

## Study of dechlorination by natural adsorbents (chitin and chitosan)

***El Mostafa Erradi (a), Jaafari Karim(a) , Ayoub Cherrat(b)***

*a E2M-LCCA, Chemistry Department, Faculty of Sciences, Chouaib Doukkali University, BP. 20, 24000, El Jadida, Morocco*

*b Laboratory of Physical Chemistry of Materials (LPCM), Faculty of Sciences, Chouaib Doukkali University, BP. 20, 24000, El Jadida, Morocco*

### Abstract

This study aim to the preparation of three adsorbent natural materials: crude chitin, chitin and chitosan extracted from shellfish, to study the elimination of Chlorides from a synthetic effluent. The process of adsorption of chlorides on these supports is described following the linearized method of the model described by Freundlich and Langmuir. The study of the influence of some physico-chemical parameters on the dechlorination process has been undertaken. And in order to approach the conditions of water dechlorination, we were also interested in the study of the influence of the presence of the counter-ions on the ability to remove chloride ions on chitosan. Moreover, we looked for the optimal conditions of desorption using a basic solution.

\* Corresponding author:

[elmostafa.bfss@hotmail.com](mailto:elmostafa.bfss@hotmail.com)

Received, 11 July 2021

Revised, 02 May 2022

Accepted 23 May 2022

**Keywords:** *crude chitin ; chitin ; chitosan*

## 1. Introduction

Chitin and chitosan are two biopolymers produced by some animals. Therefore they are biodegradable and bioresorbable, two essential properties in our time when the protection of the environment plays an important role. Chitosan has attracted more interest than chitin, because of the larger number of amine groups present on its chain [1-2]. The first applications have been developed in the fields where chitosan presented a notable interest, particularly in pharmacology, cosmetology, medicine and especially in water treatment [3-4]. Chlorides are naturally present in groundwater and rivers, at the rate of a few milligrams per liter or grams per liter for brackish water. This work contains two main parts:

The first part is mainly reserved for:

- Putting into practice the method of preparing gross chitin, chitin and chitosan
- Optimization of dechlorination conditions (elimination of chlorides) for each support.
- The determination of the adsorption capacities of the three supports.
- The second part is devoted to:
- To study the effect of the presence of counter ions, which are generally present, in different proportions, in natural waters ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{F}^-$ ), on the ability to remove chlorides from a synthetic effluent by adsorption on chitosan.
- Determine the optimal conditions of desorption of chitosan

## 2. Materials and methods

### 2.1 Preparation of adsorbents

#### • Gross Chitin

The shrimp waste containing the soft part, the head and the shell were washed with distilled water, and then are putted in an oven at 50 °C until total dry. Thereafter, they are crushed and washed several times with distilled water until neutrality. After filtration, they are returned to the oven at 50 °C for drying and storage. We must try at 50 °C in order not to modify the structure of the organic fraction of the waste and this until obtaining a constant mass [5].

#### Chitin.

Chitin is a copolymer made up of repetition units D-glucosamine and N-acetyl D-glucosamine linked  $\beta$ -(1 $\rightarrow$ 4), whose chemical structure is shown in Figure 1. It is Prepared following the method previously used by K. Ryachi[5]: the crustacean waste was firstly crushed, to have an uniform particle sizes ( $\phi < 710\mu\text{m}$ ), then they were soaked in a 3% sodium hydroxide bath maintained at 50 °C to remove the remaining proteins, and in another bath of hydrochloric acid (1.25 M) at 20°C to remove calcium or phosphate salts that cause shell hardness.

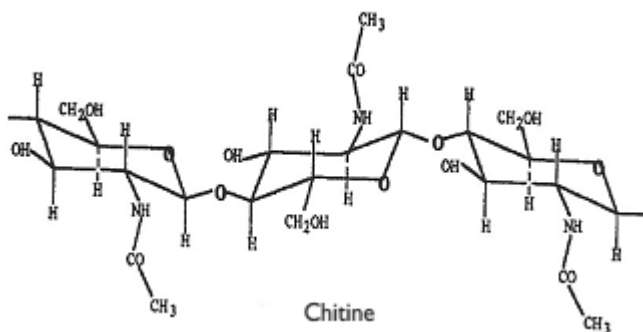
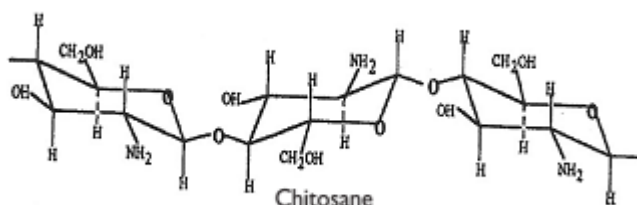


Figure 1: Chemical structure of Chitin

- **Chitosan**

Chitosan, the deacetylated derivative of chitin, is a linear  $\beta$ - (1  $\rightarrow$  4) copolymer of N-acetyl D-glucosamines and D-glucosamines as shown in Figure 2. It is obtained after deacetylation of Chitin. Deacetylation is a delicate step, which is made by using basic hydrolysis steps in aqueous solution. This is the most common method of preparation, which is consisting to soak the chitin already prepared in a 50% NaOH bath at 100 ° C for a period of 4 hours under mechanical agitation [6,7]. At this point, when the product obtained is not white enough or slightly colored, we bleach it for one hour in an acidic hydrogen peroxide bath (HCl/H<sub>2</sub>O<sub>2</sub>: 1/9: V/V)[6,7]. The characterization of adsorbent materials by physico-chemical techniques (XR, IR, ..... ) confirms that we have obtained chitin and chitosan [8],[9].



**Figure 2:** Chemical structure of chitosan

## 2.2 Preparation of the synthetic effluent

The mother solution of each ion ( $\text{CO}_3^{2-}$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  et  $\text{NO}_3^-$ ) was prepared from the mineral substance in its most soluble form ( $\text{Na}_2\text{CO}_3$ ,  $\text{NaF}$ ,  $\text{Na}_2\text{SO}_4$  et  $\text{KNO}_3$ ) (Merck product of 99% purity), and the daughter solutions were obtained by a dilution of the stock solution.

- **Dosing of chlorides**

The dosing of chlorides was carried out using the potentiometric method by measuring the potential difference between a specific and selective to the chloride ion and a reference electrode with a calomel:  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$  saturated at a pH of between 5 and 8, using a pH ionometer Consort model C3030 at temperature, constant total ionic strength of the medium and an ISA solution (Ionic Strength Adjustor). Determination of the chloride ion concentration by direct reading on a calibration curve.

- **PH measurement**

The pH of the solutions was measured using a WTW 522 pH meter with a combined electrode. Before each use, the equipment is calibrated using two Beckman buffers framing the value which will be measured.

- **Technic used for water dechlorination**

The adsorption experiments were carried out in aqueous solution for each support in discontinuous. We introduce in beakers containing the synthetic effluents to be treated, known quantities of each adsorbent according to the parameter under consideration. As previously reported, the particles size of the adsorbent is less than  $710\mu\text{m}$ . the pH is adjusted to 0.1 unit using solutions of NaOH (0.5 M) or  $\text{CH}_3\text{COOH}$  (0.5 M). The assembly is subjected to mechanical stirring and samples were taken as a function of time, the samples were filtered using a membrane with a porosity of  $0.45\mu\text{m}$ , then stored in a refrigerator at 4 ° C in polyethylene bottles. The analysis were carried out within 24 hours.

### 3. Results and discussions

#### 3.1 Calibration curve of chloride

The table below represents respectively the values of the potentials read according to the chloride ion concentration for the various dilutions and slopes of the curve.

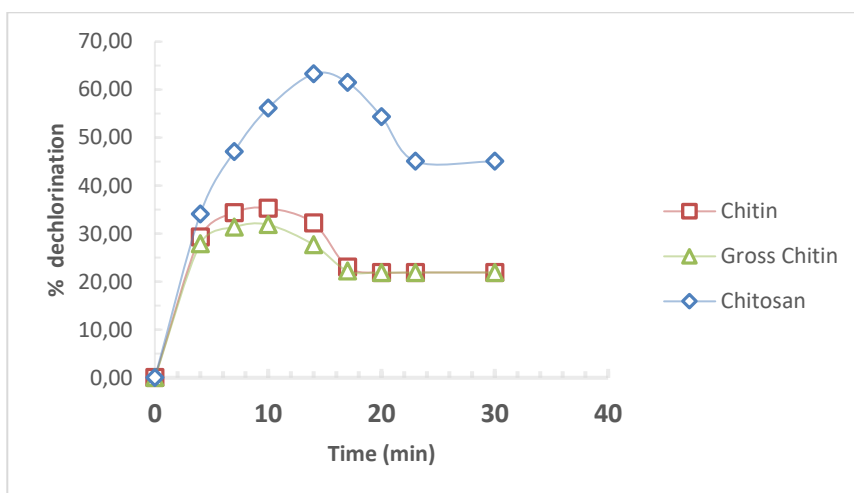
**Table 1:** Potentials Measured according to the Chloride Concentration

	standard	standard	standard	Concentration	Concentration	Temperature	slope	slope
	1	2	3	à 0 mV	à 0 mV	°C	Δ E (1-2)	Δ E (2-3)
				(slope 1-2)	(slope 2-3)		mV	mV
[Cl <sup>-</sup> ] mg/l	10	100	1000	9,89*10 <sup>-3</sup> g/l	9,53*10 <sup>-3</sup> g/l	20	-57,2	-56,4
[Cl <sup>-</sup> ] mV	0	-58	-114					

Depending on the range of concentrations of the samples to be analyzed, prepared extemporaneously, by dilution of the chloride ion stock solution to several calibration solutions (10-2, 10-1 and 1g / l). In a beaker made of plastic material (polyethylene), containing the magnetic bar, we introduce Vml of calibration solution and V ml of buffer solution. Place the beaker on the agitator, immerse the electrodes and start agitation. Ensure that no air bubbles are interposed between the membrane of the electrode and the solution. After stirring for at least 3 minutes or until the electrode stabilizes, read the potential in millivolts. The stabilization time of the electrode is variable according to its state, its age and the concentration of the analyzed solutions. Between each measurement, rinse the electrode with distilled water and drain. On the abscissa, report the millivolt potentials and in the ordinate the concentrations, in milligrams per liter, of chloride ion. Establish the calibration curve from the obtained points. The slope of the calibration curve varies with the temperature of about 1 mV at 5 ° C. For example, it is theoretically – 56.15 mV at 20 °C, de – 59.15mV at 25 °C and – 60,15 mV at 30 °C. This value should be about 59 mV for Cl more negative, this means that the difference between E 1 and E 10 ie  $\Delta E = E_1 - E_{10}$  is in the range 54 mV to 60 mV at 20° C. It is therefore necessary to check that the temperature remains constant during the determination of standard solutions and samples. Moreover, the agitation must be identical for the standards and for the samples.

#### 3.2 Kinetics of adsorption

The chlorinated waters were stirred in the presence of each support and figure 3 shows the evolution of the chloride elimination as a function of time for the three supports. We observed that the kinetics is very fast for the three adsorbents. Indeed, the equilibrium time for Chitosan is of the order of 14 minutes and does not exceed 10 minutes for gross Chitin and Chitin. This kinetics is very fast in comparison with other works concerning the adsorption of pollutants on mineral surfaces which require a very long equilibrium time, sometimes reaching at fifty days [10, 11]. This is probably due to the involvement of the organic fraction and the residual mineral fraction in the adsorbent materials. Jaafari[12] who studied the adsorption of nitrates on Chitosan and Boukhelifi [13] who studied the adsorption of heavy metals on gross Chitin, mentioned an equilibrium time comparable to ours. We also note that there is partial desorption of chloride ions for the three supports. This is probably due to the dissociation of the weak bond formed between the contaminant and the ligand, under the effect of stirring.

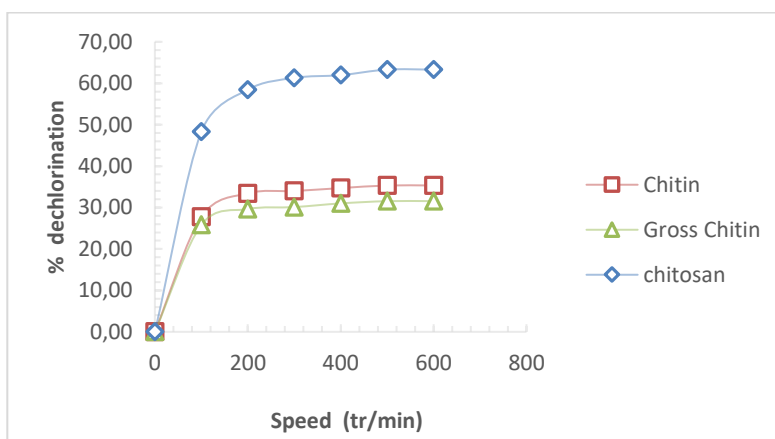


**Figure 3:** Adsorption kinetics ( $m=4$  g/l,  $[Cl^-]_0 = 190$  mg /l and  $T = 20^\circ\text{C}$  and  $\text{pH} = 6.8$   $V=500$  rpm)

### 3.3 Determination of optimal adsorption conditions

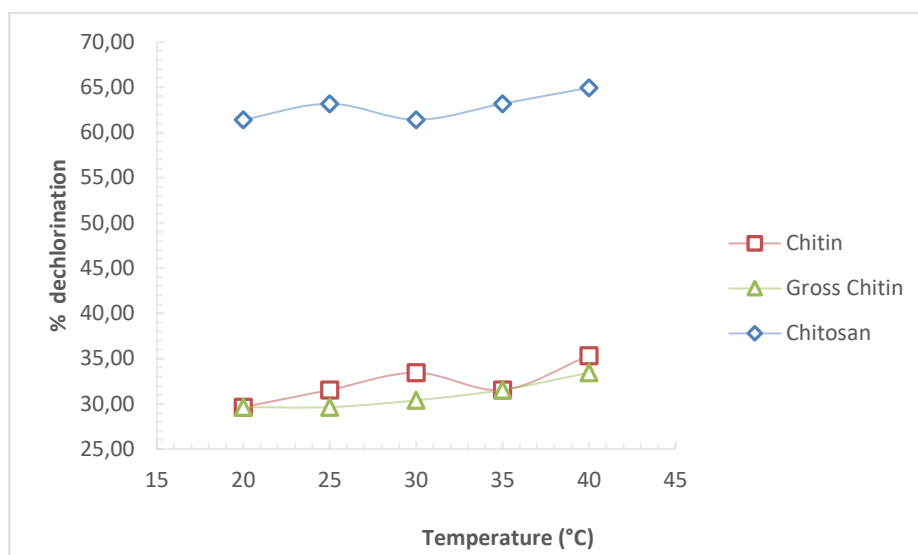
- **Effect of agitation speed on adsorption of chlorides by the adsorbents**

The evolution of the percentage of dechlorination as a function of the stirring speed (figure 4) shows that the optimum stirring speed for the three supports is reached starting at 500 rpm. This is due to the good dispersion of the supports in the solutions to be treated.



**Figure 4:** Stirring effect on the adsorption capacity ( $[Cl^-]_0 = 190$  mg/l,  $m = 4$  g/l,  $T = 20^\circ\text{C}$  and  $\text{pH} = 6.5$ )

After a 14 minutes contact time for Chitosan and 10 minutes for Chitin, samples are taken, and the adsorbed concentration (ie) is deduced from the difference between the initial concentration ( $C_0$ ) and the residual concentration in the aqueous phase ( $C_r$ ). The variation of the stirring speed changes the adsorption capacity. The augmentation of the stirring speed increases the turbulence within the solution and destroys the thickness of the film surrounding the adsorbent particles. So the adsorption phenomenon is therefore limited by the solid liquid transfer, because the stirring speed affects the adsorption capacity. Similar results have been obtained during the adsorption of Uranium and Vanadium on Chitosan and its derivatives in the work realized by Saucado and coll. And Guibal and coll[14,15]. Similarly McKay and coll[16] and Findon and coll[17] showed that the adsorption of Copper and Mercury on Chitosan is highly dependent on agitation.



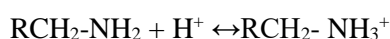
**Figure 5:** Effect of temperature on the adsorption capacity ( $[Cl^-]_0 = 190 \text{ mg / l}$ ,  $m = 4 \text{ g / l}$ ,  $V = 500 \text{ rpm}$  and  $pH = 6.5$ )

#### • Effect of the temperature

Following figure 5, we deduced that in the temperature range tested, the phenomenon of chloride adsorption for the three supports used is insensitive to the temperature and that Chitosan always remains the most efficient compared to Chitin and the gross Chitin.

#### • The Influence of the initial pH

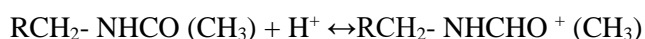
The tests were carried out by varying the pH from the value 2 to 9. Results representing the retention rates of the chloride ions on each adsorbent are illustrated in figure 6. It can be deduced from this curve that the adsorption occurs over the entire pH range, reaches a maximum for a pH of about 6.5 for all the supports. In 1998 Jaafari and coll[18] found similar results with commercial supports. The percentage of elimination decreases on both sides of this interval, which can be explained : For the case of Chitosan, in acidic medium, the amine functions hydrolyze spontaneously according to the following reaction :



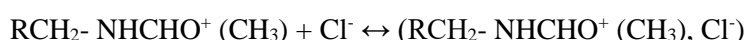
The elimination of Chlorides is made afterwards according to the following reaction :



For the case of Chitin, in acidic medium, there is protonation according to the following reaction :



The reaction between the adsorbent and the chloride ions is an acid-base reaction:



In a strongly acidic or strongly alkaline medium, the  $OH^-$  and  $H^+$  ions attack other sites of the organic molecule and other reactions are involved. This causes a major transformation of the prepared products and the dissolution of the responsible calcic phase responsible of the fixation of pollutants. We can add to this the partial solubilisation of chitosan in strongly acidic medium [19].

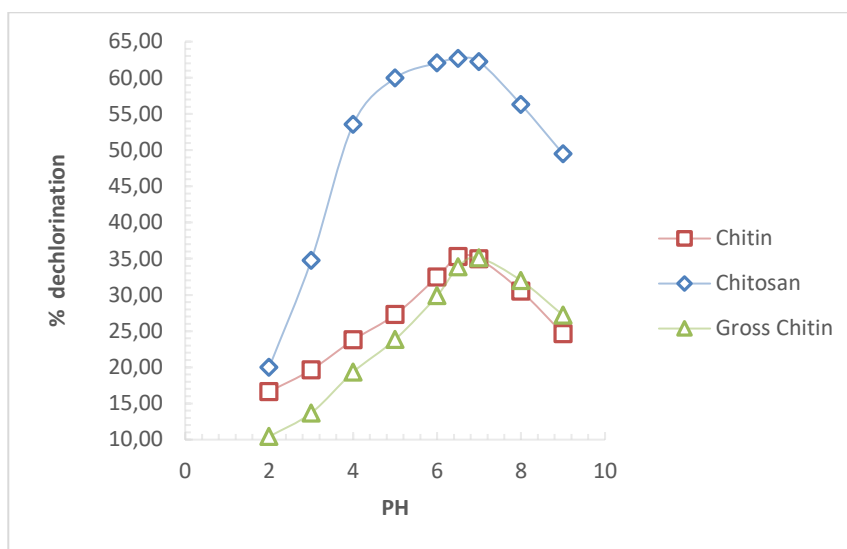


Figure 6: Effect of pH on the adsorption capacity ( $[Cl^-]_0 = 220 \text{ mg/l}$ ,  $m = 4.5 \text{ g/l}$  and  $T = 20^\circ \text{C}$ )

#### • Effect of the mass

The evolution of the percentage of chlorides elimination as a function of time for different masses of each adsorbent (figure. 7) shows that mass is one of the most important factors which could limit the adsorption. In fact, the adsorption sites increase with the increase in the mass of the support used until an equilibrium is obtained for a mass of  $4 \text{ g/l}$ .

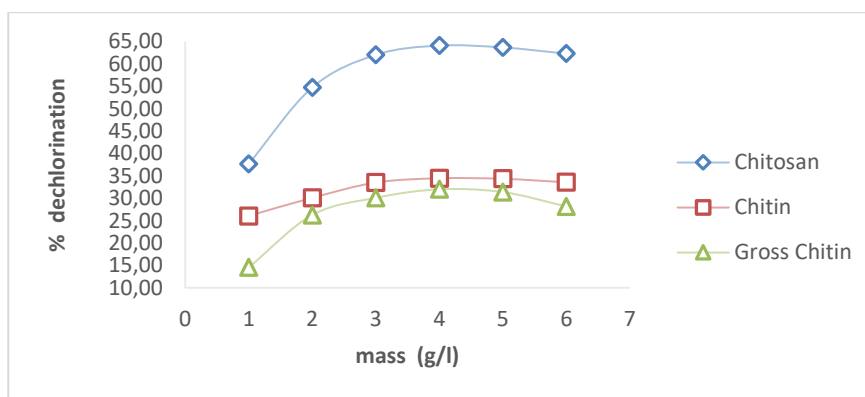
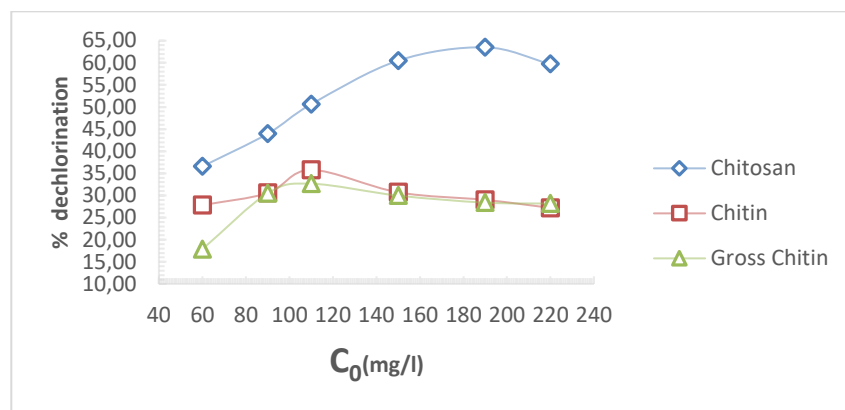


Figure 7: Effect of mass on the adsorption capacity ( $[Cl^-]_0 = 220 \text{ mg/l}$ ,  $V = 500 \text{ rpm}$ ,  $T = 20^\circ \text{C}$  and  $\text{pH} = 6.5$ )

#### • Effect of the concentration

Figure 8 shows the effect of the initial concentration on the adsorption capacity of each support. It shows that the elimination improves when the chloride concentration increases. The maximum adsorption capacity was 32.66, 35.78 and 63.49%, respectively for gross Chitin, Chitin and Chitosan, for a concentration between 110 and 190  $\text{mg/l}$ . We notice that the adsorption of chlorides increases with the increase of the initial dose of Chlorides; this can be explained by favouring the contact of chloride ions with the support. In the case where the optimal concentration is exceeded, we noted a decrease in the adsorption capacity; this is probably due to the effect of the ionic strength of the system [20,21]. Indeed the increase of the initial concentration causes an increase of the ionic strength, which reduces the adsorption through the effect of the coefficient of activity by the formation of a protective layer which prevents the accessibility to

the sites available in the material. This behavior can also be explained by the insufficiency of the active sites compared to the chloride ions. Similar results have been illustrated by Avnimelech [22].



**Figure 8:** Effect of the concentration on the adsorption capacity ( $m = 4.5 \text{ g/l}$ ,  $v = 500 \text{ rpm}$ ,  $T = 20^\circ \text{C}$  and  $\text{pH} = 6.5$ )

### 3.4 Determination of the kinetic constants of adsorption

The kinetics of adsorption is limited by two essential parameters: the chemical kinetics based on the reaction mechanisms involved in the fixation of the contaminant on the adsorbent and the physical kinetics limited by the external diffusion. Indeed, the speed of adsorption can be slowed by the external diffusion of the species through the saturated layer of the adsorbent. The speed of chloride retention on each adsorbate is a key feature in dechlorination efficiency determination. The determination of the order of the reaction was carried out with an initial chloride concentration of  $220 \text{ mg/l}$ , a support mass of  $4.5 \text{ g/l}$  and a stirring speed of  $500 \text{ rpm}$ . La vitesse de l'adsorption des ions  $\text{Cl}^-$  sur les adsorbants, s'écrit : The speed of adsorption of  $\text{Cl}^-$  ions on the adsorbents is written :

$$V_r = -d[\text{Cl}^-]/dt$$

Where  $V_r$  : Apparent adsorption rate of  $[\text{Cl}^-]$  relative to the reaction volume in  $\text{mg/l} \cdot \text{min}$ ; and  $[\text{Cl}^-]$  : Residual concentration of chlorides at time  $t$  in  $\text{mg/l}$ .

In the case of kinetics of order 1:

$V_r = K_{\text{ads}}[\text{Cl}^-]$  which allows us to write:

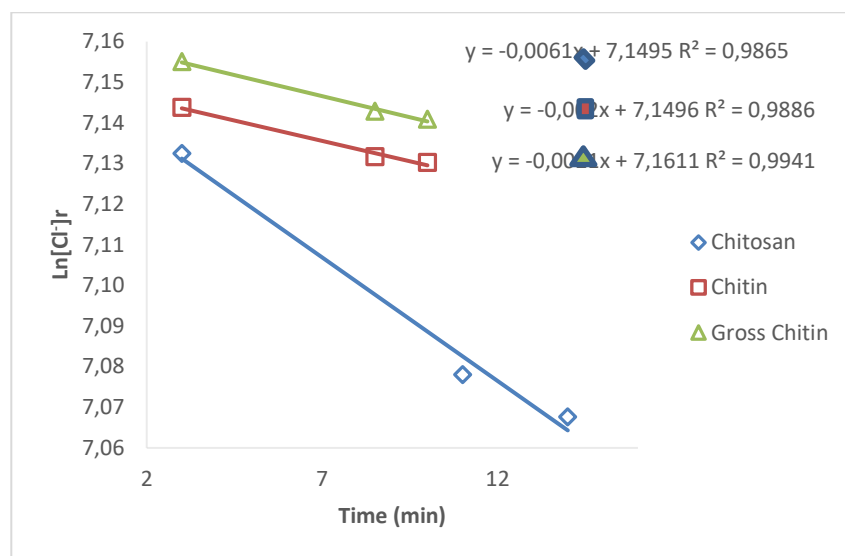
$K_{\text{ads}}[\text{Cl}^-] = -d[\text{Cl}^-]/dt$  where  $K_{\text{ads}}$  is the kinetic constant for order 1 kinetics.

**Table 2:** Kinetic adsorption constants for different supports.

Adsorbent	$C_{\text{ads}}(\text{mm}^{-1})$	Ordered originally	$R^2$
Chitosan	0.0656	5.5891	0.9804
Chitin	0.0175	5.4181	0.9824
Gross Chitin	0.026	5.5206	0.9845

The linearity of the curve representing the equation  $\ln[\text{Cl}^-]_t = f(t)$  shows its validity (Figure 9), and therefore shows that the process is following a first order kinetics. Moreover, it has been verified that the kinetic constant depends of the initial concentration. The values of the speed constant of adsorption  $K_{\text{ad}}$  of chlorides by the adsorbate are calculated from the slope of the straight lines. The results are recorded in Table 2.





**Figure 9:** the order of the adsorption Isotherms reaction of Langmuir and Freundlich

The adsorption capacity of each support depends on the initial chloride concentration in solute and is expressed in adsorbed quantity per unit mass of the adsorbent. The adsorption isotherms are obtained from the linearized equations of Langmuir[23] and Freundlich[24].

Equations of Langmuir

$$(1/q) = (1/q_m) + (1/(q_m b C_e))$$

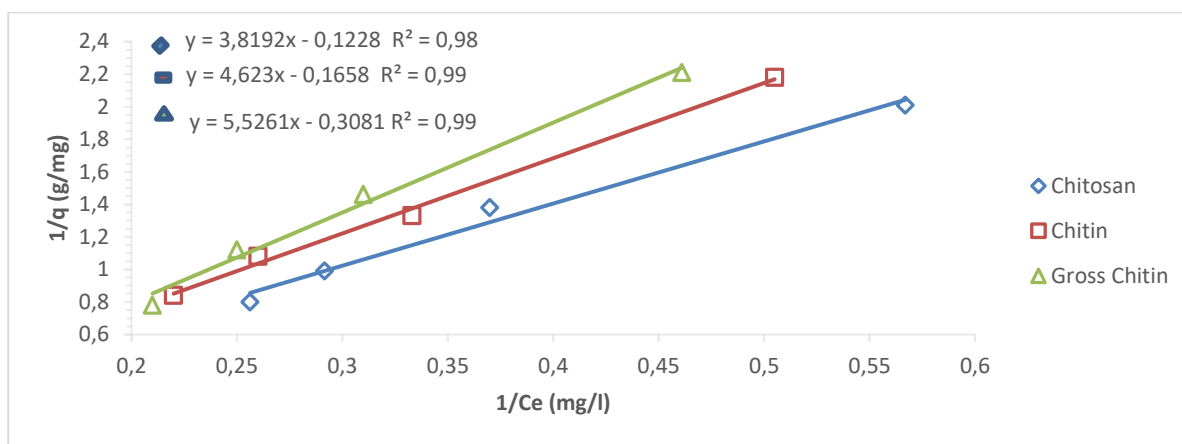
Equation of Freundlich :

$$\text{Log}q = \text{Log}K + (1/n) \text{Log}C_e$$

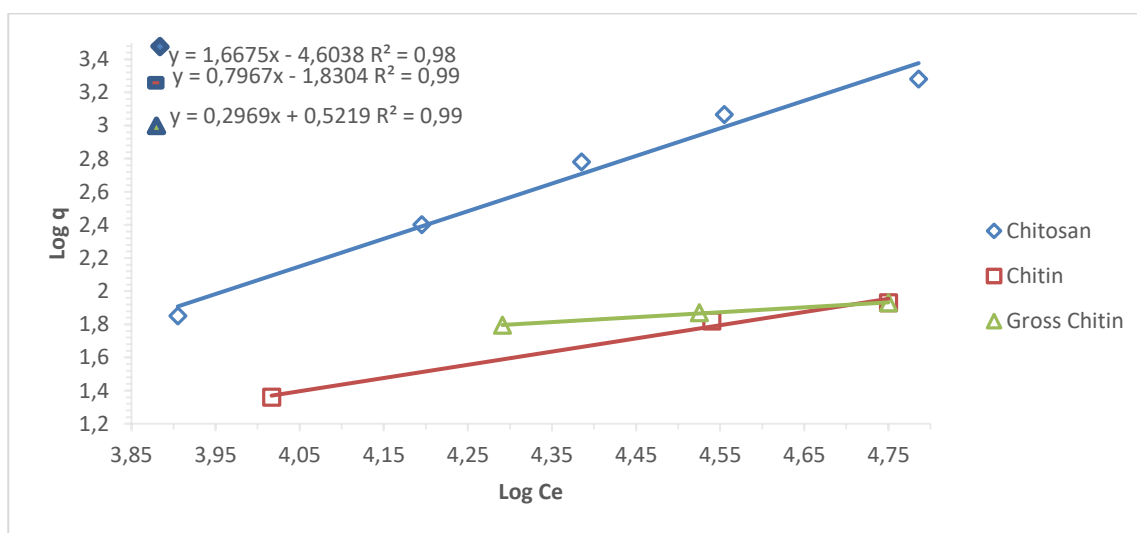
- $q$ : amount of chloride adsorbed at equilibrium (mg / g of adsorbent);
- $C_e$ : equilibrium concentration mg/l;
- $q_m$ : maximum adsorption capacity (mg of Cl⁻/g of adsorbent);
- $b$ : Langmuir constant relative to adsorption energy (l/mg);
- $K$ : Freundlich constant associated with the adsorption capacity (l/g adsorbent);
- $1/n$ : Freundlich constant associated with adsorption affinity.

To determine the maximum capacities and the adsorption equilibrium constants that characterize the couples (adsorbent chlorides), we have exploited the results of the adsorption kinetics represented on a  $1/q = f(1/C_e)$  curve. The straight line obtained has slope of  $1/bq_m$  and ordinate at the origin  $1/q_m$ . This allows the determination of the two equilibrium parameters  $q_m$  and  $b$  of the Langmuir equation. For Freundlich, the curve of the equation mentioned before allows to determine:

- The constant  $K$  which is obtained from the value of the ordinate at the origin.
- The maximum adsorption capacity  $q_m$  obtained by placing  $C_e = C_0$  (initial concentration of the contaminant).
- The slope of the straight line which allows to calculate the constant  $n$ .



**Figure 10:** Langmuir Isotherm for the three supports



**Figure 11:** Freundlich Isotherm for the three supports

The values of the maximum adsorption capacities calculated from the Freundlich and Langmuir isotherms of the three supports confirm the classification found experimentally. It shows that Chitosan is the best adsorbent followed by Chitin and gross Chitin. The Langmuir and Freundlich constants are determined from Figures 10 and 11 and grouped in Table 3.

**Table 3:** Langmuir and Freundlich constants

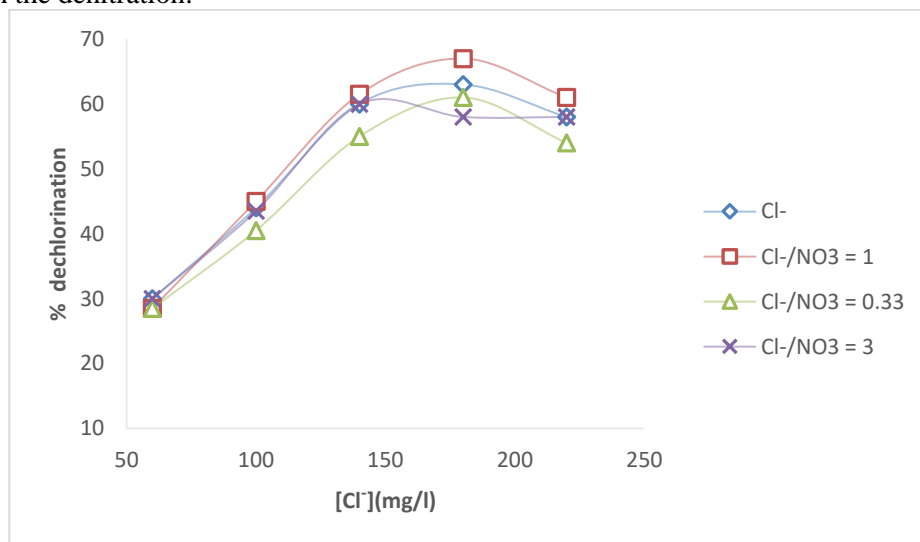
	parameters	Gross Chitin	Chitin	Chitosan
Langmuir	$q_m$ (mg/g)	3.24	6.03	8.14
	$b$ (l/mg)	0.05	0.03	0.03
	$R$	0.99	0.99	0.98
Freundlich	$K$ (l/g)	1.68	6.24	99.86
	$n$	3.37	1.25	0.60
	$q_m$ (mg/g)	6.89	6.89	26.58
	$R$	0.99	0.99	0.98
Experimental values after Fig. 8	$Q_m$ (mg/g)	7.81	7.64	24.35

### 3.5 Effect of the presence of counterions on dechlorination

It is necessary to know if the presence of the counterions has an influence on the adsorption of the chlorides. For this dechlorination tests were carried out on an amount of 5 g/l of Chitosan at a pH of 6.8 with a stirring speed of the order of 500 rpm and a concentration of 190 mg/l of Chlorides.

- **Effect of the presence of nitrate ions**

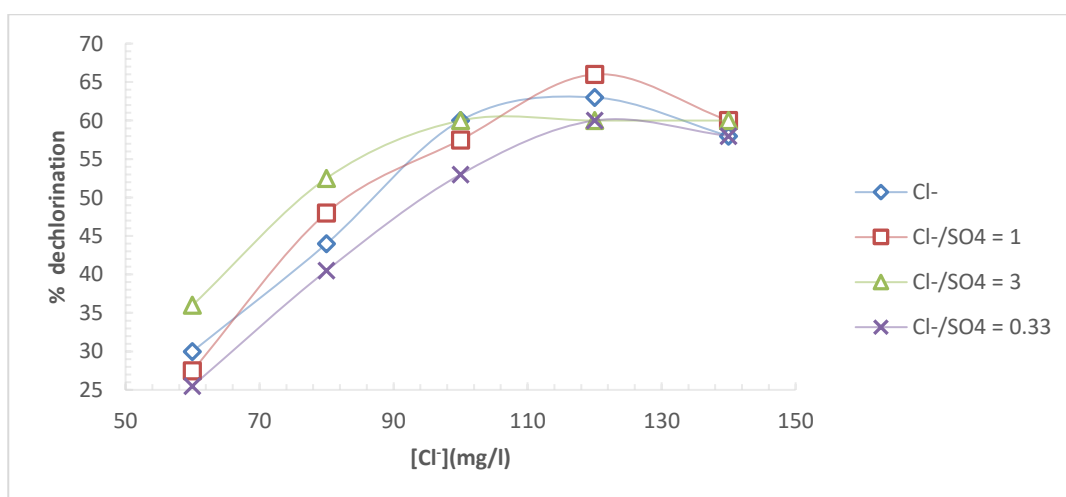
The dechlorination curve in the presence of Chloride ions alone increases with the increase in Chloride concentration to a maximum, reaching 65% at 300 mg/l of Chlorides. We can note that the dechlorination in the presence of  $\text{NO}_3^-$ , for different ratios  $\text{Cl}^- / \text{NO}_3^-$ , has an almost similar evolution, which allows us to say that the chloride ions have no significant effect on the denitration.



**Figure 12:** Effect of the presence of nitrate ions on the adsorption of chlorides

- **Effet de la présence des ions sulfate**

Under the conditions studied, dechlorination in the presence of chlorides alone increases with the increase of their concentration until an optimum of 190 mg /l.

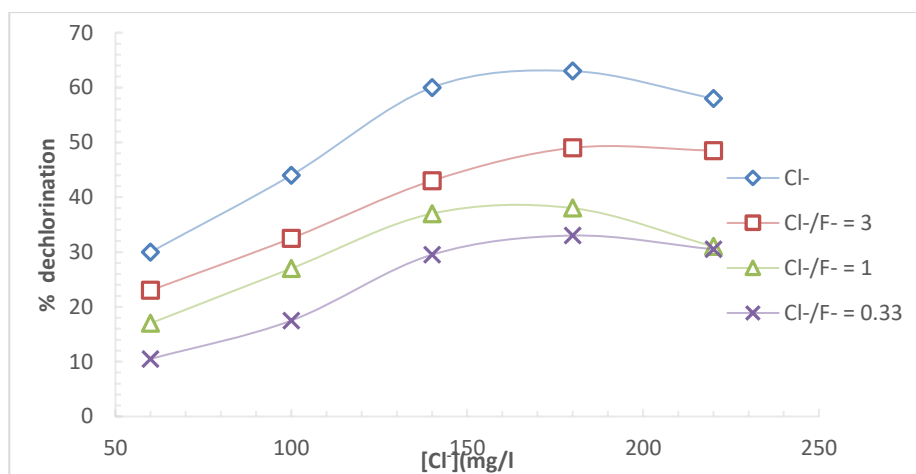


**Figure 13:** Effect of sulfate ions on chloride adsorption

We also notice that after the addition of sulphate ions with different ratios  $\text{Cl}^- / \text{SO}_4^{2-}$  the same rate is obtained as in the presence of chlorides alone, then we can conclude that the sulphate ions have no significant effect on the dechlorination and that the membrane is also selective for sulphates.

- **Effect of the presence of fluoride ions**

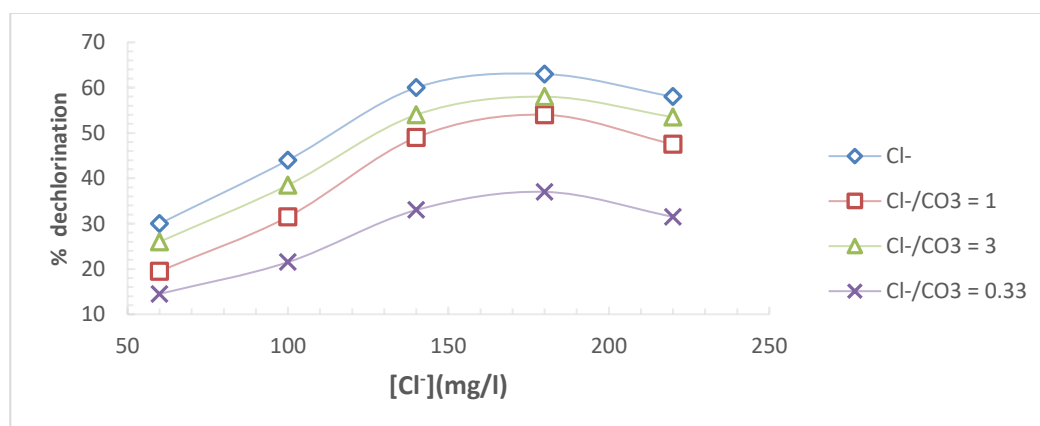
There is a large difference between the dechlorination obtained according to the ratios  $\text{Cl}^- / \text{F}^-$  chosen. The capacity to remove chlorides in the presence of fluorides decreases as the  $\text{Cl}^- / \text{F}^-$  ratio decreases, in other words, dechlorination decreases with increasing fluoride concentration to values much lower than 63%, which means that Chitosan absorbs also fluorides especially at high concentrations. The fluoride ions have a very strong competitiveness vis-a-vis the dechlorination.



**Figure 14:** Effect of fluoride ions on the adsorption of chlorides

- **Effect of the presence of carbonate ions**

By analyzing the dechlorination curves in the presence of the carbonates, we notice that the percentage of elimination decreases when the concentration of carbonates increases. The adsorption of the carbonate ions is then in competition with that of the chloride ions.



**Figure 15:** Effect of carbonate ions on chloride adsorption

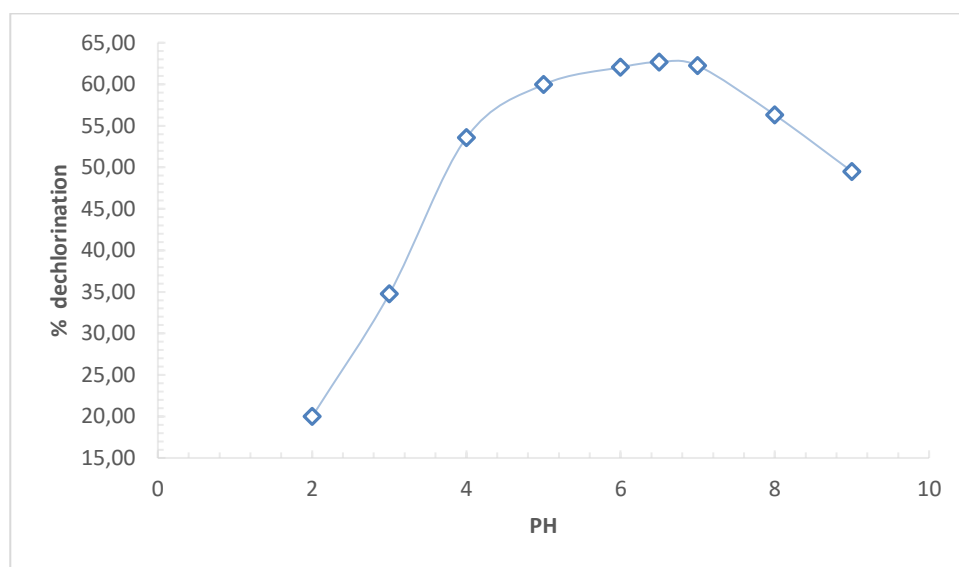
### • Interpretation

Under the conditions studied, the results show that the presence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions does not significantly change the adsorption capacity for the different concentrations of these two ions, in contrary of the  $\text{CO}_3^{2-}$  and  $\text{F}^-$  ions, whose adsorption is competitive with that of chloride ions. These results confirm those obtained by Jaafari[30]. The difference in the selectivity of ions adsorption can be explained by comparing their rays when hydrated. The classification of these rays given by Bernard et Coll in 1996 [25] is as follows:

$$r(\text{SO}_4^{2-} (0.258 \mu\text{m})) > r(\text{Cl}^- (0.177 \mu\text{m})) > r(\text{NO}_3^- (0.169 \mu\text{m})) > r(\text{CO}_3^{2-} (0.156 \mu\text{m})) > r(\text{F}^- (0.126 \mu\text{m})).$$

The selectivity of Chitosan is correlated with the size of the entity to be adsorbed. And we can conclude that the selectivity of Chitosan is based on the important parameter that is the ray of the hydrated ion.

### 3.6 Desorption of the support by the sodium hydroxide



**Figure 16:** Effect of pH on adsorption capacity ( $[\text{Cl}^-]_0 = 190 \text{ mg/l}$ ,  $m = 5 \text{ g/l}$  and  $T = 20^\circ\text{C}$ )

We choose to do the desorption with soda.

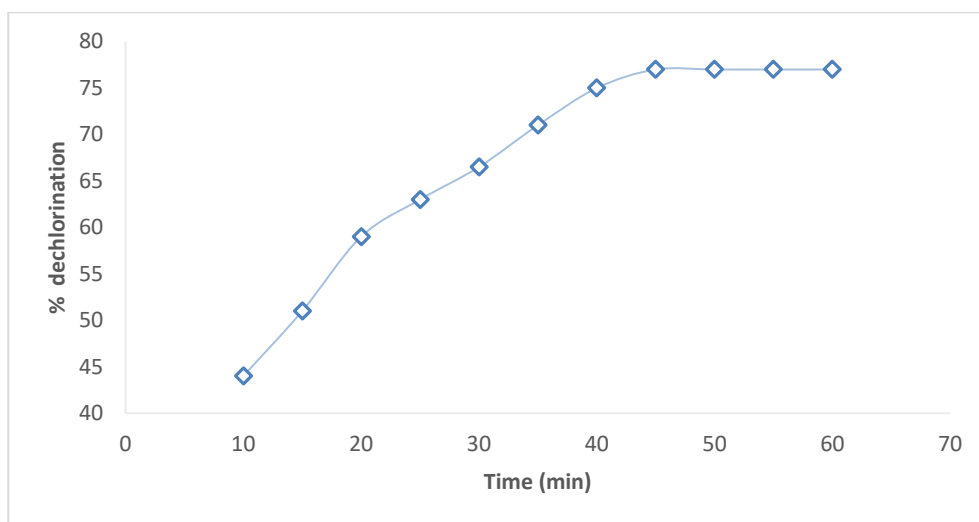
- The desorption tests were carried out on a quantity of Chitosan which was saturated by contact with a water rich in Chlorides (190 mg/l).
- The adsorption is carried out with slightly acidic medium (pH = 6.8 - almost neutral).
- The desorption consists of bringing the nitrate-saturated support carrier into contact with a basic solution for one hour before evaluating the concentration of chlorides desorbed in this solution.

### • Kinetics of desorption

Preliminary tests to determine the minimum time of desorption are made using:

- 10 g of support saturated on chloride;
- 100 ml of the sodium hydroxide solution (4 M);
- stirring at 300 rpm for different durations

This kinetic study shows that desorption is maximal after 45 minutes.

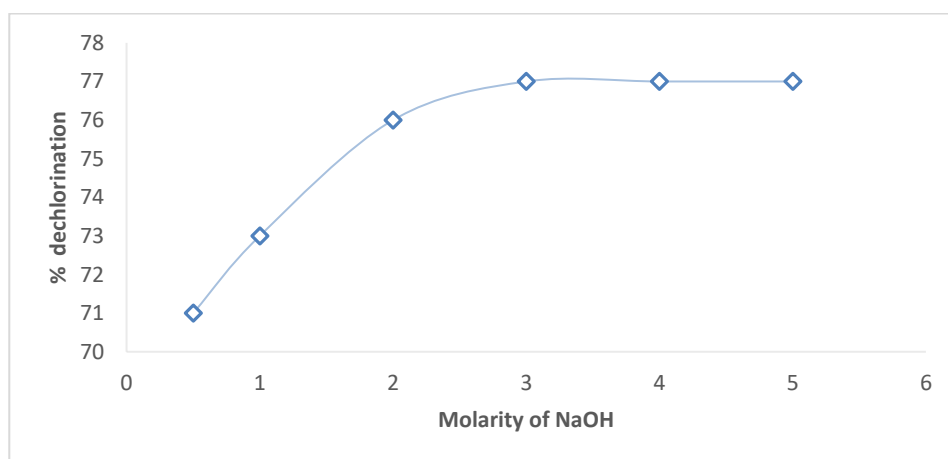


**Figure 17:** Kinetics of chloride desorption on Chitosan

- **Effect of sodium hydroxide concentration on the desorption**

To determine the optimum concentration of sodium hydroxide, the desorption is carried out on:

- 10 g of support saturated of chlorides;
- 100ml of the sodium hydroxide solution at different concentrations;



**Figure18:** Effect of sodium hydroxide concentration on desorption

A stirring at 300 rpm for 60 minutes; In Figure 18, we notice a fast and effective desorption even for low concentrations of NaOH. The maximum desorption (77%) is obtained for concentrations of sodium hydroxide higher than 3 M.

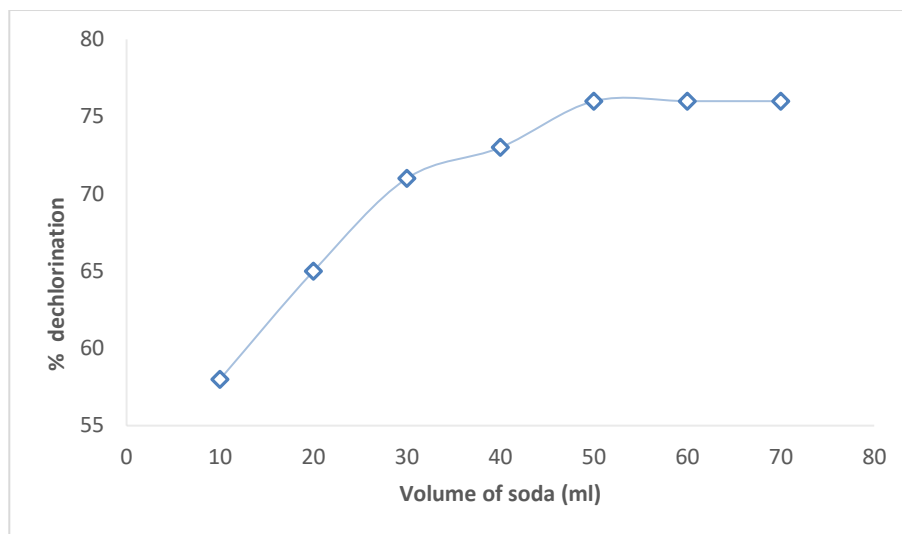
- **Efficiency of desorption for different volumes of sodium hydroxide solution**

In order to know the optimal volume of the sodium hydroxide solution to regenerate 10 grams of the saturated support, we proceed in the same way, using:

- 10 g of support saturated with chlorides;
- A 3M sodium hydroxide solution at different volumes;

- Stirring at 300 rpm for 60 minutes.

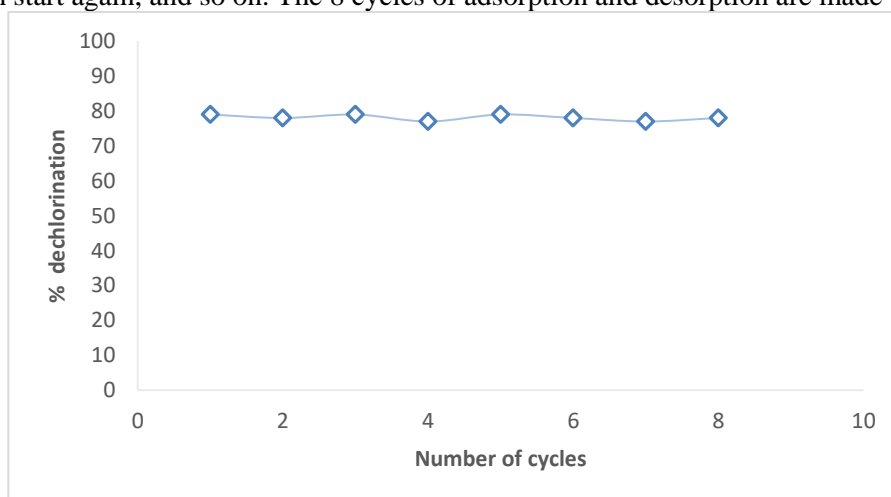
For a mass of 10 g of Chitosan, the maximum desorption efficiency is reached from a volume of 50 ml in 3M sodium hydroxide solution.



**Figure 19:** Efficiency of desorption for different volume of sodium hydroxide (3M)

Adsorption-desorption cycles

10 g of Chitosan are brought into contact with a solution containing 190 mg/l of chlorides, with a stirring speed of 300 rpm and at a pH of 6.8. After filtration and for desorption, the support was putted into a basic solution of 100 ml of NaOH (3 M) at 300 rpm. After the desorption, the pH is readjusted with a solution of  $H_2SO_4$  at pH 6.8 and the next adsorption phase can start again, and so on. The 8 cycles of adsorption and desorption are made on:



**Figure20:** Chloride regeneration rate for 8 adsorption-desorption cycles

- 10 g of chitosan;
- 100 ml of a sodium hydroxide solution (3M);
- Stirring at 300 rpm for 14 minutes for adsorption and 45 minutes for desorption;
- adsorption is carried out at a pH of 6.8.

The chlorides desorption rate from the saturated chitosan by chlorides is substantially constant for the 8 cycles performed (Figure 20).

### 3.7 Discussion

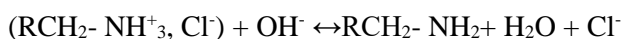
In slightly acidic medium, a protonation of the organic functions present in the structure of chitosan is obtained and the charge of the complex formed is compensated by the fixing of the chlorides according to the following reaction:



The elimination of chlorides is made afterwards according to the following reaction:



The addition of a strong base to the complex formed allows its neutralization and consequently the release of the chlorides according to the following reaction:



### 4. Conclusion

- In the light of this study it appears that the elimination of chlorides by the three supports is characterized by very fast kinetics and that the adsorption process follows a first-order kinetics. The efficiency of the dechlorination depends particularly on the mass of the adsorbent material, the chloride concentration and the pH of the solution. Optimum adsorption is obtained for slightly acidic pH (pH = 6.8 - almost neutral) and at room temperature (20 ° C). The adsorption equilibrium results show that this equilibrium is suitably described by the Freundlich and Langmuir models for gross chitin, chitin and chitosan and the maximum adsorption capacities allowed us to classify the three supports in ascending order: chitosan > chitin > gross chitin. The competitiveness of the counter-ions vis-à-vis to the elimination of chlorides depends on several factors:
- The ray of the hydrated ion considered. Indeed, the classification according to the selectivity follows the following order  $\text{F}^- > \text{CO}_3^{2-} > \text{NO}_3^- > \text{SO}_4^{2-}$  which is the same for the rays of the hydrated ions.
- The amount of counter-ions particularly fluorides and/or carbonates which give more stable complexes than that formed with chlorides. Indeed, the increase in the concentration of the counter-ions makes it possible to shift the equilibrium towards the fixation of the counter-ions and the release of the chlorides.

Chloride desorption from the saturated support is possible and effective with the addition of NaOH. Indeed, the addition of the strong base to the complex formed after the dechlorination allows its neutralization and consequently the release of chlorides.

### References

- [1] Zhang. Jun, Youling. Yuan, Jian.Shen. Sicong., (2003). European Polymer Journal, 39, p. 847-850.
- [2] Kittur. F. S, Prashanth. K, Sankar.Kv., Tharanathan. R. N., (2002).Carbohydr. Polym, 49, p. 185-193.
- [3] Srinivasa P. C, Ramesh M. N,Kumar. K. R, Tharanathan. R. N.,(2004). Journal of Food Engineering, 63,p. 79-85.
- [4] Inger. M. N, Vold. Kjell. M, Varum.Eric. Guibal, Olav. Smidsrd., (2003).Carbohydrate Polymers, 54, p. 471-477.
- [5] Ryachi. K, Bencheikh. A., (1998).Ann. Chim. Sci. Mat, 23, p. 393-396.
- [6] Tolaimate. A, Desbrières. J, Rhazi.M, Alagui. A, Vincendon. M, Vottero.P., (2000). Polymer, 41, p. 2463-2469.
- [7] Tolaimate. A, Desbrieres. J, Rhazi.M, Alagui. A., (2003). Polymer, 44, p.7939-7952.
- [8] Sehchi. M, Masaru. M, Reikichi. I,Susumu. Y., (1983). Journal of appliedPolymer Sciences, 28, p. 1909-1917.
- [9] Liu. X. D, Tokura. S, Haruki. M,Nishi. N, Sakairi. N., (2002).Carbohydrate Polymers, 49, p. 103-108.



- [10] R. N. J. Comans., (1987). Wat.Res., 21 (12). p. 1573-1576.
- [11] Sadiq. M, Zaidi. T. H., (1981).Water Air and Soil Pollution, 16 (3), p.293-299.
- [12] Jaafari. K., (2001). ThèsedeDoctorat d'état Fac. Sc. El-Jadida- Maroc
- [13] Boukhelifi. F., (2001). Thèse de Doctorat. Fac. Sc. El-Jadida- Maroc
- [14] Saucedo-Medina. T. I., (1992).Thèse de Doctorat, Université de Provence Aix-Marseille I, École des Mines d'Alès, France.
- [15] Guibal. E, Saucedo-Medina. T. I,Rossy. J, Roulph. C, Le Cloirec. P., (1993). Water. S. A.19, 2, p. 119-126.
- [16] Mckay. G, Bino. M. J., (1985).Chem. Eng. Res. Des, 63, p. 168-174.
- [17] Findon. A, Mckay. G, H. S. Blair.,(1993). J. Envir. Sci. Health A28 (1), p.173-185.
- [18] Jaafari. K, Elmaleh. S, Coma. J,Benkhouja K, (2001). Water S. A., Vol. 27, No 1, p. 9-13.
- [19] Muzzarelli. R. A. A., (1977).“Chitin”, Pergamon Press, Oxford,New York.
- [20] Guibal. E, Dambies. L, Milot. C,Roussy. J., (1999). Polymer International,48, p. 671–680.
- [21] Guibal. E, Milot. C, Roussy. J.,(2000). Separation ScienceandTechnology, 35, p. 1020–1038.
- [22] Avnimelech. Y, Ravech. A.,(1982). J. Environ. Quality, 11 (1), p. 69-72.
- [23] Langmuir I., (1915). Modelisation of adsorption” Phys. Rev, 6, p. 79-80.
- [24] Freundlich H., (1906). On adsorption in solution. Z. Phys. Chem., 57, p.358-471.
- [25] Bernard. M, Burnot. F., (1996).Usuel de chimie générale et minérale.Dunod, Paris, p. 562

---

(2022) ; <https://revues.imist.ma/index.php/morjchem>