECH4-co-products	20	1.10	5.50
ECH5-co-products	20	1.31	6.55
ECH6-co-products	20	1.09	5.45
ECH7-co-products	40	2.38	5.95
ECH8-co-products	40	2.30	5.75

Table 4 shows that chitosan extraction yield from shrimp shells is almost double that the obtained with the heads. This result may be explained with the structure of carapace shrimp with more chitin in composition than that of the heads, i.e., 63% in the carapaces and 36% in the heads.

Table 4: Chitosan extraction yield from shrimp shells and heads by the hydrothermo-chemical method.

Sample	dry Weight(g)	Mass of the chitosan (g)	% Mass of the chitosan from waste dryness prawns
ECH9-Carapace	20	1.576	7.88
ECH10-head	20	0.89	4.45

After extraction and drying, the chitosan is present in the form of very fine powder that is soluble in solvents with a pH <7.

3.2. Analysis of the prepared chitin by infra-red Spectroscopy

The FTIR spectrum for the chitin prepared is represented in the Fig. 3, and Table 5 shows the comparison of the main bands with the reference Sofiane B.[23].

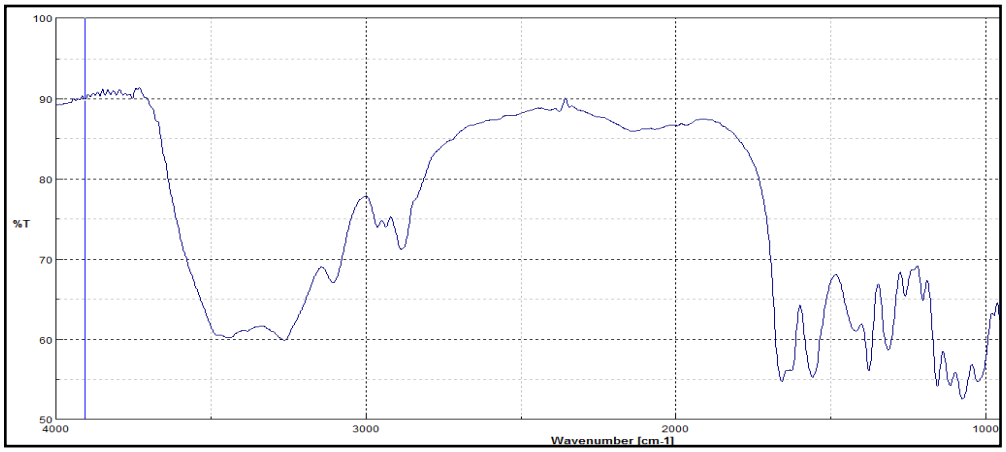

Figure 3: Infra-red spectrum of prepared chitin between 4000 cm^{-1} and 400 cm^{-1}.

Table 5: Principal bands of infra-red spectrum of prepared chitin

Absorption bands (cm^{-1})	Attributions	
Prepared chitin	Commercial Chitin	
3454	3450	Elongation of the N-H bond and O-H
2925 and 2972	2940 and 2980	Stretching vibration of C-H bonds in the CH_2 or CH_3 groups
1362	1375	The C-H bond deformation vibration in the CH_3 group
1481	1440 and 1480	The C-H bond deformation vibration in the CH_2 group
1654	1650	Vibration of valence of C=O (amide 1)
1558	1550	Vibration of deformation of connection N-H (amide 2)
1310	1320	Vibration of valence of the connection C-N
1099 and 1137	1080 and 1160	Vibration of valence of connection C-O-C
1022	1030	Vibration of valence of connection C-O-H

There is a good agreement between the experimental and bibliographical results.

3.3. Analysis of the prepared chitosan by infra-red Spectroscopy

The FTIR spectrum for the prepared chitosan is represented on Fig. 4. The comparison between the principal bands obtained and those of the reference Keddou épouse Addar M. 2008 [24] are indicated in the Table 6. The good agreement of the spectrum representative bands with reference to suggest that the extracted product is Chitosan.

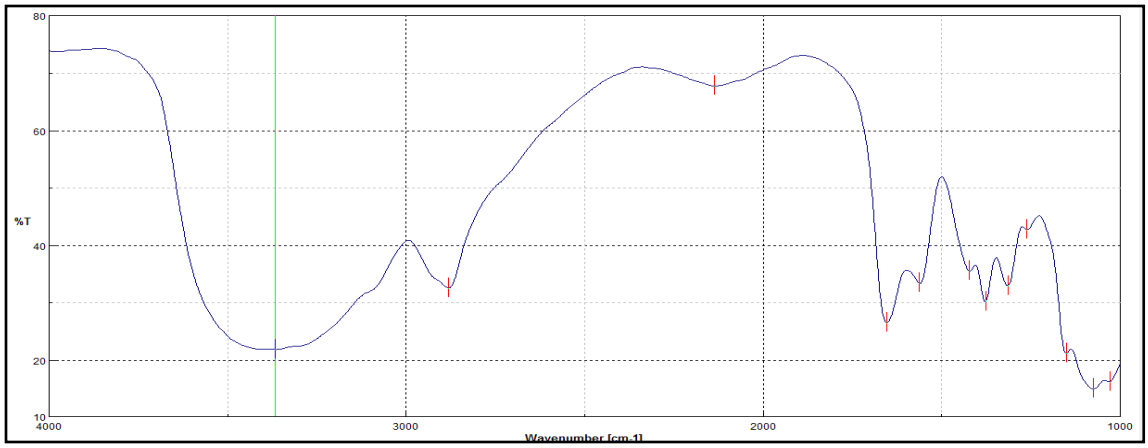

Figure 4: Infra-red spectrum of the chitosan.

Table 6: Principal bands of infra-red spectrum of the prepared chitosan

Absorption bands (cm^{-1})		Attributions
The prepared chitosan	Commercial Chitosan	
3465	3480	Elongation of the N-H bond and O-H
2881	2890 and 2923	Stretching vibration of C-H bonds in the CH_2 or CH_3 groups
1376	1381	The C-H bond deformation vibration in the CH_3 group
1423 and 14464	1421 and 1470	The C-H bond deformation vibration in the CH_2 group
1643	1637	Vibration of valence of C=O (amide 1)
1562	1601	Vibration of deformation of connection N-H (amide 2)
1315	1310	Vibration of valence of the connection C-N
1076 and 1149	1091 and 1154	Vibration of valence of connection C-O-C
1029	1020	Vibration of valence of connection C-O-H

3.4. Comparison of spectra of chitin and chitosan

According to the table 7, we notice a difference on some absorption bands: the principal band which is to 3455 cm^{-1}, which corresponds to the elongation of connection N-H and OH. The amide I band which appears to 1650 cm^{-1} for the chitosan is weaker than chitin (1658cm^{-1}) this explains why the deacetylation is always associated with a weakening of the band amide I.

3.5. The degree of acetylation and deacetylation of the chitin and the chitosan

The acetylation and deacetylation degree of the chitin and the chitosan prepared by the two methods of extraction are indicated in the Table 8. The results show that the deacetylation degree (DD) of chitosan extracts by the hydrothermo-chemical method are higher (60 to 86%) than the classical method (35 to 36%), and also with the commercial chitosan (55.78%).

Table 7: Principal bands of the chitin and the chitosan prepared.

Absorption bands (cm^{-1})		Attributions
The prepared chitin	The prepared chitosan	
3454	3465	Elongation of the N-H bond and O-H
2925 and 2972	2881	Stretching vibration of C-H bonds in the CH_2 or CH_3 groups
1362	1376	The C-H bond deformation vibration in the CH_3 group
1481	1423 and 1464	The C-H bond deformation vibration in the CH_2 group
1654	1643	Vibration of valence of C=O (amide 1)
1558	1562	Vibration of deformation of connection N-H (amide 2)
1310	1315	Vibration of valence of the connection C-N
1099 and 1137	1076 and 1149	Vibration of valence of connection C-O-C
1022	1029	Vibration of valence of connection C-O-H

The hydrothermo-chemical technique in two stages makes possible to decrease the time of production of at least four times compared to the classical technique in three stages (three to four days). Moreover, the consumption of chemical products and energy in the digestion process also decreases significantly.

Table 8: Degree of acetylation and deacetylation of the chitin and the chitosan

Sample	Matter/ (Extraction Method)	Wavenumber 1655 cm^{-1}	A	Wavenumber 3450 cm^{-1}	A	DA%	DD%
chitin 1	Co-prod./(a)	1654	0.71	3450	0.57	93.65	6.34
chitin 2	Co-prod./(a)	_	_	_	_	_	_
chitosan 1	Co-prod./(a)	1649	0.55	3448	0.65	63.62	36.37
chitosan 2	Co-prod./(b)	1651.5	0.56	3452	0.65	64.77	35.23
chitosan 3	Co-prod./(b)	1644.62	0.47	3484.13	0.99	35.70	64.30
chitosan 4	Co-prod./(b)	1642.70	0.32	3489.28	1.42	16.94	83.06
chitosan 5	Co-prod./(b)	1639.62	0.71	3469.13	1.83	29.17	70.83
chitosan 6	Co-prod./(b)	1643	0.62	3467.10	1.3	35.86	64.14
chitosan 7	Co-prod./(b)	1635.70	0.58	3476.3	1.89	23.07	76.93
chitosan 8	Co-prod./(b)	1634.2	0.6	3471.35	1.83	24.65	75.35
chitosan 9	Head /(b)	1638.41	0.82	3463.28	1.83	33.69	66.31
chitosan 10	Carapace/ (b)	1632.7	0.41	3492	2.2	14.01	85.99
The Commercial chitosan		1637	0.08	3480	0.136	44.22	55.78

Extraction method: (a): chemical classic**,** (b): hydrothermo-chemical.
Matter: Co-prod. = Co-product: raw-material. ; A: Absorbance

3.6. Effect of the amount and deacetylation degree of the chitosan on the adsorption of Reactive Red 23

Figure 5 shows that RR23 percentage adsorbed increases with the amount of the chitosan up to an optimal value of 300 mg for the chitosan with DD 83%, and to 400 mg for the chitosan with DD 64%.

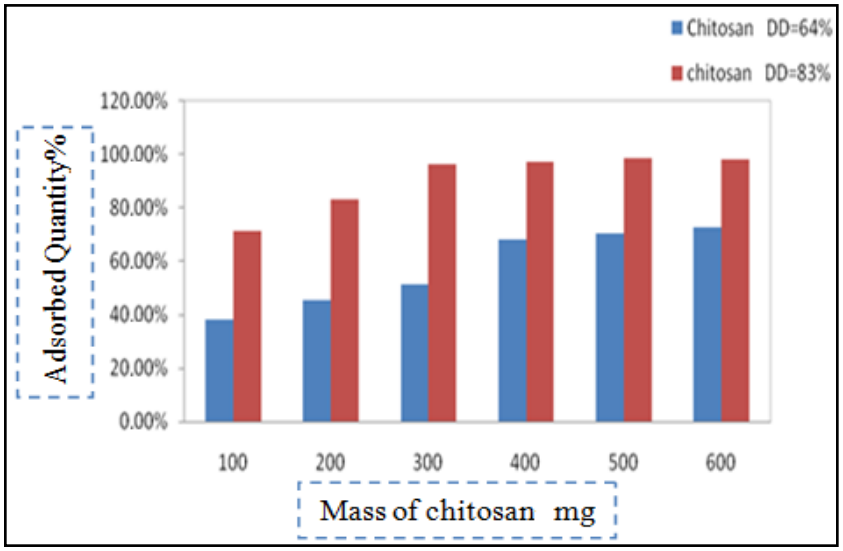

Figure 5: Effect of the amount and deacetylation degree of the chitosan on the adsorption of the "Reactive Red 23"(C_0 = 10 mg / l; 100mg <m (chitosan) <600 mg; Agitation = 150 rpm; Time = 90min; Temperature = 33° C).

3.7. Effect of the pH on the adsorption of Reactive Red 23

The plot of the amount of dye adsorbed with pH, Fig. 6, shows three distinct regions: for pH lower than 3.33 the adsorbed quantity remains almost constant, 37.5 mg/g; in pH ranging between 3.33 and 8.15 the amount adsorbed decreased approximately linearly until 12.5 mg/g; and for higher alkalinity the Q_e maintains the value 12.5 mg/g. This behavior is related with the positive charge acquired by the chitosan surface in acidic medium that attracts the anions of dye ($R\text{-}SO_3^-$). After saturation of the active sites there is repulsion, Fig 7, between the surface and grouping ($R\text{-}SO_3^-$).

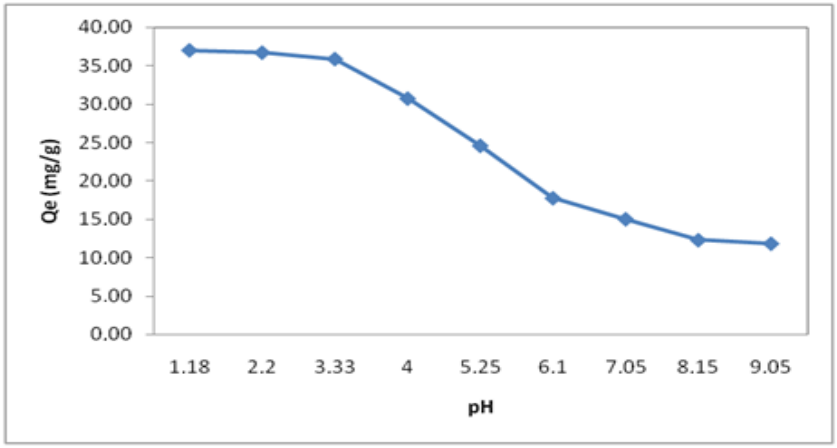

Figure 6: Effect of the pH on the adsorption of the "Reactive Red 23".
(1 <pH <9, m (chitosan) = 200 mg, C_0 = 150mg /l, Agitation 150 rpm, Time = 90 min, Temperature = 24 ° C and λ_{max}= 511 nm).

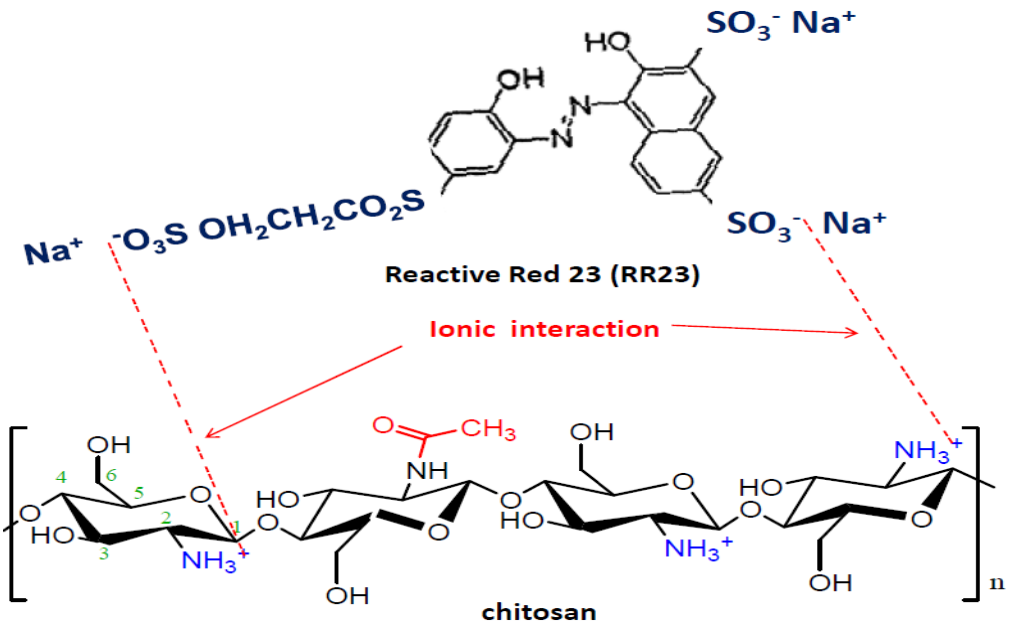

Figure 7: Interaction between Reactive Red 23 and chitosan.

3.8. Kinetics of chitosan adsorption

Figure 8 shows the adsorbed quantity of the dye by the chitosan according to the time of contact at 26°C.The adsorption increases linearly to about 180 minutes, and thereafter tends to the corresponding saturation level, 38 mg/g.

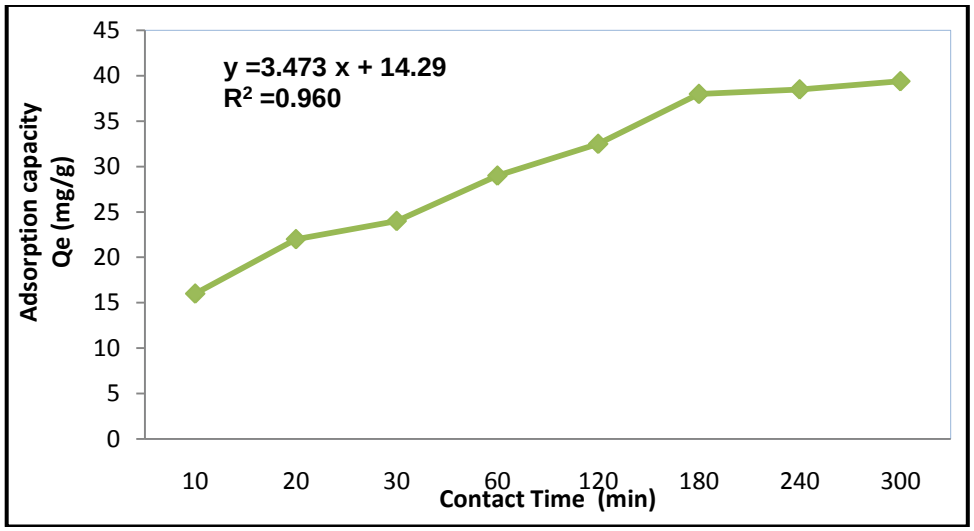

Figure 8: Kinetics of chitosan adsorption for the dye "Reactive Red23" into chitosan.
(C_0 = 150 mg/l, m(chitosan) =200 mg, Temperature =26 ° C and the contact time: between 30 and 360min).

3.9. Effect of the initial concentration of Reactive Red 23 on the adsorption capacity

The shape of the curve in the Fig.9 shows that there is a strong increase in the quantity of the dye adsorbed on the chitosan according to the concentration of the dye until reaching a bearing, beyond adsorption becomes constant. This can be explained by the fact why starting from a certain quantity of the fixed dye, the sites of adsorption of the dye will be saturated. It is noted that the optimal concentration of the dye is obtained that starting from the bearing, the latter is equal to 150 mg/l.

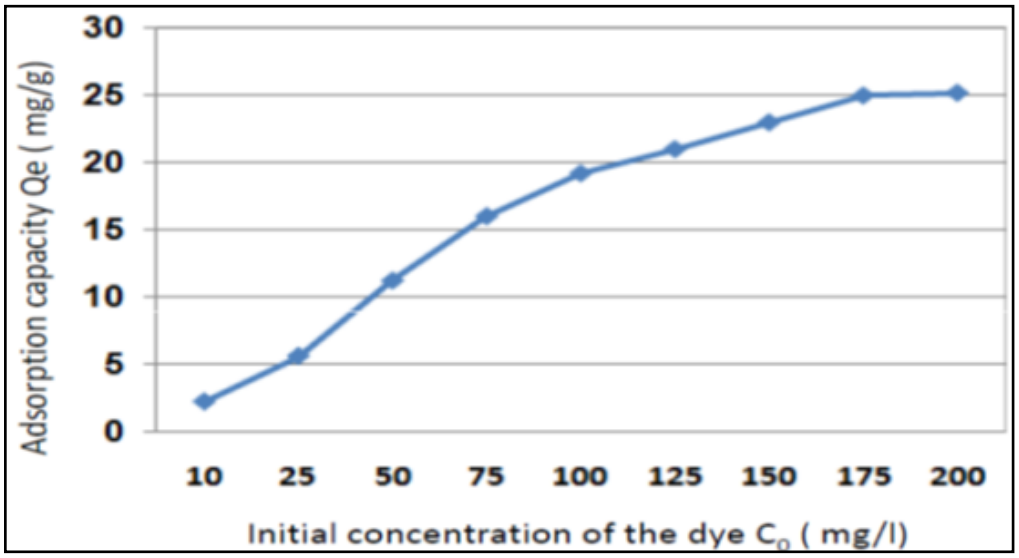

Figure 9: Effect of the initial concentration of the dye "Reactive red 23".
(Temperature = 24 ° C, m(chitosan) = 200mg, 10 <C_0<200 mg / l, Agitation 150 rpm, Contact time : 90min)

The application of the model of Langmuir (8) corresponding to the following relation:

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{b\,Qm} \qquad (8)$$

The model has ends on a line with a first-order equation affirming that the mechanism of adsorption concerned in these experiments is described in a satisfactory way by this model affirming the formation of a molecular monolayer (figure 10).

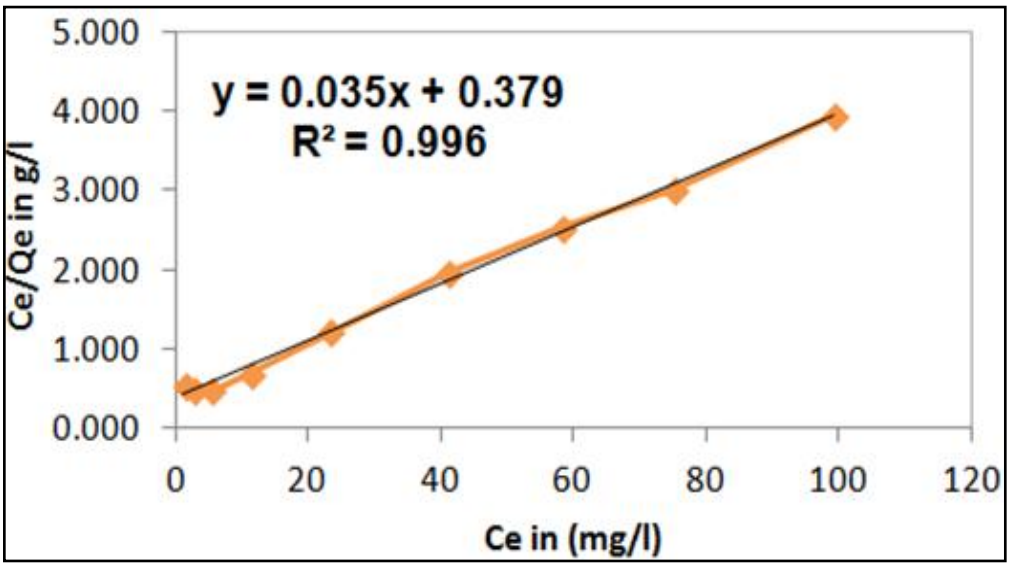

Figure 10: Application of the model of Langmuir in the adsorption of the "Reactive red 23"
(Temperature = 24 ° C, Contact time: 90min, m(chitosan) = 200mg, 10 <C_0<200 mg / l, Agitation 150 rpm)

According to the curve Q_m= 28.57 mg/g and b= 0.09. Thus the maximum quantity to adsorb is of 28.57 mg/g.

Conclusion

The main aim of our work was, at the origin, to develop co-products of prawns resulting from the factories of dehusking. One of the ways of valorization which is very interesting is the extraction of the chitosan, a biopolymer which has a broad spectrum of use. Thus we used this product in the field of the depollution of the industrial effluents in charge of toxic substances such as the dyes. The valorization of co-produts of Nordic prawns "*Pandalus borealis*" by extraction of the chitosan according to the hydrothermo-chemical technique suggested in two stages makes it possible to decrease the time of production of at least four times compared to the classical technique in three stages (three to four days). It is of the interest to be simpler and surer. Moreover it makes it possible to produce a chitosan with a better yield and a high degree of deacetylation (between 60% and 85%).

The study of the adsorption of Reactive Red 23 on the chitosan prepared give very encouraging results such as a better capacity of adsorption for a weak time of balance. The process of adsorption according to the isotherm obtained presents a good correlation with the model of Langmuir affirming the formation of a monolayer. Finally starting from the got results, we can recommend that the chitosan could be used like a good adsorbing in the discoloration of the industrial effluents. It shows better characteristics compared to the usual adsorbents, in particular for the anion, reactive dyes and for heavy metals.

From the point of view of safeguarding of the environment and to as well carry out an industrial ecology for the valorization of the industrial waste as well for the adsorption of dyes resulting from the textile industry and in order to increase by advantage its capacity of adsorption and to reduce the costs of exploitation, it seems important to associate it in composites or nanocomposites with other adsorbents what is programmed in our studies in progress.

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