

# Decontamination of a solution of chromium IV by marine algae (ulva-lactuca)

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**Abstract - Wastewater contaminated by heavy metals remains today one of the major problems to solve in industrialized countries. Various conventional methods are used to remove heavy metals from the existent wastewater. They are based on chemical precipitation phenomena, ion exchanges, and adsorption or bio-sorption.**

**The treatment by plants (phytopurification) is a natural treatment for a variety of aquatic or semi aquatic organized and structured artificially to maximize their holding capacity for various pollution parameters. Many studies aim to increase the removal of heavy metals by plants to clean up wastewater. In this study we are interested in the ability of the algae "ulva-lactuca" to eliminate the chromium (Cr) from a previously prepared solution and the factors that may influence the absorption [1,2,3].**

**The parameters studied were pH, mass, contact time between polluted water and algae (biomass and its impact on the bio-sorption also other physico-chemical parameters). The results show the bio-sorption percentage  $R\% = 84\%$  is observed at  $pH = 5$  and  $m = 4g$  amount of living biomass, and the elimination percentage of Cr is equal to  $96\%$  at  $pH = 5$ ,  $m = 1g$  and  $C_0 = 38.32 mg/l$  and the amount adsorbed can reach  $1.81 mg/g$  for crushed algae. These results are consistent with those obtained with the Langmuir model.**

**Keywords: algae, contaminated water, chromium, ICP-AES, Langmuir.**

## I. INTRODUCTION

It is well recognized that the presence of heavy metals in the environment can be detrimental to a variety of living species, including man. Chromium is one of the most toxic metals affecting the environment. Mining and metallurgy of chromium, chromium electroplating, battery and accumulator manufacturing, pigments and ceramic industries waste waters contain undesired amounts of chromium (VI) ions. The main techniques which have been utilized for treatment chromium (VI) bearing waste streams include precipitation, evaporation, adsorption, ion exchange, membrane processing, solvent extraction, etc. These methods have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems [4]. Using microorganisms as biosorbents for heavy metals offers a potential alternative to existing methods for detoxification and recovery of these components from industrial waste waters. The special surface properties of microorganisms enable them to absorb different kinds of pollutants from solutions [5].

Absorption in natural or uncontrolled situations typically involves a combination of active and passive transport mechanisms starting with the diffusion of the metal ion to the interior of the microbial cell. Once the metal ion has diffused to the cell interior, it will bind to the polymer attached heavy metals which exhibit some chemical affinity for the metal [6,7]. This step contains a number of passive accumulation of processes and may include absorption, ion exchange, coordination, complexation, chelation and micro-precipitation. Generally, such metal ion absorption is fast, reversible, and not a limiting factor in bioremoval kinetics when dealing with dispersed cells. Absorption is often followed by a slower metal binding process in which an additional metal ion is bound, often irreversibly. This slow phase of metal uptake can be due to a number of mechanisms, including covalent bonding, surface precipitation and redox reactions, diffusion into the cell interior and binding to proteins and other intracellular sites [8,9,10]. The marine algae can sequester heavy metal ions by the same absorption mechanisms as other microbial biomass. The mechanism of binding metal ions by inactivated algal biomass may depend on the species and ionic charges of metal ion, the algal organism and the chemical composition of the metal ion solution [11,12].

Our interest in the wastewater treatment of these marine algae is mainly due to their nature biopolymers (polysaccharides, proteins, and lipids) rich in amines, alcohols, sulfates, and carboxylic groups responsible for the fixation of heavy metals functions [13,14,15,16,17,18].

The aim of this work is to evaluate the bio-sorption capacity of chromium (VI) in living marine algae (ulva lactuca). Our choice is at the same time, guided by ecological and economic considerations which impel us to look for natural sorbents, absorbent, these algae are abundant in nature and exploitable in the raw state or after a simple treatment. After saturation, residues of algae will be recovered and eventually incinerated or stored in appropriate places.

## II. MATERIALS AND METHODS

### A. Harvest and Preparation of algae

Marine green algae (ulva-lactuca) were collected using peaches to plankton net in October 2013 at room temperature  $22^\circ C$  on the Moroccan Atlantic coast at the level of the beach of Rabat ( $34^\circ 03'$  North latitude, and  $6^\circ 46'$  West longitude at an altitude of 79 m). These algae have been rinsed with sea water and then Stored in plastic bags of polyethylene previously

rinsed with distilled water acidified with nitric acid pure, upon arrival at the laboratory, the algae are again rinsed with distilled water.

These algae were dried in an oven at a temperature of 70 ° C for 48 hours until the weight of the fibers becomes constant; Then they were crushed and the resulting particles serve for the remainder of our study.

**B. Preparation of metallic solutions**

The cadmium solutions were prepared by dissolving mass  $m = 0,101g$  of  $K_2Cr_2O_7$ , in demineralised water. The initial solution of concentration  $[Cr]=38,17mg/L$  was diluted to obtain other solutions of different concentrations. The solution pH was adjusted by means of HCl and NaOH solutions (both of concentrations 0.1M and 1M), using a pH-meter. The percentage of biosorption is given by equation (1) [19]:

$$R\% = \frac{C_0 - C_t}{C_0} * 100 \tag{1}$$

With:  $C_0$ : the initial concentration of the metal in the aqueous solution.

$C_t$ : the concentration of the metal to the equilibrium of extraction in the supernatant solution.

**C. Determination of contact at equilibrium time**

To determine the time after which algae comes into equilibrium with the polluted aqueous solution Cr, An amount of living algae was put in contact with a volume of 50 ml of a synthetic solution of chromium (VI) ( $[CR(vi)] = 20.81 mg/l$ ). The swabs Resulting from the contact time of 1 day of interval and 6 days were analyzed by ICP - AES.

**D. Effect of agitation**

Effect of agitation experiments were performed suspending 1 g of biomass, or its equivalent fixed in agar, in 50 ml of Cd(II) solutions. The metal concentration 38, 17 mg/g . Suspensions were kept in constant agitation at desired and constant pH = 5 and room temperature  $t^\circ = 22^\circ C$  After 15, 30, 60, 90, 120, 150, 180 min, the mixture (algal biomass+ metal) was filtrated with membrane filters (0,45 um). Afterwards, the final metals concentrations in the remaining solution were determined and metal uptake ( $Q_t$ ) was calculated using the following mass balance equation [20]:

$$Q_t = (C_0 - C_t) \frac{V_l}{M_s} \tag{2}$$

Where  $C_0$  is the initial metal concentration (mg l<sup>-1</sup>),

$C_t$  the equilibrium metal concentration (mg l<sup>-1</sup>),

$V_l$  the solution volume (l).

$M_s$  is the dry alga weight (g).

**III. RESULTS AND DISCUSSION**

**A. realised pH Effect**

As known, the initial solution pH has a great influence on the elimination of metallic ions by adsorption phenomenon. Therefore its effect was considered for ion Cd(II) by varying its value as follows:

pH 2, 3, 4, 5, 6, and 7.

The obtained results are shown in Fig. (2), as follows:

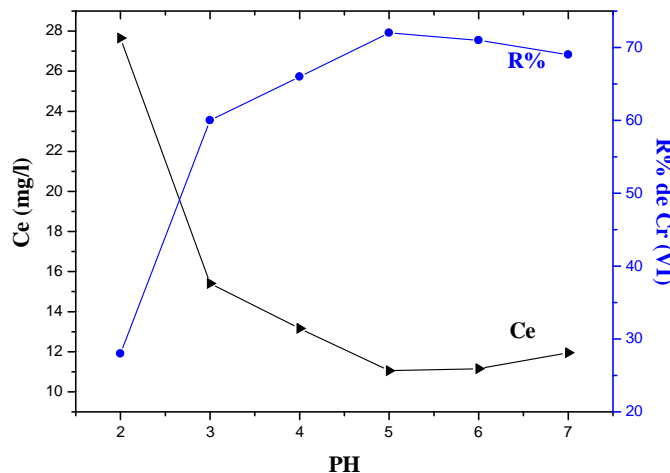


FIG.1. EFFECT OF pH ON THE ABILITY OF CHROMIUM ABSORPTION BY ALGAE ULVA LACTUCA.

Earlier studies on heavy metal biosorption have shown that pH is an important parameter affecting the biosorption process. Chromium (VI) uptake by algal biomass (ulva lactuca) is also a function of solution pH. Chromium (VI) uptake by algal biomass (ulva lactuca) is also a function of solution pH. The effect of initial pH on the adsorption of cadmium on algal biomass (ulva-lactuca) was studied at 38,17mg/l initial chromium(VI) ion concentration and at 22°C. As seen from Fig. 1, the absorption of chromium (VI) increased with pH up to 5.0 and then declined with further increase in pH. The maximum equilibrium uptake value was found as R=72% at pH 5. The equilibrium binding capacity decreased to the value of R = 28% by decreasing pH value to 2.0. Solution pH influences both cell surface metal binding sites and metal chemistry in water. At low pH, cell wall ligands were closely associated with the hydronium ions H<sub>3</sub>O and restricted the approach of metal cations (as a result of) which causes the repulsive force. As the pH increased, more ligands such as carboxyl, phosphate and amino groups would be carried negative charges with subsequent attraction of metallic ions with positive charge and absorption onto the algae surface. Similar results have been reported from other research teams [21,22,23,24,25].

B. *the mass effect on chromium (VI) absorption*

Finding the minimum mass which may absorb the maximum of chromium (VI) comprises contacting a solution of Cr concentration C<sub>0</sub> = 38, 17 mg.l<sup>-1</sup> and pH = 5, with different masses of seaweed. The results are shown in figure 2.

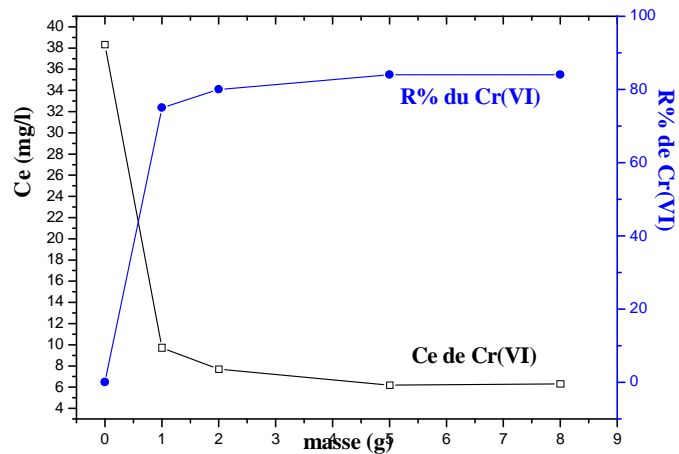


FIG.2. INFLUENCE OF THE AMOUNT OF ALGAE (ULVA LACTUCA) ON THE CAPACITY ABSORPTION OF CHROMIUM (VI).

These curves there is chromium (VI) concentration absorbed increases with the mass of the alga, the maximum retention is obtained for a mass of 5 grams of algae <ulva-lactuca> by 50 ml of solution. For this quantity, the percentage of elimination saves its value maximum (R = 84% for m = 5 g of chromium (VI)). For other quantities, the percentage of elimination increased from 63% to 84% for the masses of fibres from 1 to 8 g of ulva lactuca. The increase in the retention rate of hexavalent chromium on the basis of the increase in the mass of fibres is mainly due to the presence of functional groups capable of fixing heavy metals. This trend is quoted by [26].

C. *effect of contact time on the removal of chromium (VI)*

Figure 3 shows the percentage of chromium (VI) absorbed by the <ulva-lactuca> living time. The experimental conditions are as follows: mass of Spirogyra SP. m = 5 g, initial concentration of chromium (VI) C<sub>0</sub> = 20, 81 mg.l<sup>-1</sup> ambient temperature t = 22 ° C, and pH of the solution in the range of 5.

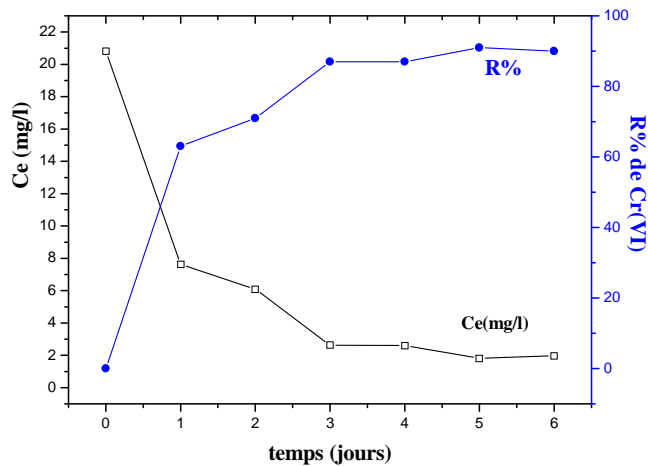


FIGURE 3. INFLUENCE OF THE CONTACT ON THE BIOSORPTION CAPACITY TIME CHROMIUM (VI) BY ALGAE ULVA LACTUCA.

-figure 3 shows a rapid increase in the percentage of elimination of chromium (VI) for  $0 < t < 3$  days, which can be explained by high affinity of the alga for chromium (VI). It also shows for  $t > 3$  days, there is a stability of the amount of chromium (VI) absorbed by our algae, which can be explained by a saturation of the functional group able to fix heavy metals, So more than the time of balance is reached after 4 days or more are times of balance.

D. Effect of agitation

Agitation is one of the important parameters for biosorption application. Fig. (1) Shows that the adsorption of the cadmium is very rapid during the first minutes, indicating a great affinity between the biomasses of green algae for these cations. In fact, the results show an elimination of 96 % after only 30 minutes. The retention capacity increases with time and reaches the equilibrium after 40 minutes with a removal of 98% ( $Q_{eq} = 1,83$  mg/g).

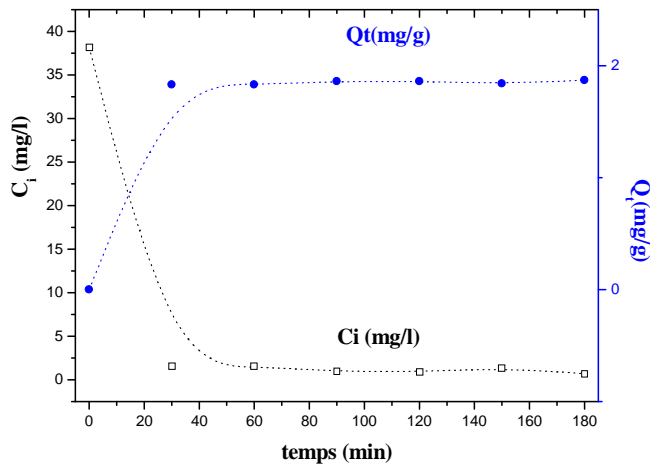


FIG.4. INFLUENCE OF AGITATION OF HEAVY METAL (CR) BIOSORPTION BY GREEN BIOMASSES.

E. Modeling of adsorption isotherms

Langmuir adsorption isotherm

Langmuir adsorption isotherm [27] assumes that the solid surface has a finite number of identical sites which shows homogeneous

surfaces. Langmuir equation and its linearized form may be represented as:

$$Q_{eq} = \frac{Q_m \cdot K_L \cdot C_i}{1 + K_L \cdot C_i} \tag{3} \text{ (non - linear form)}$$

$$\frac{1}{Q_{eq}} = \frac{1}{K_L \cdot Q_m \cdot C_i} + \frac{1}{Q_m} \tag{4} \text{ (linear form)}$$

where  $q_e$  (mg/g) is the amount of the adsorbed ion per unit weight of the dried plant adsorbent at equilibrium,  $C_e$  is the equilibrium concentration of ion (g/L) in the solution,  $q_L$  is Langmuir maximum adsorption capacity (mg/g) and  $K_L$  is Langmuir constant (L/g) related to a free energy of adsorption. The isotherm constants  $q_L$  and  $K_L$  were calculated from the slope and the intercept of the plot between  $1/q_e$  and  $1/C_e$ . Langmuir equation is thermodynamically consistent and follows Henry's Law at low concentrations. As  $C_e$  becomes lower,  $K_L C_e$  is much less than unity and  $q_e = K_L C_e$ , which is analogous to Henry's Law.

**Freundlich adsorption isotherm**

Freundlich [28] equation shows the best fittings to the adsorption data for natural heterogeneous adsorbents. Freundlich adsorption isotherm equation and its linear form can be written as follow :

$$Q_{eq} = K_F \cdot C_i^{1/n_f} \tag{5} \text{ non linear form}$$

$$\ln Q_{eq} = \ln K_F + \frac{1}{n_f} \ln C_i \tag{6} \text{ linear form}$$

where,  $q_e$  is the amount of the solute adsorbed per unit weight of adsorbent (mg/g);  $C_e$  is the equilibrium concentration of the solute in the bulk solution (g/L);  $K_f$  is Freundlich constant, which is a comparative measure of the adsorption capacity for the adsorbent, and  $n_f$  is an empirical constant related to the heterogeneity of the adsorbent surface. The isotherm constants  $n_f$  and  $K_f$  were calculated from the slope and the intercept of the plot  $\ln q_e$  versus  $\ln C_e$ . For a favourable adsorption,  $0 < n_f < 1$ , while  $n_f > 1$  represents an unfavourable adsorption, and  $n_f = 1$  indicates a linear adsorption. If  $n_f = 0$ , the adsorption process is irreversible.

Values for the constants of different models, for a temperature of 22 ° C, are given in table 1.

Table 1: Relating to the Cr (VI) chromium biosorption on crude fibre of ulva lactuca constants of Langmuir and Freundlich

Modèle	Expression linéaire	Paramètres du modèle
<b>LANGMUIR</b>	$y = -0,0209x + 0,5594$	<b>Qm = 1,86 (mg/g)</b> <b>KL=0,026 (ml/g)</b> <b>R2= 0,99</b> <b>0&lt;RL=0,5&lt;1 isotherme de Langmuir est Favorable</b>
<b>FREUNDLICH</b>	$y = -0,0328x + 0,6194$	<b>Kf =1,85 (L/g)</b> <b>nf =30,4</b> <b>R2=0,97</b> <b>nf&gt;1 : adsorption faible</b>

**IV. CONCLUSION**

Marine algae <ulva-lactuca> are used in the elimination of heavy metals from polluted waters. We have shown that the absorption of heavy metals by these algae dependent on operating parameters as the pH of the solution, the concentration of polluting metal, the amount of algae used and the time of stays of the alga in the solution.

We have also shown that balance, algae-solution metal, is reached after 5 days and the binding capacity increases as the initial pH of the solution get higher, the absorption maximum is reached at pH = 5, m = 5 g and the percentage of elimination is equal to 84% for C0 = 38, 32 mg.l1 of chromium (VI).

This study showed that from the correlation coefficient R2 values, it can be concluded that the Langmuir model is the most suitable for the experimental results obtained in the two adsorption isotherms and the amount adsorbed at equilibrium is 1.86 mg/g. Taking into account the results, we can conclude that marine algae <ulva-lactuca> may constitute an effective ecological instrument in the process of water decontamination or closed basins polluted by certain metals such as chromium (VI).

**REFERENCES**

[1] Mo Ali, RD Tripathi, Rai ONU, A. Pal, SP Singh. (1999). -Caractéristiques physico-chimical et le niveau de lac Nainital (UP, Inde) pollution: Rôle des macrophytes et le phytoplancton dans la biosurveillance et la phytoremédiation des ions métalliques toxiques. Chemosphere, 39 ; 2171-2182.  
 [2] VK Gupta, A. Rastogi, VK Saini, N. Jain. (2006). -Biosorption de cuivre (II) à partir de solutions aqueuses par des espèces Spirogyra. J. Colloïd Interface Sci., 296; 59-63.  
 [3] A. El-Sikaily, A. El Nemr, A. Khaled, O. Abdelwehab. (2007).- Retrait de chrome toxiques des eaux usées utilisant algue verte Ulva lactuca et son charbon actif. J. Hazard. Mater., 148; 216-228.

- [4] R. Ahmed, T. Yamin, M.S. Ansari, S.M. Hasany, (2006). -Sorption behaviour of lead(II) ions from aqueous solution onto Haro river sand, *Adsorpt. Sci. Technol.* 24; 475–486.
- [5] Sheng, P.X., Ting, Y.P., Chen, J.P., Hong.(2004). -Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interf.* 275; 131–141.
- [6] P. King, N. Rakesh, S. Beenalahari, Y. Prasanna Kumar, V.S.R.K.(2007) Prasad, Removal of lead from aqueous solution using *Syzygium cumini* L.: equilibrium and kinetic studies, *J. Hazard. Mater. B* 142 ; 340– 347.
- [7] Parest Pavasant, Robanchob Apirati Kul, Vimonrat Sungkhum, Prateep Suthiparinayáonont, Surophong Wattanachira, Taha F. Marhaba. (2006) Biosorption of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ , and  $Zn^{2+}$  using dried marine green macroalga *Caulerpa lentillifera*. *Bioresource Technology* 97; 2321 – 2329.
- [8] -Y. Sag, Z. Aksu, T. Kutsal, Design and Operation of Bioreactors — The Med-Campus Programme of the European Communities-Lecture Notes, Ege University Biotechnology Centre, Turkey, 1993, p. 195.
- [9] -G. McKay, Y.S. Ho, J.C.Y. Ng, *Sep. Pur. Methods* 28 (1999) 87.
- [10] Volesky, B., 2001. Detoxification of metal-bearing effluents; biosorption for the next century. *Hydrometallurgy* 59 ; 203-216.
- [11] VK Gupta, AK Shrivastava, N. Jain. (2001).-Biosorption du chrome (VI) à partir de solutions aqueuses par des algues vertes *Spirogyra* espèces *Res eau.*, 35 ; 4079-4085.
- [12] V.K. Gupta, A. Rastogi. (2008). -Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. *Journal of Hazardous Materials.* 152 ; 407–414.
- [13] Narsi R. Bishnoi , Rajender Kumar, Sunil Kumar, Suman Rani.( 2007). -Biosorption of Cr (III) from aqueous solution using algal biomass *Spirogyra* spp. *Journal of Hazardous Materials.*145; 142-147.
- [14] Bishnoi, N.R., Kumar, R., Kumar, S., Rani, S., 2007. Biosorption of Cr(III) from aqueous solution using algal biomass *Spirogyra* spp. *J. Hazard. Mater.* 145; 142–147.
- [15] María Mar Arecoa, Sergio Hanelab, Jorge Duranb, María dos Santos Afonsoa. (2012). -Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga *Ulva lactuca* and the development of a sustainable matrix for adsorption implementation. 213– 214 ; 123– 132.
- [16] E. Fourest, JC Roux. (1992). -Lourde biosorption de métal par du mycélium fongique sous-produits: les mécanismes et l'influence du Ph *Appl. Microbiol. Biotechnol.*, 37; 399-403.
- [17] ZY Lia, SY Guo, L. Li. (2006). -Étude sur le processus, isotherme thermodynamique et mécanisme de Cr (III) l'absorption par *Spirulina platensis*. *J. alimentaire Eng.*, 75; 129-136.
- [18] G. Naja, C. Mustin, B. Volesky, J. (2005). -Berthelin. Une haute résolution titreur: une nouvelle approche à l'étude des sites de liaison de biosorbants microbiennes. *Res eau.*, 39 ; 579-588
- [19] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, TF Marhaba. (2006). -Biosorption de  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  et  $Zn^{2+}$  en utilisant séché macroalgue vert marine *Caulerpa lentillifera*. *Bioresour. Technol.*, 97; 2321-2329.
- [20] YP Kumar, P. King, VSRK Prasad. (2006). -Retrait de cuivre de la solution aqueuse à l'aide *Ulva fasciata* sp. Une algue verte marine. *J. Hazard. Mater.* 137; 367-373.
- [21] VK Gupta, A. Rastogi. (2008a). - Biosorption de plomb à partir de solutions aqueuses par espèce algues vertes *Spirogyra*: équilibre et d'adsorption cinétique. *J. Hazard. Mater.*, 153 ; 407-414.
- [22] VK Gupta, A. Rastogi. (2008b). -Sorption et de désorption des études de chrome (VI) à partir de la biomasse de cyanobactérie *Nostoc* non viable. *J. Hazard. Mater.*, 154 ; 347-354.
- [23] VK Gupta, A. Rastogi. (2008c). -Biosorption du plomb dans des solutions aqueuses de non algues vivant biomasse *Oedogonium* sp. et *Nostoc* sp. - Une étude comparative. *Colloïdes Surf. B: Biointerfaces*, 64 ; 170-178.
- [24] DAKIKY, M., M. KHAMIS, A. MANASSRA, M. MEREB (2002). -Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Adv. Environ. Res.*, 6, 533-540.
- [25] A. El Sikaily., A. El Nembr., A. Khaled and O. Abdelwehab (2007). Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon. *Journal of Hazardous materials* 148 216 – 228.
- [26] R.S. Bai, T.E. Abraham. (2001). -Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*. *Bioresour. Technol.*, 79 73–81
- [27] I. Langmuir. (1918). -The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40 1361–1403
- [28] H. FREUNDLICH, (1926). -*Colloid and Capillary Chemistry*», translated from the 3rd German Edn. by H.S. Hateld, Methuen, London