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### THE EXAMINATION OF THE PERFORMANCE OF A NATURAL BIOMATERIAL FOR THE ELIMINATION OF CHROME IN AQUEOUS

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**KEYWORDS:** adsorption, lignin, response surface methodology, natural biomaterial, chromium (VI)

#### ABSTRACT

The wastewater pollution by trace metals remains today one of the major concerns of the government. This study aimed to examine the adsorption of chromium ions in aqueous solution by lignocellulose biomaterial prepared from eucalyptus bark in batch mode.

The working method implementation was carried out using a dual approach: experimental and numerical, based on an experimental design for response surface.

It was chosen to develop a statistical model of polynomial type interactions with 3 parameters to describe the adsorption process and determine elimination optimization conditions for chromium (VI) ions in aqueous media.

According to the estimated results and the experimental data, the lignocellulose biomaterial prepared from eucalyptus bark appears to have a strong affinity for the chromium ions at low pH values.

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#### INTRODUCTION

At present, the reuse of treated wastewater is important to provide sustainably water needs for irrigation. This reuse raises the question of health and environmental risks for the simple reason that the availability of a poor water in microbial germs and pollutants especially trace metals is far from certain. In Settat, various industries predominantly characterized by numerous small industrial structures, including metallurgy, surface treatment, textile and electroplating have a major contribution to water pollution by chrome. This product transported by water, in addition to its toxicity to wildlife and flora, is unusual to accumulate, especially in aquatic ecosystems; is one of the major polluting metals. [1]

The concentration of Cr (III) and Cr (VI) in industrial effluents ranges from 0.5 to 270 mg / L [2]. The World Health Organization (WHO) recommends that toxic limits of chromium (VI) in wastewater is 0.05 mg / l, [3].

In the United states, the daily maximum concentrations allowed by the Environmental Protection Agency for effluent existing metal finishing industries discharge to a municipal sewer system is: 2.77 mg L<sup>-1</sup> Cr. [4]

Various techniques have been used for the removal of heavy metals, including precipitation, coagulation, ion exchange, and separation by reverse osmosis membrane etc ... [5A].

These techniques, although effective nevertheless has some disadvantages:

(i) sludge production, (ii) high consumption of often toxic reagents (iii) loss of raw material [5B]. In a context of sustainable development, this work aims to examine the performance of a lignin-based biomaterial as a potential adsorbent.

The adsorption process has been recognized as a cost effective method for the removal of trace metals in wastewater especially low metal concentration.

Adsorption is a surface phenomenon in which atoms or molecules of a species called adsorbate (gas or liquid) are fixed on the surface of a solid adsorbent according to various known processes. It will be favored on materials having large surface area and a high density of functional groups on the surface.



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The adsorbents can be of mineral, organic or biological, agricultural waste, biomass and polymeric materials. [6] Numerous studies have shown that the lignin has the potential to act as an adsorption material because of its high adsorption capacity [7].

Lignin is an amorphous and three-dimensional polymer. It is not soluble in water and without optical activity. Phenolic functions lignins are designated as the main adsorption sites.

The lignin has a high specific surface (180 m<sup>2</sup> / g), therefore, it has the potential to be used as bio-sorbing material to remove pollutants from various liquid media. [8]

The use of lignocellulose residues as adsorbent material to remove heavy metals from wastewater can be explained by several reasons.

- The desire to preserve the environment,
- The ability to operate plant materials
- Cheaper, biodegradable, abundant
- No energy requirement

In this paper, the adsorption of Cr (VI) ions from the lignin-based biomaterial was evaluated.

The adsorption conditions such as the dose of adsorbent, the pH and concentration of metal ions in the solution, were optimized. With this goal in mind, we tested the use of lignocellulose residue prepared from eucalyptus bark starting from the following considerations:

1-Dupont and Guillon who have conducted studies on the adsorption of Cr with cellulose and lignin pure at acidic pH found no significant adsorption on cellulose. [9]

2- The environmental chemistry is often limited to the study of chromate ion instead of dichromate ion. The chromate form is the most widespread of Cr (VI)

### MATERIALS AND METHODS

#### 1.1. Geographical framework

Mzamza stands as a particularly interesting study site as characterized by an ecosystem, under increasing human pressures that result in malfunctioning of terrestrial ecosystems and biodiversity loss [10]. The site hosts the wastewater treatment plant STEP is located 8km from the city of Settat. Its climate semiarid passes to tempered winter. The annual average rainfall is 400 mm. The area has an agricultural vocation with a surface area of 8000 hectares, crossed by the river Bou Moussa;

The site includes douars ouled Saad, ouled Boukallou, Dladla, etc.) and the surrounding areas.

#### 1.2. Design and experimental procedure

##### 1.2.1. Preparation of the adsorbent (*Eucalyptus bark powder*)

In this study the biomaterial was obtained from bark forest of eucalyptus trees (Settat, Morocco). It was improved by subjecting the bark to a treatment that consists of impregnation for 24 hours in a solution of phosphoric acid and urea to modify the functional adsorption sites of the biomaterial, followed by washing with hot water (80 ° C) until a colorless solution was observed at room temperature. The content is dried in the sun followed by drying in an oven at a temperature range of 90-100°C and converted to powder using a grinder, and sieved using a bottom sieve to obtain a material of 0.25 mm diameter approximately.

##### 1.2.2. Adsorption batch procedure

To investigate the selectivity of the biomaterial to the anion and chromate and in order to test its anion removal capacity, effluent samples were prepared with concentrations of about 10 to 25 mg.L<sup>-1</sup>. The effect of pH on the adsorption was investigated in the pH range of 2 to 8. The pH adjustment is carried out by adding H<sub>2</sub>SO<sub>4</sub> or NaOH in the solutions with known initial concentrations known of metal ions.

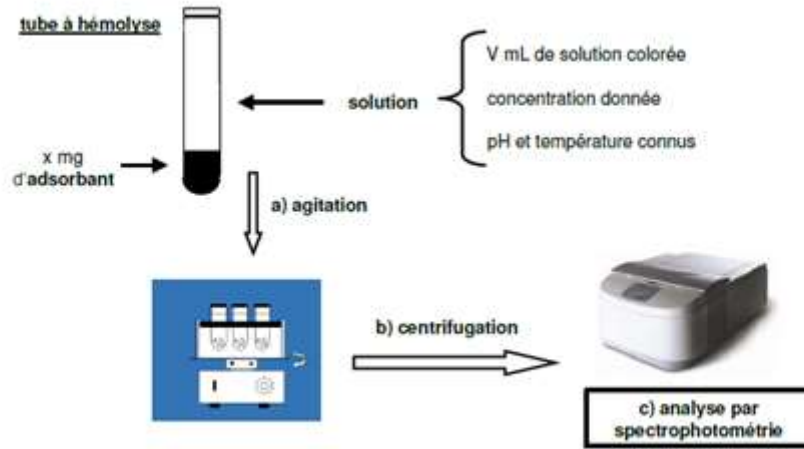
The tests were carried out by stirring 100 ml of solutions with different masses of biomaterial in beakers of 250 mL under constant stirring of 150 rev • min<sup>-1</sup> for 120 min at 25 ° C.

Solutions were separated from the lignin through a 0.45 filter membrane. The mixture was left on a mechanical shaker for 120 min.

2mL of each sample volumes were withdrawn, centrifuged and the residual concentration of chromium ions was determined.

Analysis by ICP / MS:

The concentration of chromium in the liquid phase was measured by an atomic emission with a spectrometer inductive- coupled plasma (ICP-AE; Liberty AX Turbo 150).



*Fig1. Static analytical method called batch*

**2.2.3. Evaluation of adsorptivity**

The amount of adsorption in equilibrium,  $q_e$  (mg / g), is calculated according to the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

Where  $C_i$  and  $C_e$  are the concentrations of Cr (VI) (mg / L) before and after adsorption, respectively,  $V$  is the volume in liters of the adsorbate and  $m$  is the mass of the adsorbent expressed in grams. The percentage removal of Cr (VI) ions was calculated from the following equation:

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

**RESULTS AND DISCUSSION**

**3.1. Design of Experiments**

**3.1.1. Studied process parameters**

In order to plan our experiments, the full factorial design at two levels is the simplest to implement. Its experimental matrix is denoted  $2^k$ , where  $k$  is the number of factors studied (here  $k = 3$ ). The number of experiments to be performed is equal to  $2^3 = 8$ .

Levels and process parameter ranges studied (A, pH B - initial concentration of Cr (VI) ( $C_0$ ) and C - adsorbent dose (m)) affecting the elimination of chromium used in the experiment are given in Table 1.

*Table 1: factorial adsorption of chromium (VI) on the adsorbent*

Variables	Symbol	Domain and level	
		-1	+1
Hydrogen potential pH	A	2	8
Initial concentration $C_0$ (mg L-1)	B	10	25
Adsorbent dose (g)	C	0.1	0.5

**3.1.2. Matrix of the experimental design.**



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The experience matrix below (Table 2) summarizes the experimental conditions and the response obtained for each experiment.

**Table 2: Response matrix for the removal of Cr (VI)**

1	1,0	-1,0	1,0	68,1
2	1,0	-1,0	-1,0	18,5
3	-1,0	-1,0	-1,0	74,6
4	-1,0	-1,0	1,0	96,7
5	-1,0	1,0	-1,0	45,5
6	-1,0	1,0	1,0	71,2
7	1,0	1,0	1,0	37,4
8	1,0	1,0	-1,0	20,1
1	1,0	-1,0	1,0	68,1
2	1,0	-1,0	-1,0	18,5
3	-1,0	-1,0	-1,0	74,6
4	-1,0	-1,0	1,0	96,7
5	-1,0	1,0	-1,0	45,5
6	-1,0	1,0	1,0	71,2
7	1,0	1,0	1,0	37,4
8	1,0	1,0	-1,0	20,1

### 3.2. Data and statistical analysis:

#### 3.2.1. The regression equation

The results were analyzed using the Statgraphics software.

The associated mathematical model full factorial design at two levels that can be applied is a linear regression model that takes into account the effect of factors and the effect of interactions. Its form:

$$Y = b_0 + b_1 A + b_2 B + b_3 C + b_{12} AB + b_{13} AC + b_{23} BC \quad (3)$$

Y is the response variable  $b_0, b_1, b_2, b_3$  are the linear coefficients,  $b_{12}, b_{13}, b_{23}$ , are the terms of second order interaction.

A, B and C are, respectively, the encoded scale factors studied following parameters: pH, initial concentration and adsorbent dose

Using multiple regression coefficients of equation (3) was estimated, and gave the following equation:

$$R_e(C_r) = 53,1 - 17,175 \times pH - 9,675 \times C_0 + 13,55 \times m + 2,55 \times pH \times C_0 + 3,225 \times pH \times m - 2,925 \times C_0 \times m \quad (4)$$

#### 3.2.2. Analysis of variance (ANOVA).

**Table 3: Analysis of Variance for Re (Cr)**

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:pH	2359,84	1	2359,84	13110,25	0,0056
B:Co	748,845	1	748,845	4160,25	0,0099
C:m	1468,82	1	1468,82	8160,11	0,0070
AB	52,02	1	52,02	289,00	0,0374
AC	83,205	1	83,205	462,25	0,0296
BC	68,445	1	68,445	380,25	0,0326
Total error	0,18	1	0,18		
Total (corr.)	4781,36	7			

R-squared = 99.99%

R-squared (adjusted for D. F.) = 99.97%

Mean absolute error = 0.15

The probability p is less than 0.05, indicating that the model terms are significant at the 95% probability level. The "Pred R-Squared" of 0.9918 is in reasonable agreement with the "Adj R-squared" of 0.9988. "Adeq

#### 3.2.3. Pareto Chart

The Pareto chart illustrates the variable order of importance affecting the adsorption of Cr (VI).



The effect of variables can be estimated from their sign (+ or -) and magnitude. There are two potential variables (pH and the initial concentration of Cr (VI)), which has a negative sign and the other variable (assay biosorbent,) has a positive sign

Figure.2 shows the pH parameter has the highest significance level.

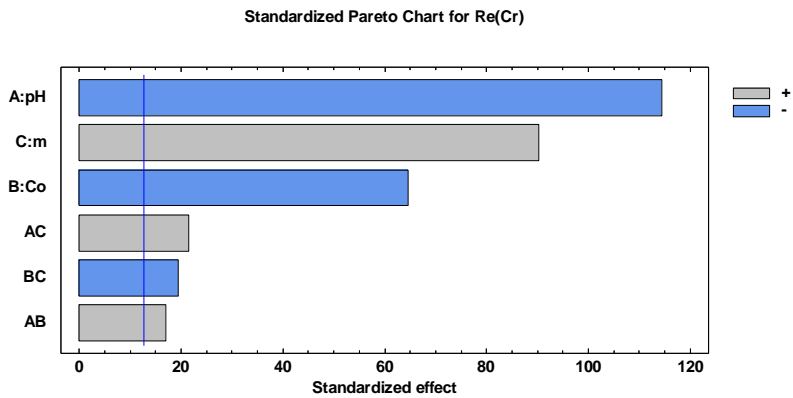


Figure.2 Pareto Chart

### 3.3. Optimal experimental conditions for the adsorption of chromium

A response surface methodology based on the development of a factorial design was used to optimize the treatment

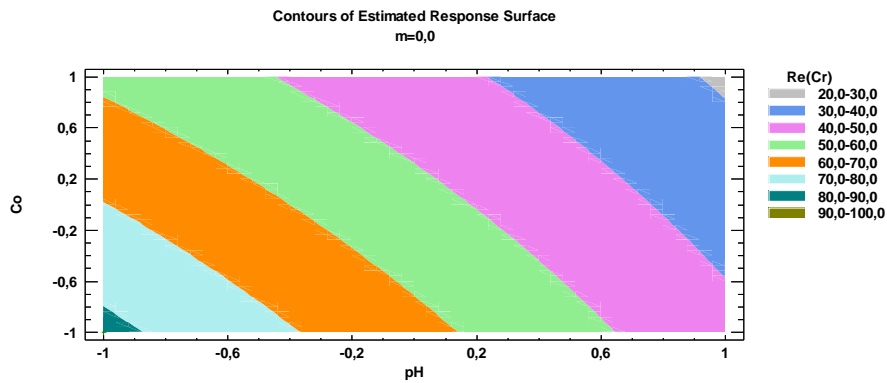
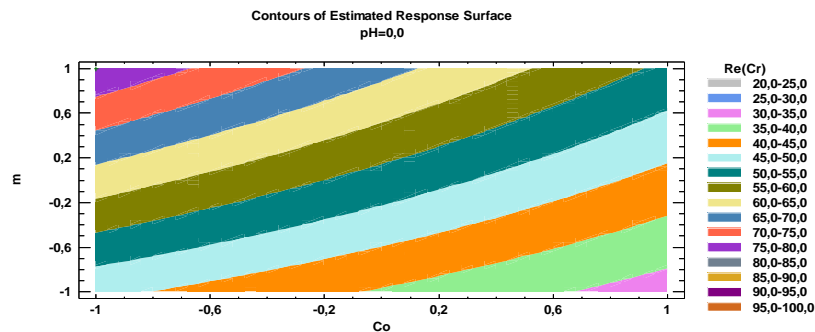
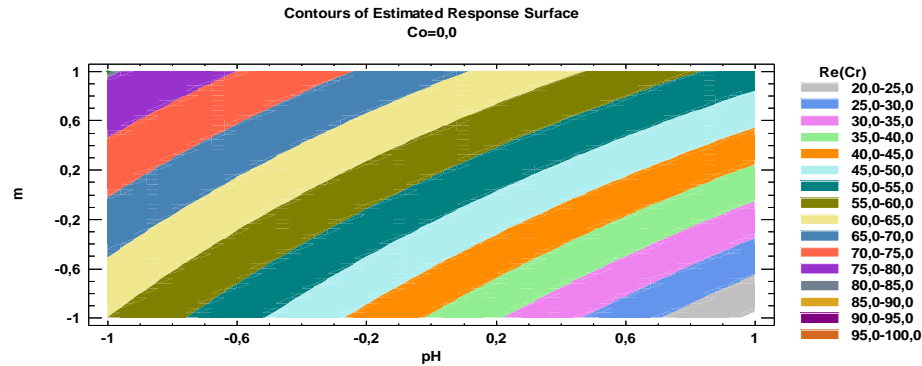


Figure.3



The optimal conditions for the removal of Cr (VI) from the aqueous solution with the biomaterial are:  
Initial concentration of Cr (VI): 10 mg / L, pH: 2.00,  
The adsorbent dose:  $m = 0.50$  g.  
Under these conditions, the maximum removal of Cr (VI) is 96.725

### 3.4. Mechanisms adsorption

#### 3.4.1. Effect of pH on the removal of chromium ions

The ionic form of chromium as well as the charge of the biomaterial surface play an important role in the adsorption phenomenon.

These two states are directly related to the pH value.

The pH of the aqueous solutions is an important parameter in controlling the adsorption of heavy metals methods.

To elucidate the role of net charge on the surface of the adsorbent in the dye fixation, we proceeded to determine the zero point or pHPZC charge.

##### 3.4.1.1. Point of zero charge

The pHPzc or pH of zero or zero charge corresponds to the pH value, for which the net charge of the adsorbent surface is zero (the amount of negative charges on the adsorbent surface of exactly the amount positive charges). [11]

This parameter is very important in the adsorption phenomena, especially when the electrostatic forces are involved in the mechanisms.



The pH<sub>pzc</sub> is the point where the final pH curve as a function of the initial pH cut the line of :

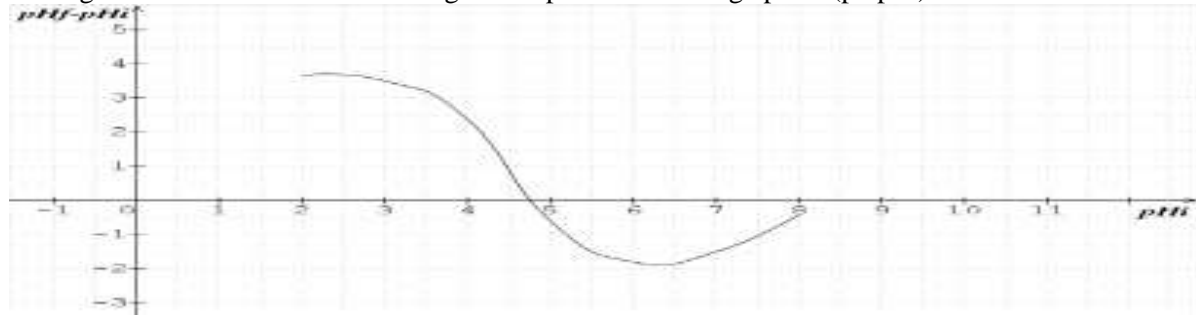
Final pH = initial .pH

The pH at the charge of zero was measured at different initial pH (2-8).

*Table 4. Comparison between the initial and final pH*

initial pH	final pH
2,00	5,67
3,00	5,50
4,00	5,37
5,00	4,40
6,00	4,0
7,00	5,5
8,00	7,6

The figure below shows the curve to give the pH of zero charge point (pH<sub>pzc</sub>).



*Fig 6. pH of zero charge of biomaterial (experimental conditions: adsorbent dose: 0.5 g in 1L, Temperature: 25 ° C)*

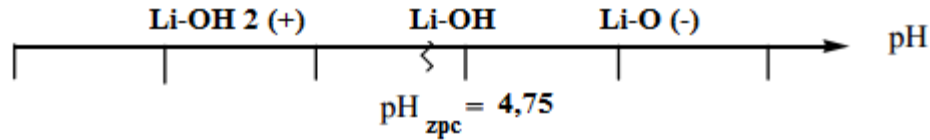
### 3.4. 1.2. Surface charge

The presence of functional groups on the polymer results in both positive and negative charges. The surface charge is usually defined by the value of the zero charge point of pH (zero load) or pH (pH<sub>pzc</sub>). The adsorbent acts as a neutral pH of zero charge.

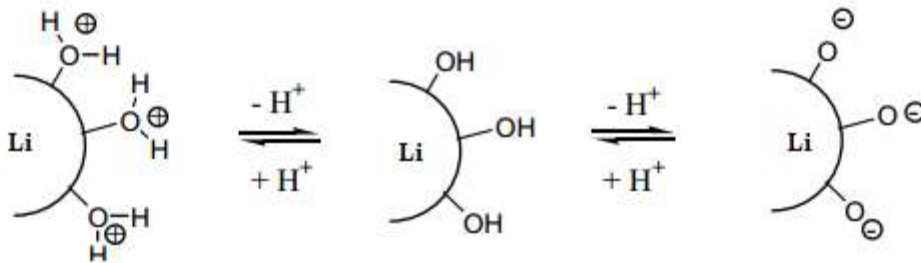
This quantity indicates when:

- pH = pH<sub>pzc</sub> the surface is electrically neutral because Li-OH type surface groups are the predominant form and the ionic forms LiO<sup>-</sup> and LiOH<sub>2</sub><sup>+</sup> compensate each.
- pH > pH<sub>pzc</sub> is the anionic form LiO<sup>-</sup> dominating over others,
- pH < pH<sub>pzc</sub> is the cationic form LiOH<sub>2</sub><sup>+</sup> dominates over the others.

It is possible to establish the predominance diagram species of lignin as a function of pH,



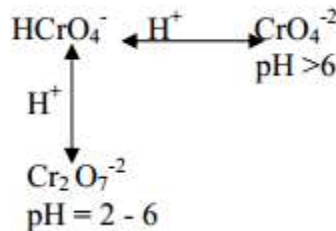
Scheme (1): Diagram predominance lignin species vs. pH



Scheme (2): Charging biomaterial surface in function of pH.

The adsorption of anions is favored at  $\text{pH} < \text{pH}_{zpc}$  [13].

Depending on the pH of the solution, the hexavalent chromium Cr (VI) can exist mainly in: chromate ( $\text{CrO}_4^{2-}$ ) or ( $\text{Cr}_2\text{O}_7^{2-}$ ) and hydrogen chromate ( $\text{HCrO}_4^-$ ) according to the equation: [15,16]



Ionic size  $\text{HCrO}_4^-$  is less than  $\text{Cr}_2\text{O}_7^{2-}$  [16]. Therefore,  $\text{HCrO}_4^-$  ions were released and easily absorbed on the surface of lignin, relative to  $\text{Cr}_2\text{O}_7^{2-}$  ions.

The speciation diagram for chromium (VI) can be obtained using the reactions and the following equilibrium constants [17].

Equation	log K (25 °C)
$\text{HCrO}_4^- \leftrightarrow \text{H}^+ + \text{CrO}_4^{2-}$	-6.5
$2\text{HCrO}_4^- \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	1.52
$\text{HCrO}_4^- \leftrightarrow \text{H}^+ + \text{Cr}_2\text{O}_7^{2-}$	0.07

At pH 2, the surface of the biomaterial is highly protonated. This leads to a net positive charge on the surface which enables electrostatic interaction with the predominant anionic form of Cr (VI), ie  $\text{HCrO}_4^-$  [14]. However, the percentage removal of Cr (VI) by the biomaterial gradually decreased as the pH increases. With increasing pH from 3.0 to 8.0, the degree of protonation on the surface of the biomaterial is gradually reduced and consequently the elimination of reduced chromium.





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It may be observed that from  $\text{pH} > 6$ , a  $\text{HCrO}_4^-$  ion transition to  $\text{CrO}_4^{2-}$  occurred. In the field of basic pH, the material used has a low adsorption capacity of chromate ions. This could be due to the presence in the solution of  $\text{OH}^-$  ions and  $\text{CO}_3^{2-}$  which reduce the number of sites accessible to these anions. It can be concluded that the active form of Cr (VI) that can be absorbed by the lignin in this study is  $\text{HCrO}_4^-$ .

### 3.4.2. Initial influence concentration

The adsorption equilibrium was found to be dependent on the initial concentration

It was found that the adsorption of hexavalent chromium on lignin was strongly dependent on the initial values of metal ion concentration; the results indicate that eliminating the hexavalent chromium content decreases as the concentration of the initial hexavalent chromium increased. A low initial concentration of hexavalent chromium adsorption sites available were easily occupied by hexavalent chromium, which lead to higher removal efficiencies. However, as the concentration of the initial hexavalent chromium has increased, most of the adsorption sites available became occupied, which leads to a decrease in removal efficiency. The Pareto chart of Figure 2 also shows that the initial concentration of the chromium solution has a significant effect among the studied factors.

### 3.4.3. Effect of the mass of the adsorbent

The influence of the mass of the adsorbent was studied in the range 0,1 - 0,5 g. The percentage removal of Cr (VI) from the aqueous solution has increased significantly (45-50)% to (90-95)% when the mass of the biomaterial has increased from 0.1 to 0.5 g.

It is well known that increasing the dose of adsorbent increases the availability of adsorption sites for the adsorbent-adsorbate interactions. However, the quantities of chromium ions must be in accordance with the adsorbent doses in the solution to ensure an equivalent number of adsorption sites.

Beyond a certain mass, the adsorption capacity decreases slightly possibly indicating the presence of another type of interaction between chromium ions and biomaterial. It is therefore useful to work with adsorbent doses  $\leq 0.2$  g and avoid inefficient overdose. [18]

## CONCLUSION

The following major conclusions can be drawn on the basis of the above study:

- The method of the design of experiments was adapted here in order to model the adsorption capacity of hexavalent chromium in aqueous medium as a function of pH, the initial concentration of the metal and the adsorbent dose.
- Removal of Cr (VI) from aqueous solutions depends strongly on the pH of the solution, of the dose of adsorbent and the initial concentration of Cr (VI).
- The highest removal efficiency was about 96% chromium.

The maximum adsorption capacity for the hexavalent chromium has been found to about 19.5 mg g<sup>-1</sup> in an acid medium. In addition, the adsorption capacity of the biomaterial was found comparable to that of low cost commercially available adsorbents that are used for the removal of Cr (VI) from aqueous solution and confirms the feasibility of using eucalyptus bark as an adsorbent for the removal of Cr (VI).

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