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Sustainable Treatment of Heavy Metals by Adsorption on Raw Chitin/Chitosan

Boukhlifi Fatima

Abstract

The objective of this chapter was to treat metal pollution of wastewater rich in Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} ions by adsorption tests on the raw chitin/chitosan. Different origin namely shrimp (Ccre), crab (Ccra) and lobster (Clan). Raw shrimp chitin had a strong affinity for Pb^{2+} and Cd^{2+} . The adsorption capacity of zinc on the crabs chitin is twice as great as that on the shrimp chitin. The kinetic study showed that more than 50% of these ions are adsorbed before equilibrium is reached (20 minutes). The adsorption kinetics also showed that the hardness of the shells has a negative effect on the kinetics of the adsorption process. Indeed, the adsorption of Pb^{2+} on the raw chitin shrimp requires only 30 minutes, while on the raw chitin lobster; the equilibrium time is 60 minutes. To ensure a sustainable treatment, sludge generated by adsorption of heavy metals was incinerated at high temperature. Incineration has led to calcite phases, which do not represent any toxicity on the environment and it can be recycled in the industry of solid materials (ceramics, cement, etc.). However, the regeneration of sludge by the acid changes the structure of the material and gives new adsorbent supports.

Keywords: raw chitin, adsorption, heavy metals, sustainable treatment

1. Introduction

The adsorption of heavy metals on the differently charged surfaces has been widely studied; on the one hand, mineral surfaces such as oxides, clays, soils, and activated carbons; and on the other hand, organic surfaces and biological surfaces.

Mineral surfaces: the most commonly used adsorbent is activated carbon, which has become a potential absorbent for wastewater [1–5]. Huang [1] studied the adsorption of Cd on activated carbon, which showed that the elimination efficiency increases when the pH increases; Ku [2] studied the coupling between two techniques adsorption on the CA and precipitation by hydroxides, which showed that the percentage of adsorption of Zn (II) increases with pH; and the same study was carried out on Cd, which found that the maximum adsorption of Cd is at pH = 9.5. Saito [6] used CA and sulphonated cottons for the removal of Cu and Cd from wastewater. The percentage of elimination reaches 98%. Most studies done on the CA have been undertaken for water treatment. However, most of the studies carried out on oxide surfaces have been undertaken to assimilate the behavior of heavy metals in the soil or the mechanism of transport and fixation

of metals by these types of surfaces. Swallow [7] studied the adsorption of Cu and Pb on the hydrous ferric oxide, he noted that this support shows a great affinity toward Pb and Cd. Anjana [8] showed that the adsorption of Zn on Fe (III) hydroxide increases with increasing pH. Spark [9] studied the adsorption of heavy metals on oxides and oxyhydroxides, which has shown that this adsorption is very dependent on pH. The study of Cd adsorption on Fe (OH)₂, δ Al₂O₃, and Fe₂O₃ showed that the percentage of removal exceeds 80%. The hydroxide aluminosilicates were used for the adsorption of Zn (II) in alkaline medium [10]. Benjamin [11] studied the adsorption of Cd²⁺ on four oxide surfaces in the presence of certain complexing agents such as SO₄²⁻, Cl⁻, and S₂O₃²⁻, and concluded that the interaction between metal ions and the complexing ligands in the presence of adsorbent surfaces can be divided into three categories based on the origin and the interaction force.

- Metal-ligand complex can form in the solution and weakly adsorb.
- Species can interact indirectly on the surface by altering the electrical properties of the surface.
- Metal-ligand complex can be strongly adsorbed by improving the removal of metals.

With regard to the clays, among the studies carried out, the adsorption of Cd on illite by Comans [12]. Schindler [13] showed that the importance of Cu, Cd, and Pb adsorption on kaolinite increases with increasing pH. Cadena [14] studied the adsorption of Pb on bentonite, which showed that the percentage of adsorption is 35%. There are also comparative adsorption studies between clay and sand, such as the study by El Khatib [15], which found that the amount of adsorbed Pb is very important in the case of clay as in the case of sand. Petersen [16] showed that the percentage of Cu adsorption on kaolinite exceeds 90%. Spark [17] found that the concentration of kaolinite has a small effect on the pH at which the adsorption process of Cd, Zn, Cu, and Co begins. Mrad [18] showed that the adsorption of Cd on montmorillonite is accompanied by a proton departure.

Biological surfaces: the most used adsorbents are active sludge and seaweed; indeed, many studies have been carried out for the removal of heavy metals by biological surfaces. Filip [19] studied the adsorption of Cu and Cd synthetic solutions and the elimination reached was 98% Cu and 100% Cd. Sloan [20] exploited different kinds of algae to eliminate Pb, Cd, Cu, and Zn at different concentrations. Nicolas [21] studied adsorption of heavy metals on active sludge. Roy [22] carried out the adsorption of the heavy metals, Cd, Co, Cr, Pb, Ni, and Zn, on two types of biomass, and found that the green alga *Chlorella minutissima* adsorbs more than 90% of the initial quantity of Pb, while Rice Hulls has an adsorption efficiency of more than 99%. However, Brown [23, 24] showed that the main constituents of active sludge surfaces are polysaccharides and proteins, while the dewaxed sludge mainly consists of lipopolysaccharides and proteins.

Organic surfaces: several studies on the fate of heavy metals in nature have shown that organic surfaces are primarily responsible for the transport, fixation, and distribution of heavy metals in nature. Thus, Lester [25, 26] found that adsorption of metal ions from wastewater is mainly due to organic matter consisting of polysaccharides, nucleic acids, and polypeptides. Among the most important adsorbents are cellulose and polysaccharides. Thus, Irwin [27] showed that wood cedar flours mixed with a base reduce the Cd concentration from 8.7 to 0.4 mg/l of

a synthetic solution with a 95.4% removal rate. Recently, Deans and Dixon [28] carried out a comparative study of the adsorption of heavy metals on several organic surfaces, cellulose, alginic acid, chitin, chitosan, carrageenan, carboxymethyl, hydroxamic acid, terephthalic acid, and its hydroxamic, which showed that the hydroxamic acid is the most effective adsorbent for the removal of metals under different conditions. Among the polysaccharides is chitin, which plays an important role in the transport of heavy metals to sediments [29].

The applications of chitin are diverse and numerous [30], which is used in the treatment of water, for its flocculating properties or for its retention properties of heavy metals. The importance of chitin as an unused resource has increased in recent years, due to its unique structure and numerous properties. Among them is the ability of this chelating polysaccharide, which seems to be the most promising property of chitin. Chitin is prepared in the form of a flocculant for the purification of municipal water [31, 32]. It was exploited in the Cu assay by adsorption-elution on a column [33]. It has also been exploited for the collection of heavy metals in seawater and these metals are then recovered by an appropriate washing of chitin [34]. Muzzarelli [35, 36] and Yang [37] also used chitin for the removal of heavy metals from wastewater and natural waters. Finally, Later Melchor [38, 39] studied the adsorption of Cu, Pb, and Cd on pure chitin extracted from crab shells as a function of pH, temperature, and salinity of the medium, which showed that this adsorption is very efficient and very fast and is not affected by the presence of other metals.

In parallel, it is found that chitin derivatives are used for selective removal of metal ions [35]. Thus chitosan, which is only deacetylated chitin, has been known especially as the most powerful adsorbent of natural origin [40]. Chitosan is very effective for the elimination of uranium [41]. Muzzarelli [42] also studied the elimination of Co and Cu from water using three chitin derivatives: serine glucan, aspartate glucan, and glycine glucan. Kurita [43] showed that chitin derivatives are very effective for the elimination of Cu.

Studies on the raw chitin adsorption are few and concern in general the crude chitin extracted from the mushrooms. Huang [44, 45] tried to eliminate Cd by several species of chitin-rich fungi such as *Aspergillus oryzae*, *Aspergillus clavatus*, and *Candida utilis*, showing an adsorption capacity according to the model of Langmuir, it has also studied the adsorption of Cu, Cd, Zn, and Ni on 12 species of fungi. Boukhelifi et al. [46, 47] studied the elimination of metals ions Zn, Pb, Cu, and Cd by raw chitin from different sources. The affinity of each metal for the adsorbent depends on the source used. A study on the competitive adsorption of metal ions on crude chitin showed that the retention of an ion is strongly influenced by the number and nature of the other ions present in the wastewater [48]. Boukhelifi et al. [49–51] applied the raw chitin shrimp for the treatment of real industrial discharges. Wales [52] also recovered Zn, Pb, Cu, and Cd by chitin/chitosan micro fungi. Until now, the work on the raw chitin from shellfish, which represents 75% of fisheries waste are rare. From then, we were interested in this study to the valuation of gross chitin some crustaceans (shrimp, crabs, and lobsters).

This chapter studied the behavior and adsorbent properties of raw chitin against Cd, Cu, Pb, and Zn metal ions. First of all, we will study the kinetic and isothermal study of the adsorption of metal ions on the raw chitin of different origins namely shrimp (Ccre), lobster (Clan), and crab (Ccra), then the study of series adsorption of metal ions, and finally, the study of sludge recovery generated from treatment by trying to study the regeneration of the adsorbent support by several cations or by incineration.

2. Isothermal study of heavy metals adsorption

2.1 Preparations

2.1.1 Preparation of adsorbent carriers

Our study focused on an economic and abundant adsorbent, the raw chitin. This polymer exists at concentrations ranging between 20% and 50% in the skeletons of arthropods and more than 60% in the skeletons of crabs and shrimp [53, 54]. The studied crustaceans [crabs, lobsters, and shrimps (**Figure 1**)] belong to the phylum of the arthropods, it is the most important branch of the animal kingdom (75%) about 1 million species, are invertebrate animals metazoans, triploblastics, acoelomates, protostomials with metamerized body, bilateral symmetry and heteronome segmentation, covered by a protective epicuticle serving as external skeleton/exoskeleton, rigid but flexible in some places, and very rich in chitin. This richness is relative to each species. The systematics of these crustaceans is summarized **Table 1**.

The selected species, Squinado, Panulirus, and Kerathurus (**Figure 1**) are the most abundant species in Moroccan markets. Their carapaces consist of an external epicuticle followed inward by a pigmented zone, a calcified layer, another noncalcified, and an epidermis.

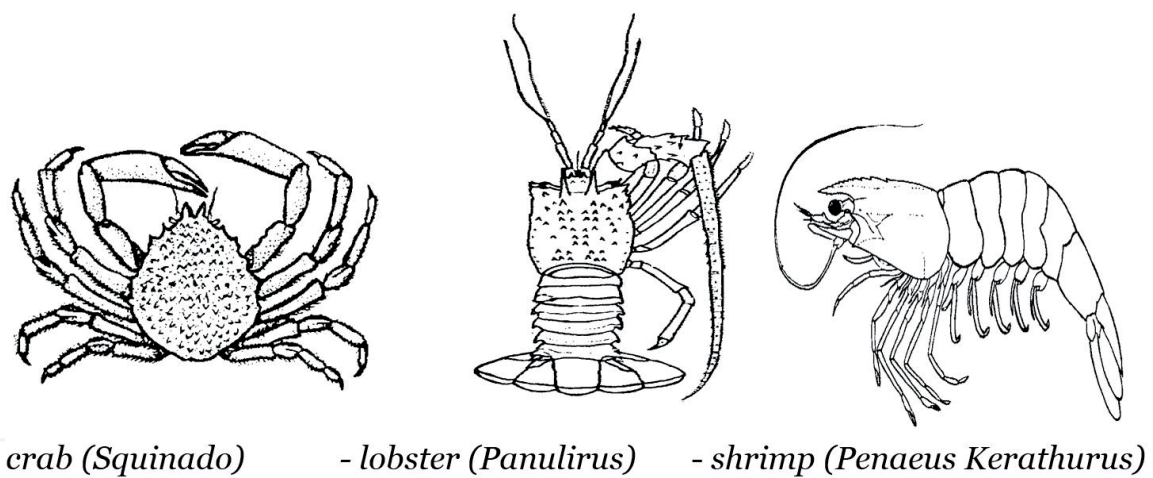


Figure 1.
Crustaceans used in the preparation of raw chitin.

	Crabs	Lobsters	Shrimps
Branch	Arthropods	Arthropods	Arthropods
Class	Shellfish	Shellfish	Shellfish
Superorder	Fucarides	Fucarides	Fucarides
Order	Decapoda	Decapoda	Decapoda
Under order	Reptantia	Reptantia	Natantia
Section	Brachyoures	Macroura	—
Kind	Maia	Palinutus	Pehaens
Cash	Maia (Squinado)	Panulirus	Penaus kerathurus

Table 1.
Systematic crustaceans used for the treatment.

The raw chitin of shrimp origin (Ccre), crab origin (Ccra), and lobster origin (Clan) is extracted from the shells of these crustaceans according to the following mode: the shells are isolated from their soft parts containing the proteins, washed with bidistilled water, dried in an oven at 100°C for 48 hours, and finally they are crushed and sieved at particle size well defined.

2.1.2 Preparation of synthetic wastewater

For each metal, a stock solution of 1 g/l [expressed in (g) metal cations per liter of test solution] was prepared using the metallic substances used in the most soluble mineral form (M^{2+} , $2NO_3^-$) \times H_2O with [M = Zn (x = 6), Pb (x = 0), Cu (x = 3), and Cd (x = 4)]. For each adsorption test, the solution containing the metals to be studied is obtained from the daughter solutions.

2.2 Experimental study of the adsorption phenomenon

Adsorption is a surface phenomenon and to evaluate the adsorption of a compound on an adsorbent, it is necessary to start the following studies:

2.2.1 Adsorption kinetics

The adsorption kinetics was established by stirring for varying periods of time, the M^{2+} solutions introduced into 250 ml Erlenmeyer flasks and added to constant amounts of the adsorbent. After a determined contact time of each suspension, they are filtered; the amount of M^{2+} not removed by the support is subsequently assayed.

2.2.2 Adsorption isotherm

The adsorption mechanism can be described using an adsorption isotherm. An adsorption isotherm is the curve, which represents the variation of the adsorbed quantity “ Q_e ” as a function of the equilibrium concentration “ C_e ” with Eq. (1)

$$Q_e = m_a / m \quad \text{et} \quad m_a = (C_0 - C_e) \cdot V \quad (1)$$

where, C_0 : initial concentration of adsorbate (mg/l); m: mass of adsorbent used (mg); v: volume of the solution (ml); and m_a : mass of retained adsorbate (mg).

The adsorption can be studied, either by examining the decrease of the concentration of the adsorbate in the solution, or by a direct determination of the amount fixed on the solid; the second case requires a washing of the solid in order to remove all the unadsorbed molecules, which can cause destruction in the case of the reversible process, and thus leads to erroneous results, and for these reasons, we opted for the first possibility.

To obtain an adsorption isotherm for a solute on an adsorbent, a constant temperature was used, by mixing a determined quantity of the adsorbent with a solution whose solute concentration is known. After vigorous stirring (500 rpm) and prolonged, the equilibrium time between the solid and liquid phases is determined. The mixture is filtered, and by appropriate dosage, the residual concentration of the solute in the solution is measured. This equilibrium concentration will be noted C_e (mg/l). The amount fixed on the adsorbent is deduced, by difference with the initial concentration. This quantity will be symbolized by Q_e (mg/g): amount of solute adsorbed per unit mass of the adsorbent. The measurement is repeated several times using solutions of different concentrations, which allow us to draw the isothermal curve. The operating conditions are summarized in **Table 2**. The supernatant is filtered and the equilibrium

Concentration of the material	1 g/l
Granulometry	$100\ \mu \leq \Phi \leq \mu\ 125\ m$
Concentration range	10–100 mg/l
Stirring speed	500 rpm
Temperature	$20 \pm 2^{\circ}\text{C}$
Stirring time	Equilibrium time of each metal

Table 2.
Operating conditions of adsorption isotherms.

Metals	Pb ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
Co (mg/l)	100.02	100.05	99.99	99.98
This (mg/l)	99.98	99.97	99.97	99.92

Table 3.
Results of the blank tests.

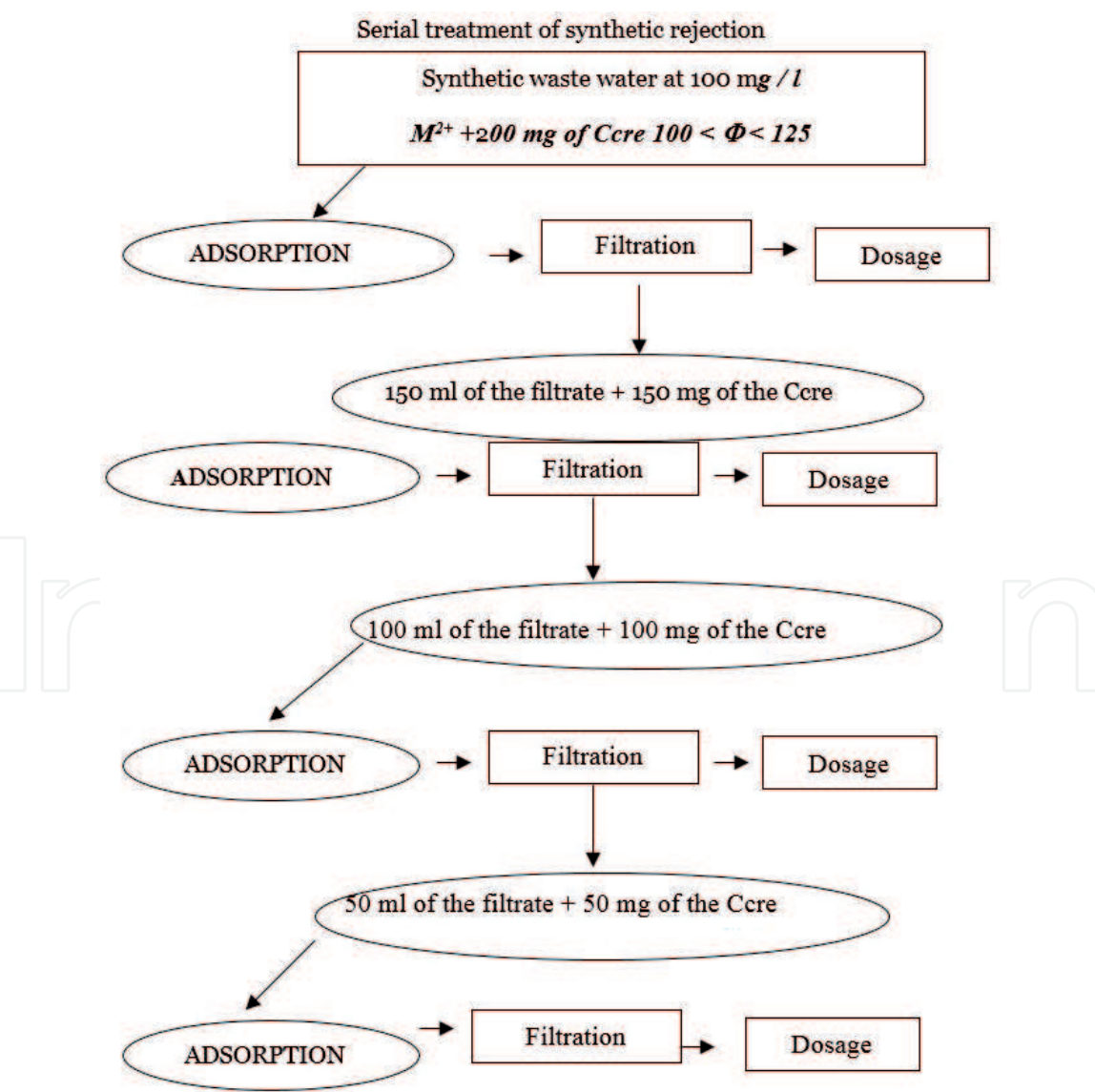


Figure 2.
Serial adsorption process.

concentration C_e is determined by a suitable assay. The precipitates $[M^{2+}/\text{adsorbent}]$ are dried in an oven for 24 hours to be mineralized. The percentage of elimination is calculate according to Eq. (2):

$$\begin{aligned} \text{Percentage of reduction} &= \text{percentage of abatement} \\ &= \text{percentage of elimination} = (C_o - C_e/C_o).100 \quad (2) \end{aligned}$$

Blank tests are carried out by stirring the same adsorbent solution (Cd^{2+} , Pb^{2+} , Cu^{2+} , and Zn^{2+}) at a concentration of 100 mg/l during equilibrium time, and this is filtered. Then dosed to determine the amount of adsorbate retained by the Erlenmeyer flasks and the filter, the results of these tests are grouped in **Table 3**.

According to this table, we can neglect the amount retained by the filter accessories.

2.3 Serial metal ion adsorption test

To demonstrate the effectiveness of the Ccre in retaining the metal ions, we proceeded to a simple treatment using 500 mg of the chitin and a series treatment using amounts of adsorbent whose sum is equal to 500 mg. Starting with an initial concentration of 100 mg/l M^{2+} , after each adsorption test, the measured filtrate is again adsorbed on the material. This operation is repeated four times for four metals according to the following flowchart **Figure 2**.

2.4 Dosage of heavy metals

Depending on the results sought and also to cross-check the information obtained, we used different techniques and equipment:

- Atomic absorption spectrophotometry with flame (cadmium, copper, lead, and zinc) by spectrophotometers VARIAN AA-475, PHILIPS PU-900, PERKIN ELMER 305, and SHIMADZU AA-680.
- Graphite furnace atomic absorption spectrophotometry (lead and cadmium) type SHIMADZU GFA-4B.

Prior to the adsorption experiments of heavy metals, it appeared useful to follow their adsorption kinetics to determine the times required to reach equilibrium.

3. Study of cadmium adsorption

3.1 Kinetic study of the Cd^{2+} adsorption

To determine the time required to reach the Cd^{2+} adsorption equilibrium, we monitored the change in Cd^{2+} concentration as a function of time. The results are shown in **Figure 3**.

This study shows that equilibrium is established rapidly for all adsorbents (**Figure 3**). It reaches its maximum for 30 and 20 minutes, respectively for Ccra and Ccre, while the adsorption kinetics of Cd^{2+} on Clan is relatively slow.

From these curves, it is also found that 50% of Cd^{2+} is adsorbed on the Ccre before the equilibrium reached 20 minutes. The equilibrium times (teq) are

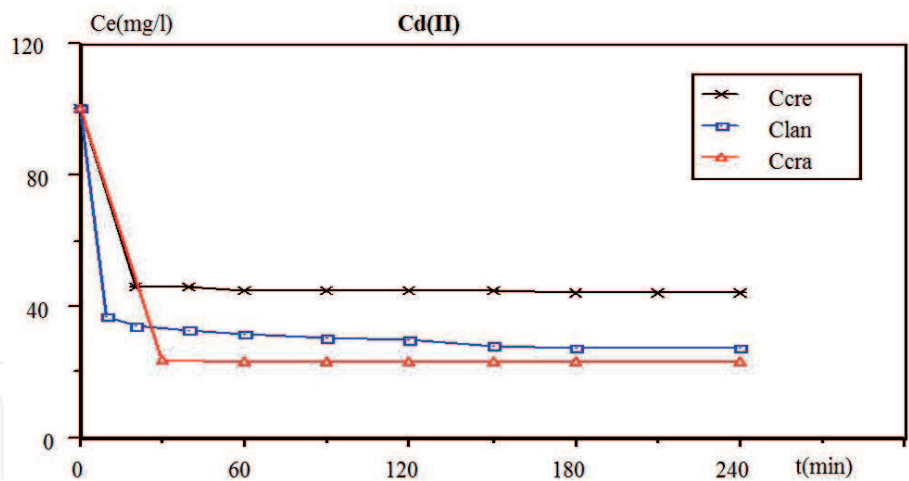


Figure 3.
Kinetic study of Cd (II) adsorption on raw chitin.

classified in the following order: $teq\ Ccre < teq\ Ccra < teq\ Clan$. This kinetics is very fast in comparison with other works cited in the literature concerning the adsorption of Cd^{2+} on mineral surfaces, which require a very large equilibrium time. For example, for the adsorption of Cd^{2+} on the illite, the equilibrium is reached after 54 days [1] and in the case of a natural clay [55, 56], the equilibrium is reached after 50 days. Melchor [39] having studied the adsorption of Cd^{2+} on chitin, mentions a time of equilibrium (40 minutes) comparable to our result.

3.2 Study of Cd^{2+} adsorption isotherms on raw chitin

The curves in **Figure 4a** show the evolution of the adsorption capacity (Q_e) as a function of the equilibrium concentration (C_e) of Cd^{2+} and **Figure 4b** shows the removal efficiency by source of chitin.

When the residual concentration increases, the isotherm of Cd^{2+} on the Ccre deviates from the other two isotherms, which presents two different curvatures. For low concentrations, the slope is steep up to 40 mg/g, which shows that adsorption is important for low concentrations as for high concentrations. Indeed, the increase of the ionic strength of the system reduces the adsorption through the effect of the coefficient of activity. More than 40 mg/g, the curve no longer follows Henry's law. The Cd^{2+} adsorption isotherm on the Ccra is almost straight; Henry's hypothesis (low surface coverage) is true for all the concentrations studied, whereas for the Clan,

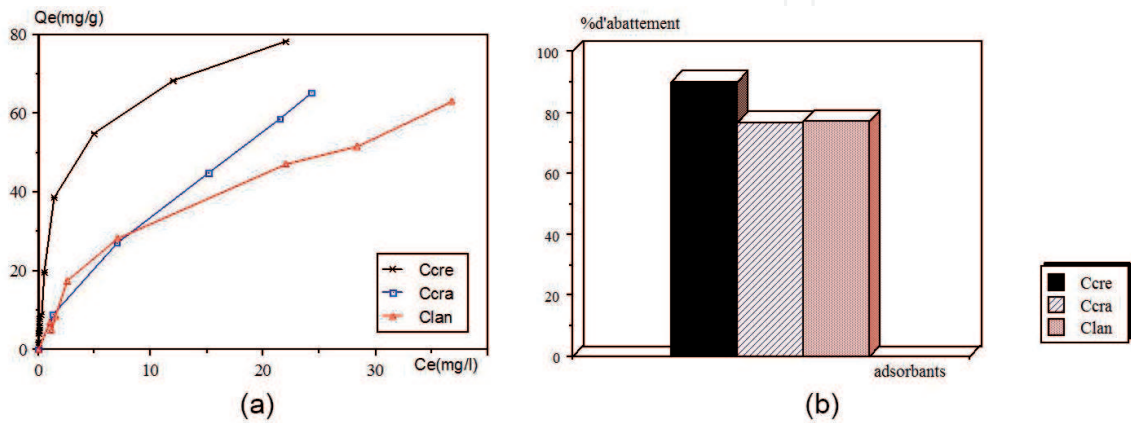


Figure 4.
(a) Experimental isotherms of Cd (II) adsorption on raw chitin, (b) Effect of the origin of raw chitin on the removal efficiency of Cd (II).

	Kf mg/g	1/n	R
Ccre	34.81	0.27	0.98
Ccra	7.38	0.69	0.99
Clan	18.92	0.34	0.97

Table 4.
Values of the Freundlich parameters deduced from the adsorption isotherms of Cd²⁺ on raw chitin.

the isothermal loss loses its linearity above 18 mg/g. For a residual concentration of 22 mg/l, the quantity retained depends on the origin of the raw chitin. Thus, it decreases successively from 78 mg/g for the Ccre to 57 mg/g for the Ccra and 47 mg/g for the Clan. From an initial concentration of Cd²⁺ equal to 100 mg/l, one can reach 22 mg/l after adsorption on the Ccre and 37 mg/l after adsorption on the Clan.

From **Figure 4b**, the percentage of removal of Cd on the Ccre reaches 90%. The selectivity of Cd for three supports is as follows: Ccre > Clan > Ccra.

The modeling of the isotherms in **Table 4** showed that the adsorption of Cd on these different supports perfectly satisfies the Freundlich model **Table 1**. The adsorption capacity of Cd on Ccre is greater than that relative to the Ccra and Clan (**Table 4**). This capacity is comparable to that found by Wales [52] by studying the adsorption of Cd²⁺ on chitin-rich fungi.

In this study **Figure 4b**, we found that the percentage of abatement decreases with increasing concentration. Thus, it varies from 78% for 100 mg/l to 98% for a concentration of 10 mg/l after adsorption on the Ccre.

4. Study of the Cu (II) adsorption

4.1 Kinetic study of Cu (II) adsorption

From **Figure 5**, we observe that the adsorption of Cu²⁺ is very fast initially and quickly reaches equilibrium time, 60 minutes for Ccra and 90 minutes for Clan. We also found that the hardness (mineral part) of the carapaces plays a role in the kinetics of the adsorption process by comparing these results with the equilibrium times found by Melchor [38].

According to Davis [57], the shape of these kinetic curves shows that the adsorption of Cu²⁺ is done according to the following model: Cu²⁺ binds rapidly in one time on the surface and groups co-ordinates very slowly to groups of chitin after scattering inside wall surfaces of the shells. Such adsorption kinetics is also

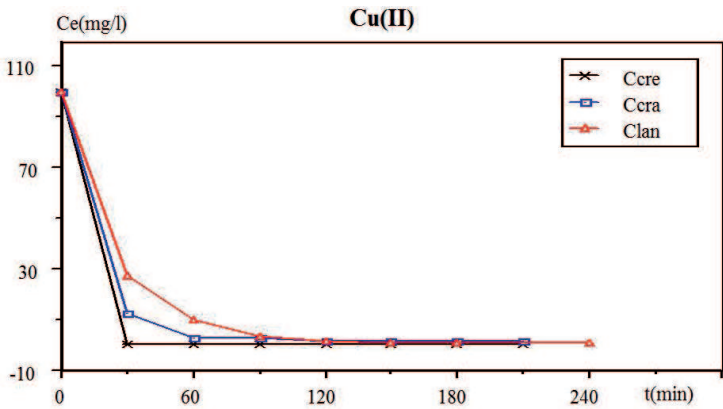


Figure 5.
Kinetic study of Cu (II) adsorption on raw chitin.

observed in the toxicological and physiological effect of copper. A similar behavior of copper retention was observed according to Balistrieri [58] on metal oxide surfaces, according to Fisher [29] on phytoplankton, and according to Xue et al. [59] on the algae.

4.2 Study of the Cu²⁺ isotherms adsorption on the raw chitin

Figure 6a shows the evolution of the adsorption capacity (Qe) expressed in milligrams of metal per gram of material as a function of the residual content (Ce) of Cu²⁺ at equilibrium. The results of calculating the average removal percentages for Cu²⁺ adsorption assays are shown in **Figure 6b**.

Examination of the different isotherms shows that Cu has a high affinity for Clan. For a residual concentration of 1 mg/l, the adsorbed amount reaches 95 mg/g for Clan and 40 mg/g for Ccre. This example proves that the adsorption of Cu²⁺ depends on the origin of the raw chitin.

From **Figure 4b**, it is clear that Cu²⁺ shows a particularly great preference for Clan. The percentage of Cu²⁺ adsorption on Clan varies between 99.07% to 5 mg/l and 93.2% to 100 mg/l, whereas on the Ccre, it varies between 81% to 5 mg/l and 68% at 100 mg/l; this shows that the adsorption of Cu²⁺ on these supports increases when the concentration decreases, and this is in agreement with the study carried out by Okieimen [60], which found that the percentage of CuCl₂ adsorption on the original Arachis Hypogaea cellulose varies between 70% to 200 mg/l and 30% to 500 m/l. Likewise, Elliott [61] having studied the adsorption of Cu²⁺ on Al₂O₃ has argued that an increase in the ionic strength of the adsorbent-adsorbent system reduces the adsorption of Cu²⁺ through the effect of the activity coefficients and the double electric surface layer.

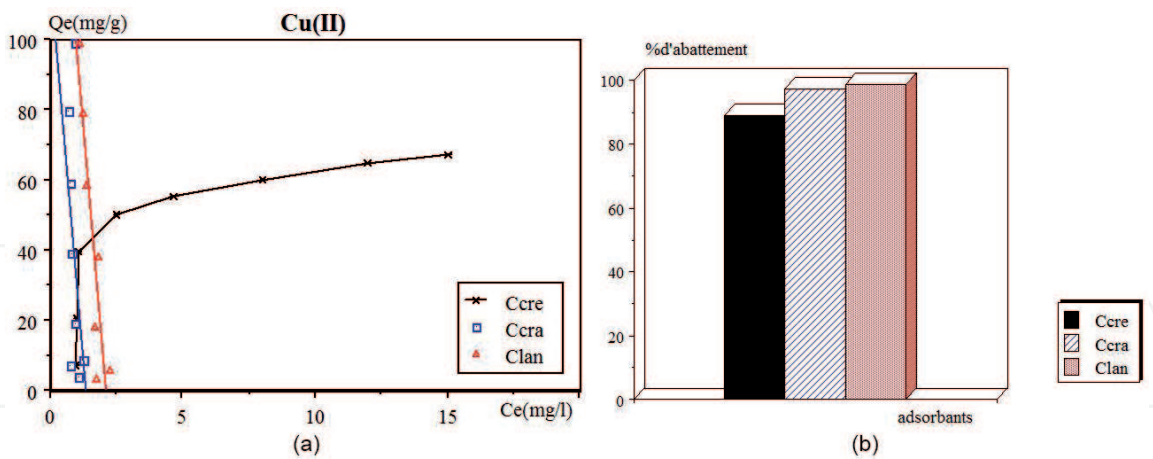


Figure 6.
(a) Experimental Cu (II) adsorption isotherms on the raw chitin, (b) Effect of the origin of the raw chitin on the Cu (II) elimination efficiency.

	Kf mg/g	1/n	R
Ccre	42.25	0.14	1.00
Ccra	17.19	−3.45	0.99
Clan	204.67	−4.58	1.00

Table 5.
Values of Freundlich parameters deduced from Cu²⁺ adsorption isotherms on the raw chitin.

The application of the linearized formula of the Freundlich equation (**Table 5**) in the case of Cu^{2+} adsorption allows us to say that this model is perfectly applicable. Indeed, the correlation coefficients R (**Table 2**) obtained are very satisfactory. Note that the adsorption capacity of Cu^{2+} on Clan is greater than that on Ccre and Ccra (**Table 5**).

Adsorption capacities deduced from Freundlich prove that copper is more adsorbed by Clan.

5. Study of the zinc adsorption

5.1 Kinetic study of the Zn^{2+} adsorption

As with other metals, the kinetic study shows that equilibrium is established rapidly. According to the curves of **Figure 7**, the contact times Ccre- Zn^{2+} , Ccra- Zn^{2+} , and Clan- Zn^{2+} required to reach equilibrium are around 40, 60, and 50 minutes, respectively. The times are very low in comparison with those necessary to reach equilibrium on mineral surfaces such as on the hydroxide of Fe (III), which requires 48 hours [8] and the goethite, which requires 42 days. Indeed, Balistrieri [58] having studied the adsorption of Zn^{2+} and Cd^{2+} on goethite, found that initially, there is a fast adsorption kinetics (a few hours) followed by a very slow diffusion controlling the penetration of the metal.

The tendency of surfaces to fix Zn^{2+} ions decreases with an increase in ion surface charge, since Zn^{2+} binds rapidly early with high affinity to the surface of the materials, and then slowly to with less activity. In addition, the increase in surface charge may induce some electrostatic repulsion. This effect on surface coverage is less pronounced with Cd^{2+} and Cu^{2+} . The same remarks were recorded for the kinetics of Cu^{2+} adsorption on algae [60].

5.2 Study of Zn^{2+} adsorption isotherms on raw chitin

Monitoring the amount of Zn^{2+} adsorbed as a function of the residual concentration (**Figure 8a**) shows that the adsorption phenomenon obeys Henry's law. For Ccra and Clan, isotherms are straight with high slopes. This time, Zn^{2+} is strongly retained by the Ccra than by the Ccre, the concentration decreases from 100 to 1.85 mg/l by adsorption on the Ccra, which proves a particular affinity of the Zn (II) to the Ccra. This affinity is stronger than that exhibited by mineral surfaces such as illite, montmorillonite, and kaolinite [2]. **Figure 8b** shows the calculation of the average removal percentages for six adsorption tests.

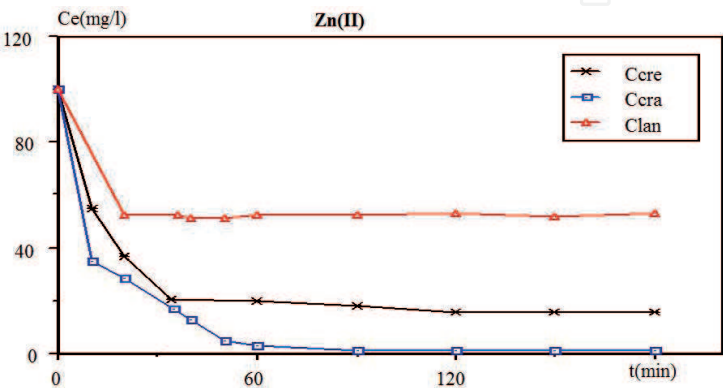


Figure 7.
Kinetic study of the Zn (II) adsorption on the raw chitin.

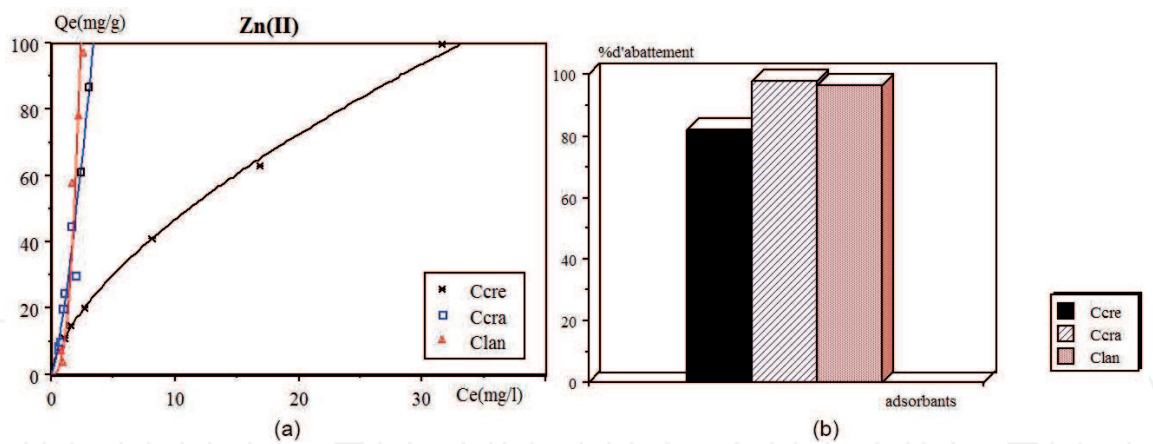


Figure 8.
(a) Experimental isotherms of Zn (II) adsorption on raw chitin (b) Effect of the origin of raw chitin on the elimination efficiency of Zn.

	Kf mg/g	1/n	R
Ccre	10.82	0.63	0.99
Ccra	23.74	1.72	0.99
Clan	11.49	1.99	0.99

Table 6.
Values of Freundlich parameters deduced from Zn^{2+} adsorption isotherms on the raw chitin.

Elimination percentages reach 98% for Ccra and 97% for Clan. These results are compared to those found for mineral surfaces such as Al_2O_3 , zeolite, and albeit whose percentages of elimination do not go beyond 30% [10].

Linear adsorption transforms according to the Freundlich model—**Table 6** show that Zn has a great affinity for hard shells. The Freundlich model makes it possible to describe the adsorption of Zn: $R^2 > 0.95$. In this case, the adsorption is hydrophobic in nature through Van Der Waals interaction and hydrogen bonds.

The perfectly applicable Freundlich model shows that the adsorption capacity of Zn^{2+} on the Ccra is twice as large as that on the Ccre (**Table 6**).

According to the isotherms of **Figure 8a**, the percentage of adsorption decreases when the concentration of Zn^{2+} increases, the same remark was recorded by Spark and Bourg [17, 62] during the study of Zn adsorption on kaolinite and clay mineral.

6. Study of the lead adsorption

6.1 Kinetic study of the Pb^{2+} adsorption

The evolution of equilibrium concentration as a function of time is shown in **Figure 9**. The kinetic study of the adsorption has shown that more than 50% of the initial amount of Pb^{2+} is absorbed on the Ccre before the time is reached 5 minutes. The concentration of Pb^{2+} decreases rapidly in a few minutes, from 100 mg/l to a concentration of less than 1 mg/l for the Ccre. A pseudo-equilibrium with the surface of the supports appears to be reached, the equilibrium times are estimated at about 18 minutes for the Ccre, 30 minutes for the Clan, and 60 minutes for the Ccra.

The study conducted by Melchor [39] on the adsorption of Pb^{2+} on chitin extracted from crabs has shown that this is a reaction of the first order and gives an equilibrium time $t = 44$ minutes relatively low compared to the time found for the raw chitin 60 minutes; this implies that the mineral part plays a role in adsorption kinetics.

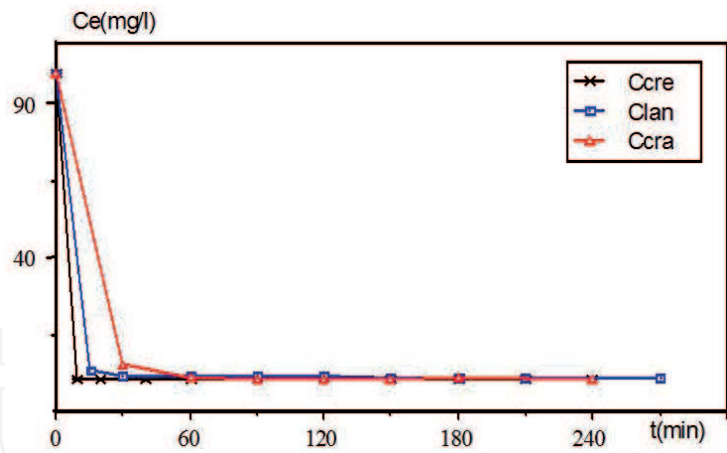


Figure 9.
Kinetic study of Pb (II) adsorption on raw chitin.

After equilibrium, more than 80% of the initial amount of Pb^{2+} (100 mg/l) is adsorbed on the Ccra, whereas only 41% of the initial amount of Pb^{2+} is adsorbed on pure chitin [39]; this shows that the mineral part of the crab shells plays a role in the retention of Pb^{2+} . The percentages of adsorption as a function of time are in good agreement with the results obtained by Yang [37].

6.2 Study of Pb^{2+} adsorption isotherms on raw chitin

According to **Figure 10a**, the curve representing the variation of the quantity of Pb^{2+} adsorbed on the Ccra as a function of residual concentration is linear up to 80 mg/g, whereas for Ccre and Clan, the adsorption obeys Henry's law in the range (10–100 mg/l).

Pb adsorption on the Ccre is peculiar, which is a very important slope that shows Ccre exhibits a strong affinity toward this metal. This feature was also noticed during the adsorption of Pb^{2+} on the zeolites [63, 64] and during adsorption on clinoptilolite [65]. Pb adsorption on all three supports perfectly the Freundlich model in comparison with the adsorption of Pb on activated carbon [66], which gives a capacity of 1.046 mg/g.

The calculation of the percentage of average abatement of Pb^{2+} (**Figure 10b**), for several adsorption tests confirms these results. So Pb is more retained by the Ccre. The concentration of Pb from 100 mg/l to only 0.37 mg/l for 10 minutes is a remarkable retention with a yield of 99.63%. From **Table 7**, the maximum

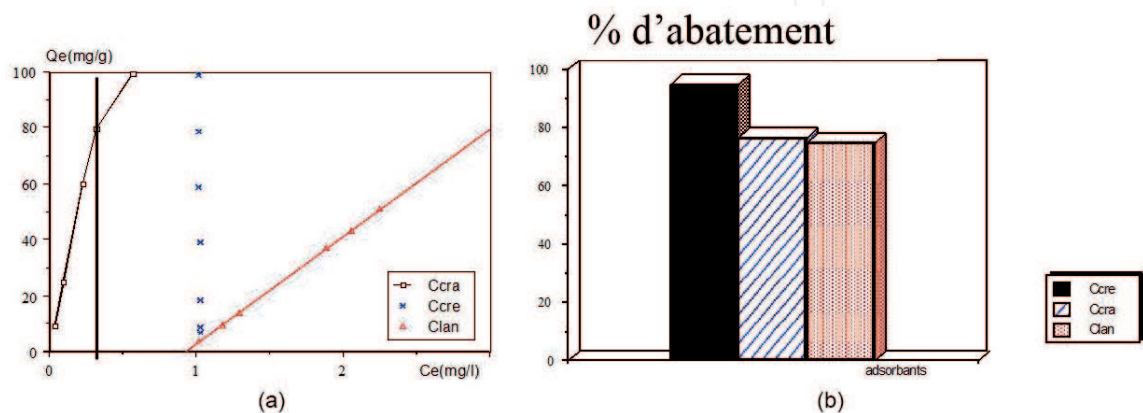


Figure 10.
(a) Experimental isotherms of Pb (II) adsorption on raw chitin, (b) effect of the origin of crude chitin on the removal efficiency of Pb (II).

	Kf mg/g	1/n	R
Ccre	9266.9	263.98	1.00
Ccra	265.07	1.04	1.00
Clan	3.59	3.69	1.00

Table 7.
Values of Freundlich parameters deduced from Pb adsorption isotherms on the raw chitin.

adsorption capacity according to the Freundlich model is 9266.86 mg/g on the Ccre, it is 35 times greater than that corresponding to the Ccra. There is also a better adsorbability for Ccra 265.07 mg/g.

We compared the rate of fixation of Pb by Ccre with adsorption results on biological surfaces such as 90% algae and rice biomass 99% Hulls [22], adsorption on mineral surfaces such as 35% bentonite and montmorillonite, which retain only 25% of Pb and to the cellulose for which the percentage of adsorption does not exceed 62.8%.

The average reduction percentage of Pb is 95% for the Ccre, and 75% for the Clan. According to the adsorption tests, the percentage of adsorption decreases when the concentration increases, the same observation was recorded for the adsorption of Pb on Kaolinite [13], a significant reduction in Pb is obtained at low initial concentrations.

7. Comparison with active charcoal powder (CAP)

The adsorbent supports are numerous and diverse, but in water treatment, activated carbon is used almost exclusively as adsorbent. To value chitin in the treatment of metallic water pollution, we have tried to compare its purification performance with that of CAP. We will then study the kinetics and adsorption isotherms of metals on CAP.

7.1 Kinetic study of adsorption of heavy metals on active coal powder (CAP)

During the treatment of liquid discharges, processes are always sought which give the maximum of treatment efficiency in a minimum of time. Since then, we have tried to compare the kinetics of adsorption on the studied materials and on the CAP. We have tried to situate ourselves under the same operating conditions as those of the raw chitin. The evolution of the adsorbed quantity as a function of time is reported in **Figure 11**.

From figure above, active carbon rapidly sets a maximum amount of metal. So for the Pb, it takes 60 minutes to reach adsorption equilibrium. Cd requires a time of about 10 minutes, while Cu and Zn only require a few minutes for their concentrations in the solution to stabilize.

Comparing the kinetic curves of the CAP with those obtained for different types of chitin, we find that the raw chitin exhibits identical kinetic behavior to that of the CAP even if the times of the adsorption kinetics on the raw chitin depend on its origin; these times are always close to those observed with the CAP, and sometimes, the equilibrium times are smaller than those of the CAP (case of the Ccre-Zn).

7.2 Comparing isothermals of metals adsorption on CAP and on raw chitin

To compare the reduction of metallic pollution by crude chitin to that by CAP, we carried out adsorption tests of heavy metals on the CAP under same conditions

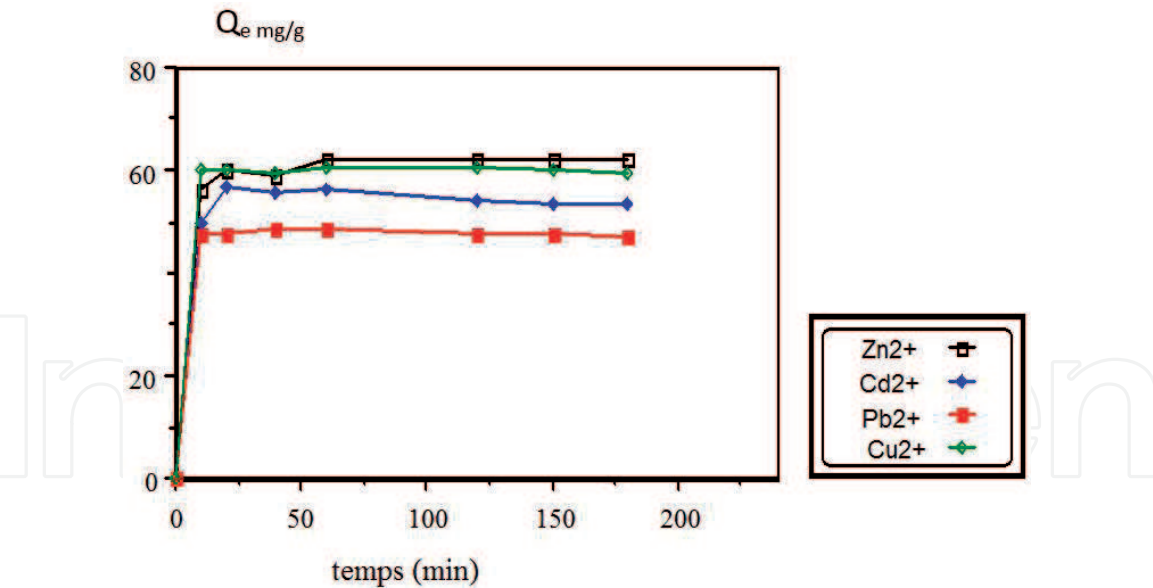


Figure 11.
Kinetic study of heavy metals adsorption on the CAP.

as those of crude chitin. **Table 8** represents the values of the Freundlich parameters for this study.

According to this table, Pb is more adsorbed by CAP than other metals, it is about 10 times more adsorbed than Cu. The retention of Zn and Cu is low, 1 g of CAP retains only 4.35 mg of Cu²⁺ and 3.38 mg of Zn. The selectivity of CAP toward these metals is as follows Pb > Cd > Cu > Zn. In order to compare these results with those of raw chitin, we have drawn up **Table 9** grouping the maximum adsorption capacities of metals on different media.

According to this table, the adsorption capacities of the metals on the CAP are low compared to the raw chitin. There is a difference between the values observed, and this difference is important in the case of Pb. Indeed, the Pb is 58 times retained by the Ccre than by the CAP, it is almost five times more retained by the Ccra than by the CAP. In the case of Cd²⁺, the gap exists particularly between the Ccre and the CAP, Cd is more than three times retained by the Ccre than by the CAP. For Cu, 1 g of the Ccre retains a quantity of Cu 10 times higher than that retained by the CAP. Similarly, Zn is more adsorbed by crude chitin than by CAP. The same remarks were made by calculating the elimination percentages for six heavy metal adsorption tests; we have used the example of Cu²⁺ and Zn, their percentages compared to those observed with the raw chitin are grouped in the following **Figure 12**.

This figure clearly shows that the adsorption of the metals on the raw chitin is much stronger than the adsorption of the metals on the CAP. From this study,

	Kf (mg/g)	1/n	R
Pb ²⁺	58.69	1.03	0.98
Cd ²⁺	9.01	0.56	1.00
Cu ²⁺	4.35	0.57	1.00
Zn ²⁺	3.38	0.59	1.00

Table 8.
Values of the Freundlich parameters deduced from the adsorption isotherms of metal ions on activated carbon.

	Pb ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
CAP	58.69	9.01	4.35	3.38
Ccre	9266.86	34.81	42.25	10.82
Ccra	265.07	7.38	17.02	23,74
Clan	3.59	18.92	204.67	11.49

Table 9.
Values of the maximum adsorption capacity K (mg/g) of heavy metals.

it follows that the CAP can be substituted by the raw chitin for the treatment of the effluents rich in heavy metals.

7.3 Interpretation and comparison of results

According to this study, we can draw strong conclusions about the existence an affinity between biosorbent materials based on shells of crustaceans and some heavy metals.

Raw shrimp chitin exhibits a strong affinity for Pb. The adsorption capacity of zinc on the raw chitin of crabs is twice as great as that on the raw chitin of shrimp. The selectivity of the metal for each of these materials was defined by the plot of the adsorption isotherms. The metal ions are retained by these materials in the following order:

- Lead: Ccre > Ccra > Clan
- Cadmium: Ccre > Clan > Ccra
- Copper: Clan > Ccre > Ccra
- Zinc: Ccra > Clan > Ccre

The kinetic study has shown that the adsorption process is relatively fast compared to the adsorption on the supports described in the bibliography (of mineral origin). More than 50% of these ions are adsorbed before equilibrium is reached (20 minutes). The adsorption kinetics has also shown that the mineral part of the raw chitin is partly responsible for the retention of heavy metals. The hardness of the shells has a negative effect on the kinetics of the adsorption process, given the time required for equilibrium. Indeed, the adsorption of Pb on the raw chitin shrimp requires only 30 minutes; while the raw chitin lobsters the equilibrium time is 60 minutes.

Studies cited in the literature have shown that to obtain a given abatement, it is necessary to introduce a sufficient quantity of the material. Thus, our treatment tests have shown that to achieve a removal rate of 99% copper contained in

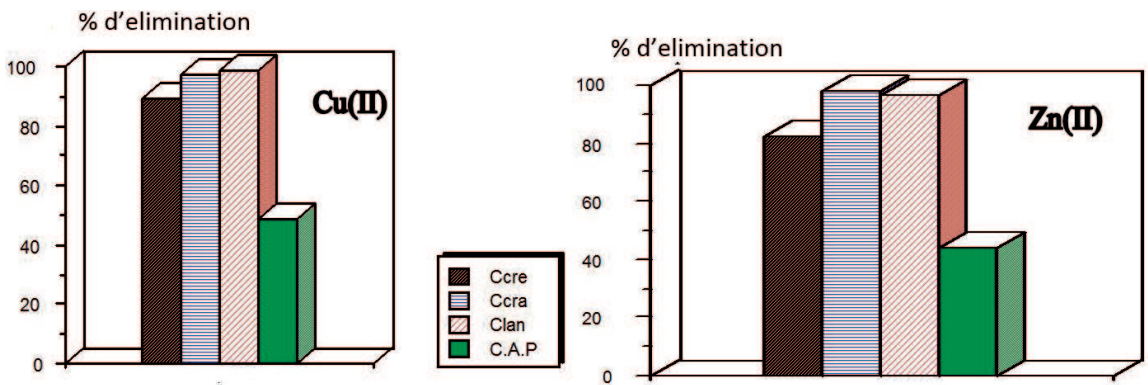


Figure 12.
Evolution of the average percentages of elimination according to the supports adsorbents.

a synthetic release with an initial concentration of 100 mg/l, it is necessary to add 1 g of raw chitin. The adsorption percentages of the metal ions on the raw chitin increase when the concentration of these ions decreases.

The comparative study with activated carbon powder (CAP) indicates that the substitution of the latter by chitin may be possible. However, chitin can be coupled to CAP during a chain of treatment of industrial discharges of various loads. As a result, the quantity of heavy metals not retained by the CAP will be retained by the raw chitin.

7.4 Comparative study of the selectivity of heavy metals adsorption on raw chitin in relation to other adsorbent cited in the literatures

From the previous results, we can classify the retention capacity of heavy metals by raw chitin according to the following sequences:

$$\begin{aligned} \text{Ccre Pb} &> \text{Cu} > \text{Cd} > \text{Zn} \\ \text{Ccra Pb} &> \text{Zn} > \text{Cu} > \text{Cd} \\ \text{Clan Cu} &> \text{Cd} > \text{Zn} > \text{Pb} \end{aligned}$$

These results are in agreement with some studies, indeed Haug et al. [67] showed that the addition of metal ions to a solution of Na alginate prepared from *Laminaria digitata* leads to the order of the next affinity: $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$. Nicolas [21] found the affinities of the following heavy metals:

$$\begin{aligned} \text{Zn} > \text{Cu} &= \text{Ni} > \text{Cd} \text{ (pyrophosphates +61 mg/g polysaccharides)} \\ \text{Cu} = \text{Ni} &> \text{Cd} > \text{Zn} \text{ (pyrophosphates +222 mg/g of proteins)} \end{aligned}$$

Melchor [38, 39] showed that pure chitin crabs exhibits affinity vis-à-vis heavy metals in the following order: $\text{Cu} > \text{Cd} > \text{Pb}$.

In general, the chitin selectivity sequence depends, on the one hand, on the origin of this chitin (algae, fungi, crustaceans, etc.) and on the other hand, on the nature of the ions, in particular the 3d orbitals. It does not depend in any case on their Cu 0.72 Å, Pb 1.2 Å, Cd 0.97 Å, and Zn 0.74 Å sizes. However, the adsorption selectivity of metal ions on mineral surfaces varies greatly from one medium to another. We give the following sequences as an example: $\text{Pb} > \text{Cu} > \text{Zn} = \text{Cd}$ and $\text{Pb} > \text{Cd} > \text{Zn} > \text{Cu}$ respectively for montmorillonite and Kaolinite [68].

8. Test of metallic ion adsorption in series

In order to study the effect of the number of treatments on the percentages of elimination of metal ions and to solve the problem of competitive adsorption, we proceeded to a series treatment starting with an initial concentration of 100 mg/l from M^{2+} . After each adsorption test, the measured filtrate is again adsorbed on the material. This operation is repeated four times for the four metals. In parallel, we do a simple treatment using the same quantity used previously. The results found will be compared to FAO standards.

The results of the monitoring of the evolution of the metal ion contents during the series treatment and after the simple treatment of the synthetic rejection are shown in **Table 10**.

This table shows that the equilibrium concentration decreases after each adsorption test. Thus, we go from 100 to 0.032 mg/l after the first test and from 0.032 to only 0.002 mg/l after second test for Pb. This value is 25 times lower than the FAO standard of 0.050 mg/l; it is a remarkable reduction of the Pb ion.

	Pb ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
Co (mg/l)	100	100	100	100
Simple treatment	0.300	1.780	1.260	3.860
First trial	0.032	22.340	23.050	31.480
Second trial	0.002	11.400	0.824	2.489
Third trial	0.001	0.465	0.780	0.915
Fourth trial	—	0.019	0.151	0.728
FAO (mg/l)	0.05	0.02	0.2	5
PVL (mg/l)	0.5	0.2	0.5	5

Table 10.
Values of equilibrium concentration in mg/l of metal ions after single treatment and after each test during serial treatment.

	Pb ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
First treatment	99.97	77.66	76.95	68.52
Fourth treatment	99.99	99.98	99.84	99.27
Simple treatment	99.54	98.22	98.74	96.14

Table 11.
Percentages of reduction of metals according to the number of tests.

In the case of Cd after the fourth test, the Cd ion content is below the FAO standard. In the case of Cu, the concentration ranges from 100 to 0.780 mg/l after third test and from 0.780 to 0.151 mg/l, after the fourth test, the equilibrium concentration is therefore lower than the FAO standard for Cu²⁺.

Finally, in the case of Zn²⁺, only two adsorption tests are required to reach the FAO standard of 5 mg/l, which is relatively higher than the standards for other metals given the biological role played by Zn²⁺ in living organisms.

After a simple treatment, using the same quantity of the adsorbent used in the series treatment, it is noted that the quantities of metal ions remaining at equilibrium are greater than those remaining after the fourth serial treatment test; this shows that serial processing is more effective than simple treatment.

In **Table 11**, we calculated the percentage of abatement after the first test, the fourth trial, and simple treatment.

According to this table, the series treatment is very effective to reduce the amount of metal ions and thus increase the reduction efficiency. For example, for Zn, we go from a percentage of 68.52% after the first test and 99.27% after fourth adsorption test.

9. Sludge management test generated from the adsorption of heavy metals

One of the problems of the environment is the accumulation of solid waste. In order not to generate a simple transfer of pollution and in order to valorize the proposed treatment process, the solid sludge component generated by this treatment process “raw chitin saturated with heavy metals” should not weigh down the pollutant mass of household waste. From then we proposed at the end of this chapter two solutions to get rid of the generated sludge:

- The first is the elimination of this sludge by calcination at high temperature.
- The second is the recovery of this sludge by trying to study the regeneration of the adsorbent support by an acid.

9.1 Examination test for sludge generated by incineration

Incineration can greatly reduce the volume and weight of household waste by transforming it into gas, heat, and sterile and inert materials, ashes and slag. Volume and weight reductions can 90 and 60%, respectively of the initial volume and weight of the garbage. The gases formed contain mainly excess air, water vapor, carbon dioxide (CO₂), nitrogen oxides (NO_x) fly ash, and in small quantities, various products from combustion: carbon monoxide (CO), organic matter, sulfur dioxide (SO₂), hydrochloric acid, etc. The incineration takes place in three phases to know: drying with evaporation of water, spraying materials organics from 200°C and gasification of combustion of the carbonaceous residue: the volatile substances emitted burn at 500°C, this combustion is considered complete at 1000°C, provided that the air/fuel contact is satisfactory and the residence time at this high temperature is sufficient.

After the adsorption tests, the precipitates obtained loaded with the heavy metals are dried at 200°C in an oven and then calcined at high temperature (800°C) using a tubular oven for 2 hours, at the entry of the sample, the release of C, CO₂, and H₂O. Generally, when burning a conventional hydrocarbon fuel, one obtains at the end of the combustion, two harmless products CO₂ and H₂O, which result from the complete oxidation of the carbon and the hydrogen contained in the fuel, by the oxygen of the air. After few seconds, this release stops. The calcined final product is white for three samples relating to three metals studied, although for the case of copper, the sample was blue. In order to identify the phases obtained, the products resulting from the calcination were characterized by X-ray diffraction.

At high temperature, the predominant phase is the calcite phase, this remark is recorded for three metals. The calcination gave rise to a new phase, which is only the metal oxide phase. The appearance of the PbO, CdO, and CuO oxide phases relating to the cure loaded, respectively by Pb, Cd, and Cu. The metal ions are finally recovered in the form of an oxide that can be used as a raw material in the field of solid materials.

9.2 Test of the chitin regeneration

An adsorbent is of real interest only if it can be easily regenerated. The raw chitin used in the retention of metals must recover its initial structure and its starting chemical composition for a possible reuse with an appreciable re-adsorption efficiency.

In most of the regeneration studies carried out on organic materials, the essential element used as regenerant is the H⁺. So, Muzzarelli [34] has exploited chitin to collect heavy metals from seawater, these metals are then recovered by appropriate washing with an acid. Huang [44, 45] studied the regeneration of fungi biomass loaded by Cd²⁺, and found that these materials can be regenerated by strong acids. Hoshi [33] exploited chitin in the determination of copper by column adsorption-elution, Cu²⁺ retained was eluted with a mixture of acetic acid and acetone. Roy [22] showed that most heavy metals can be recovered by lowering the pH of the medium, using an acid wash. In general, the efficiency of the regeneration depends on the rate of passage on the adsorbent, the direction of this passage, and the amount of the regenerating solution which is passed over the adsorbent. According to our study, it turns out that

Metal	C _{M2+ fixed} (mg/l)	C _(metal) (mg/l)	Percentage of release
Pb ²⁺	98.91	14, 820	149.8
Cd ²⁺	86.77	23.17	26.70
Cu ²⁺	94.09	23.35	24.82

Table 12.
Variation of the release percentage according to the nature of the metal.

the raw chitin has undeniable qualities of fixing heavy metals. For the regeneration tests, we chose the raw chitin of shrimp origin. Finally, the regeneration is carried out by HCl and focused on four metals, the regeneration conditions are optimized.

Let the percentage of release defined as following Eq. (3):

$$\% \text{ of release} = C_{(\text{metal})} / C_{M2+\text{fixed}} \tag{3}$$

with
C_{M2+ fixed}: concentration of M²⁺ fixed on the adsorbent before regeneration,
C_(metal): concentration of the released amount of M²⁺ after regeneration.
Concentration C_{M2+ fixed} is calculated according to the following Eq. (4):

$$C_{M2+\text{fixed}} = [(CiVi - CeVr) Ms] / MoVr \tag{4}$$

with
Mo: initial mass before treatment; Ms: mass saturated with heavy metals; Vi: volume used for saturation; Vr: volume used for regeneration; Ci: initial concentration of metals; Ce: concentration of ions at equilibrium.

The amount released by HCl remains relatively stable from a concentration of 0.08 mol/l HCl, if we increase the concentration of HCl. It should be noted that all the metals studied are easily displaced by a low concentration of H, this shows that the interactions established between the metals and the raw chitin are not strong to resist the H⁺ ions. The released quantity is maximum in the case of Pb. In the case of Cu and Cd, it is almost constant and neighbor. These results are grouped in **Table 12**, indeed the percentages of release are equal.

9.3 Comparison between the two processes and interpretation of results

The incineration of raw chitin has led to metal oxides that can be recycled in other industries; in addition, it is a fast and perfectly hygienic process. It allows a significant reduction of waste in weight and volume. Therefore, it is the best solution in the case of effluents less loaded with heavy metals and whose composition is complex. However, the regeneration of raw chitin is a cumbersome process that requires the addition of reagents (acid, salt), and the use of material, in addition, it modifies the structure of the material, but in spite of this, the regeneration is the best solution in the case of mineral effluents heavily loaded with heavy metals and whose composition is simple.

10. Conclusion

The isothermal study and kinetics of adsorption of metal ions on crude chitin has shown that the adsorption capacity of a metal depends on the origin of the latter

and that the adsorption process is relatively fast. The Freundlich model is perfectly applicable; in fact, the correlation coefficients obtained for the four metal ions are very satisfactory. The removal efficiency of the metal ions depends on the initial concentration. This yield is high for a low initial concentration; therefore, the treatment of metal pollution after dilution in industrial effluents is interesting.

The comparative study with activated carbon (CAP) showed us that the raw chitin has a greater power of elimination than the (CAP), which suggests a probable substitution of CAP by chitin. According to this study, it can also be seen that the high temperature incineration of sludge generated by the adsorption of heavy metals on crude chitin results in calcite phases, which do not represent any toxicity in the environment and at low levels of metal oxide phases that can be recycled in the industry of solid materials (ceramics, cement, etc.). However, the regeneration of crude chitin changes the structure of the material relatively well and gives new adsorbent supports.

In summary, it can be argued that all the results obtained show the good ability of crude chitin to remove heavy metals when working under adequate conditions. Thus, fisheries waste, rich in chitin, would therefore constitute materials that could, on the one hand, eliminate metal pollutants, especially Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} ions and on the other hand to substitute activated carbon in metal pollution treatment facilities.

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