Bio-Reduction of Hexavalent chromium using *Punica Granatum* leaves: optimization, kinetic and thermodynamic study

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Abstract

This work is focused on the study of the bio-reducing capacities of the Punica granatum leaves in the removal of Cr(VI) using a well-defined factorial experimentation plan. Bioreduction tests were performed according to the Batch method, studying the influence of some experimental variables such as the mass of the bio-reducer, the temperature of the mixture, the pH of the solution and the initial concentration of Cr(VI). Molecular absorption spectrophotometry (UV-Vis) was used as the Cr(VI) assay method.

This study showed optimal Cr(VI) bio-reduction at an initial Cr(VI) concentration of 100 mg. L^{-1}, for a bio-reducer mass of 0.150 g, at pH = 1 and at T = 55°C. A total reduction of Cr(VI) was observed after 10 minutes of contacting the latter with the biomass. The bio-reducer was characterized by spectroscopy (FTIR) using a Shimadzu-8700 spectrometer and by scanning electron microscope analysis (SEM-EDX) type Quanta 250. The modelling study showed that the bio-reduction kinetics obeyed the pseudo-second-order model with R^2 of 0.99992. The thermodynamic study revealed that the bio-reduction process is endothermic, spontaneous and has a stable configuration.

Keywords: Bio-Reduction, Cr(VI), *Punica Granatum* Leaves, Kinetics, Thermodynamics.

Introduction

Pollution of water resources by heavy metals threatens present and future life; it is essentially of natural origin, scientists have pointed to the volcanic activity of planet earth, volcanic materials are among the largest natural polluters, moreover, a fairly significant part of the pollution of the planet is of anthropic origin, mainly due to human activity (industrial effluents, agriculture, maritime transport and other activities). Heavy metals are toxic and non-biodegradable; bioaccumulation explains their very high toxicity[1].

There are serious environmental and health problems for human beings, so the levels of heavy metals must be rigorously controlled[2]. Cadmium, lead, arsenic and chromium are the most well-known mineral contaminants in aquatic systems and soils[3], Cr(VI) can be derived from a variety of anthropogenic activities including chromite mining, leather tanning, electroplating synthesis and electrolytic chroming, wood preservation, or else the stainless steel industry[4,5] Significant quantities of chromium are thus released into the environment; discharge waters may contain a wide range of chromium concentrations resulting in a threat to humans[6]. In solution, chromium can exist mainly in two stable oxidation states, Cr(III), ($Cr(OH)^{2+}$ or $Cr(OH)_2^{+}$ and Cr(VI) ($HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$)[7,8].

Its reduced form can form highly stable and insoluble precipitates and is considered chemically inert[9]. Cr(VI) is very toxic and highly soluble in water throughout the pH range; this solubility gives it great mobility in ecosystems so that pollution with Cr(VI) can then affect a much larger area[10]. Hexavalent chromium compounds cross biological membranes more easily compared to trivalent compounds and Cr(VI) is 500 times more toxic than Cr(III)[11]. Studies have shown that Cr(VI) ions can indeed cause chronic mutagenic disorders[12]. The methods used to treat releases polluted by Cr(VI), generally aim to reduce it to Cr(III). WHO has limited Cr(VI) in water to 50 $\mu g.L^{-1}$13. During various industrial processes the generation of Cr(VI) is created by the oxidation of Cr(III) and is rejected as industrial waste[14].

Various methods have been used by many researchers to control Cr(VI) water pollution, such as chemical precipitation, membrane separation, ion exchange and evaporation, which are still too expensive, especially when used to treat large waste streams[15] and are not effective at concentrations between 1 and 100 mg. L^{-1}16. Many research works are attempting to harness the self-regenerative capabilities of nature, decontamination technologies based on bio-reduction have proven to be a promising approach due to their low cost, cost-effectiveness and environmental friendliness, Cr(VI) is reduced to Cr(III), using the olive stones[17], various bacteria such as *Pseudomonas stutzeri*[18], microbial cellulose[19], the green microalga[20], the yeast strain[21].

In the present work, we have set ourselves the objective of carrying out a study on the valorization of a component of pomegranate (*Punica granatum*) using it as a biomaterial. *Punica granatum* has exceptional properties, which would be explained by the particular composition of its different parts due to the proven antimicrobial, antiviral, anticancer, antioxidant and antimutagenic effects of fruits.[22] It contains polyphenols, ellagic tannins and gallic and ellagic acids[23].

The results obtained in this work have highlighted the bio-reduction of Cr(VI) by the leaves of *Punica granatum*, its ability to remove chromium has never been studied and we were able to achieve 100% yields after just one hour of contact. Biomass of 0.150 g made it possible to reduce 50 ml of a 100 $mg.L^{-1}$ Cr(VI) solution in a strongly acid medium and a temperature of 55° C.

Material and Methods

Preparation of the Cr(VI) stock solution: The 1000 $mg.L^{-1}$ stock solution of Cr(VI) was prepared from the dissolution of analytical grade sodium dichromate ($Na_2Cr_2O_7.2H_2O$) in distilled water. All other concentrations were obtained by dilution.

Preparation of the bio-reducer: *Punica granatum* leaves underwent four essential sequences which are harvesting, drying, grinding and sieving; these samples came from the region of Annaba (Algeria); the drying was carried out in the shade at room temperature for three weeks. Once dry, the bio-reducer is crushed and sieved using an appropriate mesh sieve.

General Bioreduction Experimental Protocol: Molecular absorption spectrophotometry (UV-Vis) was used as an analysis method, Cr(VI) was determined after reaction with 1, 5- diphenylcarbazide in acidic medium, we used a SPECORD 200 plus UV-Vis double beam spectrophotometer, to measure the absorbance of the complex formed at λ = 540 nm[24]. Total chromium was determined by atomic absorption spectroscopy at λ = 357.9 nm using an AAS WFX-130B and the Cr(III) solution content was obtained under optimal conditions by subtracting the Cr(VI) from the total chromium.

All the bio-reduction tests were carried out according to the Batch method, the latter consisting of placing a well-defined mass of bio-reducer in beakers in contact with 50 ml of a Cr(VI) solution, the solutions are placed in a thermostatically controlled bath with electronic temperature control, the whole is kept at a constant temperature and with stirring, the variation of the Cr(VI) concentration was monitored for 60 minutes, the results obtained made it possible to establish the dependencies: Cr(VI) reduction rate as a function of time [R(%) =f(t)].

$$R\ (\%) = [(C_0 - C_e) / C_0]\ 100$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) ($mg.L^{-1}$).

Results and Discussion

Influence of the bio-reducer mass: The tests were carried out using different masses of bio-reducer ranging from (0.025g -0.150g). In a series of beakers were introduced: 50 ml of a Cr(VI) solution at 30 $mg.L^{-1}$ and well-defined mass of the bio-reducer studied, the whole was placed in a bath thermostated at 25°C and kept under fixed agitation. This study has shown that a reduced rate of about 77.40% reached 10 minutes after bringing a solution of Cr(VI) in contact with 0.150 g of pomegranate leaves, an hour later, a rate of about 90% is observed. The results obtained during this study allow us to deduce that an optimal mass of 0.150 g of the bio-reducer allows reducing almost all the Cr(VI), the more important is the mass of the bio-reducer, the faster the bio-reduction is (Fig. 1).

Effect of pH: The study of the effect of solution pH on the reduction of Cr(VI) by the leaves was carried out according to the same operating protocol as previously. The tests were carried out at different pH levels (1, 2, 3, 4, 5 and 6), with an optimal mass of (0.150 g) of the bio-reducer (Fig. 2). This study confirms faster kinetics in a strongly acidic medium (pH=1), the whole amount of Cr(VI) is practically reduced after a contact time of 10 minutes and a similar rate was observed at pH=2. From a kinetic point of view, a strongly acidic medium favours a rapid reduction of Cr(VI) ions.

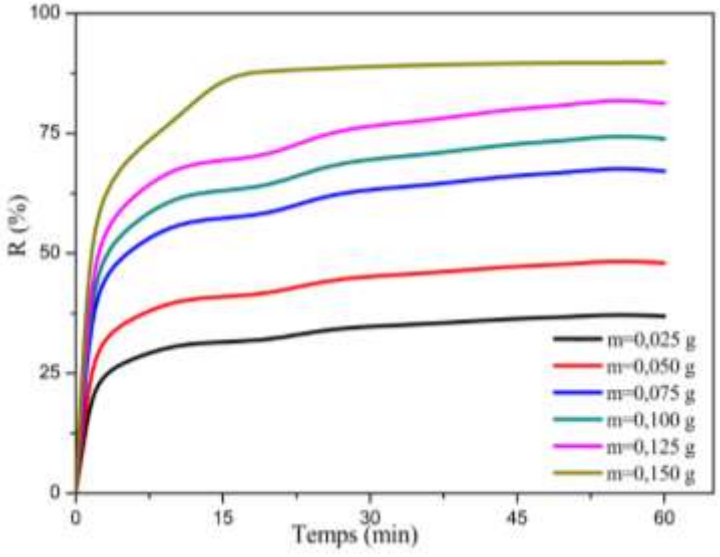

Figure 1: Effect of Punica granatum leaves mass on the bio-reduction of Cr(VI) ($T=25°C$, C_0 =30 $mg.L^{-1}$)

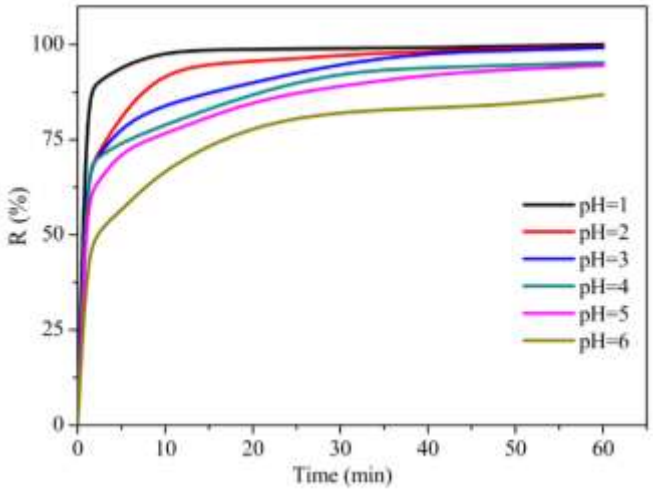

Figure 2: Effect of pH of the solution on the bio-reduction of Cr(VI) by Punica granatum leaves ($T = 25\ ^\circ C$, $m = 0.150$ g, $C_0 = 30 mg.L^{-1}$)

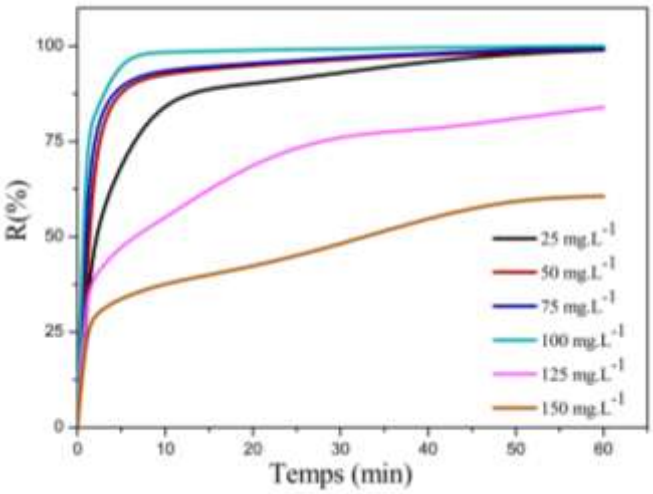

Figure 3: Effect of initial concentration of Cr(VI), on the reducing power of Punica granatum leaves (T=25°C, m= 0.150 g, pH =1)

Effect of Initial Cr(VI) Concentration: Different solutions of Cr(VI) were prepared in a range of concentrations varying between 25 and 150 $mg.L^{-1}$. Contacting an amount of 0.150 g of pomegranate leaves with Cr(VI) solutions at pH=1 with varying concentrations between (25 and 100) $mg.L^{-1}$, gives a very high Cr(VI) reduction rate close to 100 %. A C_0 concentration higher than 100 $mg.L^{-1}$, Cr(VI) is reduced drastically and the reducing capacity of the studied biomass is very much affected. The reduction rate observed for C_0 = 150 $mg.L^{-1}$ does not exceed 60 % after one hour (Fig. 3).

Temperature effect: The bio-reduction tests were carried out at different temperatures (25°C - 55°C) on a Cr(VI) solution of C0= 100 $mg.L^{-1}$, in strongly acidic media (pH=1) (Fig. 4).

The study of temperature effect on the reducing power of pomegranate leaves revealed that the best results were observed in the temperature range (45°C - 55°C), after a contact time of 5 to 10 minutes. The reduction rate of Cr(VI) reached 100% at a temperature of 55°C with better kinetics.

Optimal conditions: The results obtained following the various bio-reduction tests on Cr(VI) removal are very encouraging; we were thus able to achieve very high yields reaching 100% after one hour of contact. All the physicochemical parameters likely to interfere with the yield of Cr(VI) bio-reduction have been studied; it appears that a strongly acidic pH and a temperature of 55°C promote the reduction process (Fig. 5).

Characterization of the bio-reducer

Fourier transform infrared spectroscopy (FTIR): *Punica granatum* leaves were characterized by Fourier transform infrared spectrophotometry (FTIR), using a Shimadzu-8700 spectrometer. The spectra of the studied bio-reducer are gathered in fig. 6. The studied biomass contains several types of compounds: polyphenols, flavonoids, alkenes, aliphatic fluorinated compounds, alcohols, ethers, carboxylic acids, esters and nitro compounds linked to hydrogen[25]. The FTIR spectrum of leaves that have not been in contact with a Cr(VI) solution shows a large peak between 3000 and 3600 cm^{-1}; corresponding to the stretching

vibration of the hydroxyl and amino groups, the change in position of this peak after bioreduction of Cr(VI), indicates the binding with the metal and the increase of the hydroxyl and amino group on the leaves.

The bands between 2850 and 2980 cm^{-1} are attributed to the stretching vibrations of the alkyl groups, the peak was observed at about 1730 cm^{-1} characteristic of the C = O frequencies of the carboxylic or ester groups; The absorption peaks observed at 1615 and 1515 cm^{-1} are assigned respectively to the C = O of the amide I and amide II stretching band and the region between 1300-1450 cm^{-1} corresponds to the deformation stretching of the CH_2 and CH_3 groups, it was foreseen that the Cr(VI) must have undergone bio-reduction via complexation with a carboxyl or hydroxyl or amide functional group of the biomass by coordination with metal cations[26], a weakening of the peak around 1030 cm^{-1} characteristic of a vibration band of the amino functions and a decrease of the alkyl groups with the addition of chromium.

Scanning Electron Microscopy (SEM-EDX): A Quanta 250 scanning electron microscope coupled with energy dispersive X-ray spectroscopy (EDX) was used to study the leaf surface morphology of *Punica granatum*, SEM analysis showed that the surface of the natural leaves without the addition of Cr(VI) (Fig. 7), appeared to be smooth with a relatively regular shape; *Punica granatum* leaves brought into contact with the Cr(VI) solution underwent cell destruction (Fig.7). Change in cell morphology could be a mechanism adopted to resist Cr(VI) toxicity. A similar observation was also reported by XU et al.[27] The elemental composition of the leaves before and after the addition of Cr(VI) was determined by energy dispersive x-ray analysis (EDX). The main components are carbon, oxygen and minor amounts of Al, Si, Cl, P, K, Ca, Mg, Cu and Fe (Fig. 8).

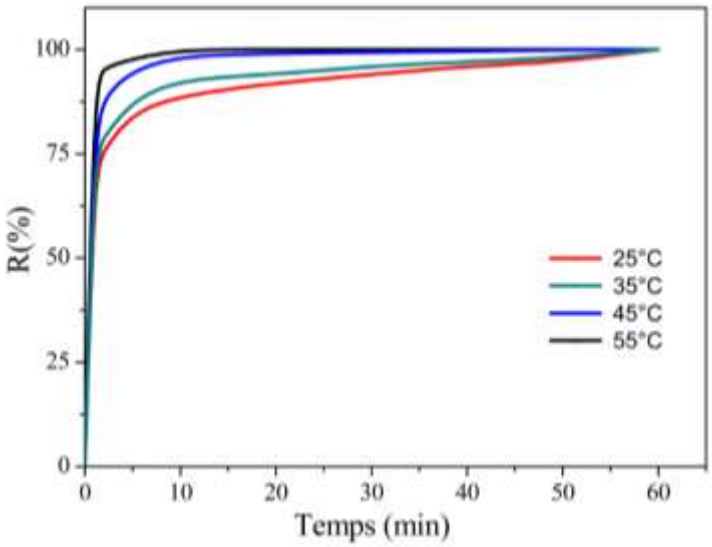

Figure 4: Effect of temperature on the bio-reduction of Cr(VI) by *Punica granatum* leaves (m=0.150 g, pH=1, C_0 =100 $mg.L^{-1}$)

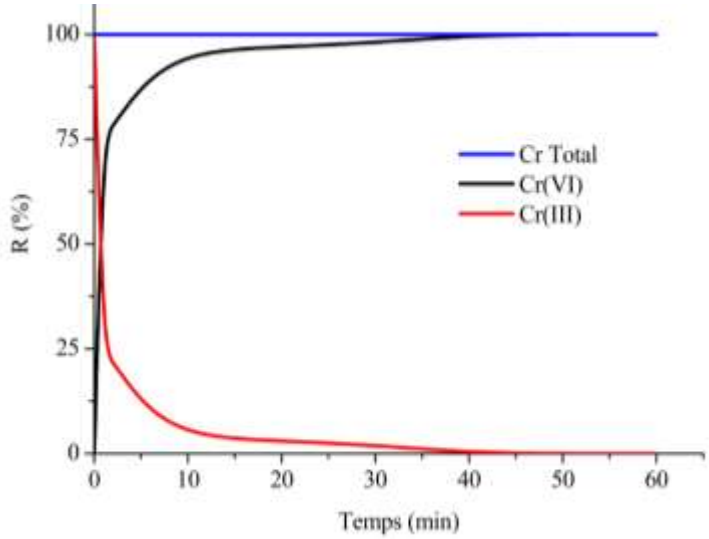

Figure 5: Optimal conditions for bio-reduction of Cr(VI) by *Punica granatum* leaves (m=0.150 g, pH=1, C^0 =100 $mg.L^{-1}$, T = 55°C)

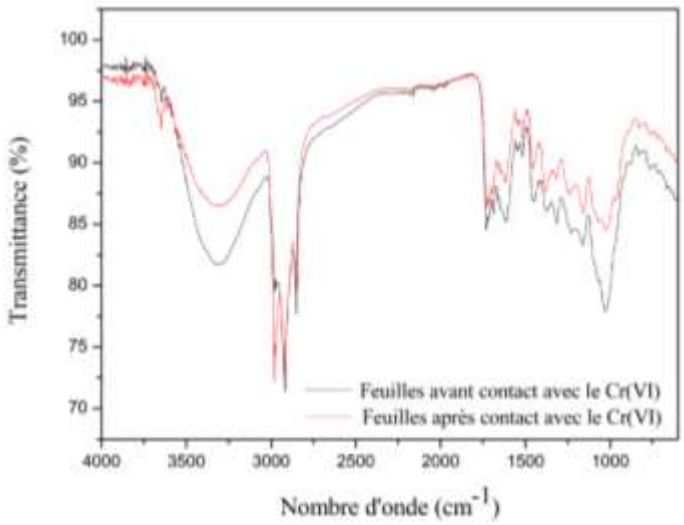

Figure 6: FTIR spectra of *Punica granatum* leaves before and after contact with Cr(VI) solution

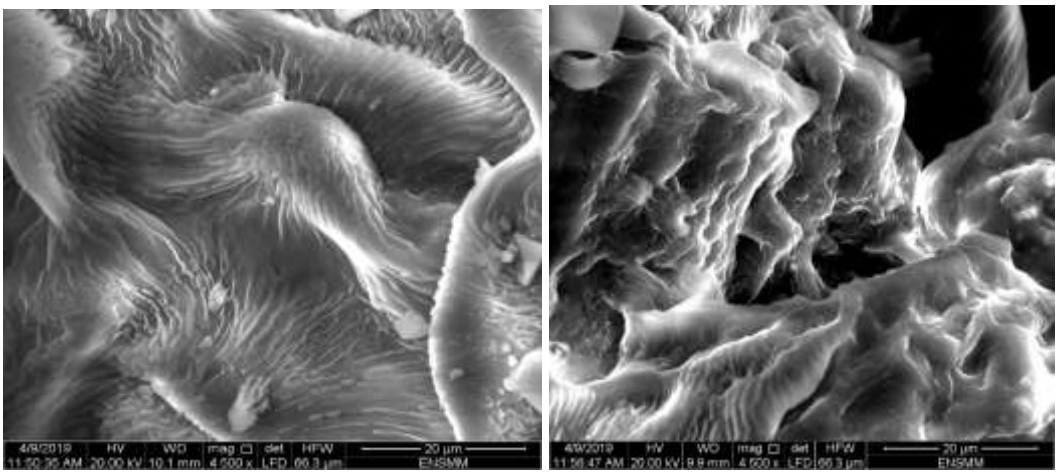

Figure 7: SEM image of *Punica granatum* leaves before and after contact with Cr(VI)

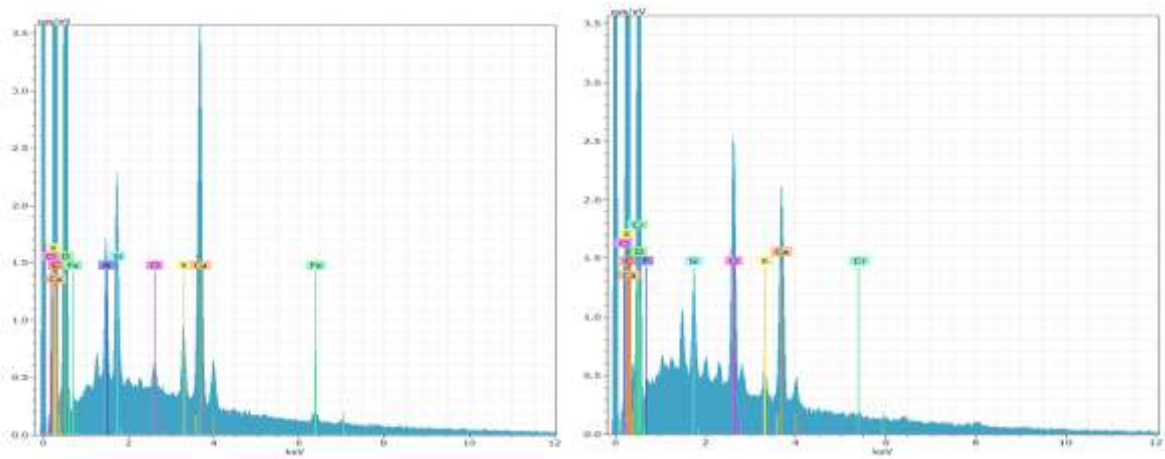

Figure 8: EDX spectrum of Punica granatum leaves before and after contact with Cr(VI)

EDX analysis showed that the reduction of Cr(VI) by the leaves is effective because the peak intensity of P and K peaks in the spectrum has decreased; however, the chromium peak is confused with the background noise. Chromium may be present as a crystalline structure and therefore cannot be detected (Fig. 8).

Modeling bio-reduction kinetics: It has been reported that the reaction takes place by complexation between functional groups on the surface of *Punica granatum* leaves and Cr(VI) ions[28]. To develop a kinetic model of the interaction, the reaction order is an important parameter for the determination of the reaction mechanisms. The reduction of

Cr(VI) by the biomass used was modelled using the equations given by Lagergren, pseudo-first-order, eq. 1[29] and the pseudo-second-order model eq. 2[30].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (2)$$

The amount of Cr(VI) reduced was calculated according to equation 3:

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (3)$$

where q_e and q_t are reduced amounts ($mg.g^{-1}$) at equilibrium and time t respectively. k_1 is pseudo-first-order velocity constant (min^{-1}). k_2 is pseudo-second order adsorption rate constant ($g.mg^{-1}.min^{-1}$). t is contact time (min). C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) ($mg.L^{-1}$) respectively. V is volume of the solution (L) and m is the amount of bio-reducer used (g).[31,32].

The results of the pseudo-first-order and pseudo-second-order models are gathered in table I and illustrated in figure 9. Fig. 9 shows that the bio-reduction of Cr(VI) using biomass used follows the pseudo-second-order model with a correlation coefficient, R^2 of 0.99992, the theoretical values of q_e are better estimated by the pseudo-second-order model than by the pseudo-first-order model which suggests that the bio-reduction of Cr(VI) is dominated by a chemical process.

Thermodynamic parameters: The thermodynamic parameters of chromium (VI) bioreduction by *Punica granatum* leaves, Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) can be determined from the slope and intersections of the Van't Hoff representation, ln K relative to $1/T$[33] and were calculated using the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

$$\Delta G^0 = -RT \ln K \quad (5)$$

Combining equations (4) and (5), we obtain equation (6):

$$lnK = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

where K is equilibrium constant. C_{solid} is Concentration of Cr(VI) in the solid phase (biomass) at equilibrium. C_{liquid} is concentration of Cr(VI) in the liquid phase at equilibrium. T is absolute temperature (Kelvin) and R is the gas constant with a value of $8{,}314 J \cdot mol^{-1} \cdot K^{-1}$.

The results of the thermodynamic study (Fig. 10) show that Gibbs energy decreases with increasing temperature as shown in table II, all ΔG^0 values are negative, indicating that the interactions between Cr(VI) and the biomaterial studied are spontaneous, the positive enthalpy values ΔH^0 are consistent with the endothermic nature of these interactions, the entropy values ΔS^0 indicate that the bio-reduction process has a stable configuration.

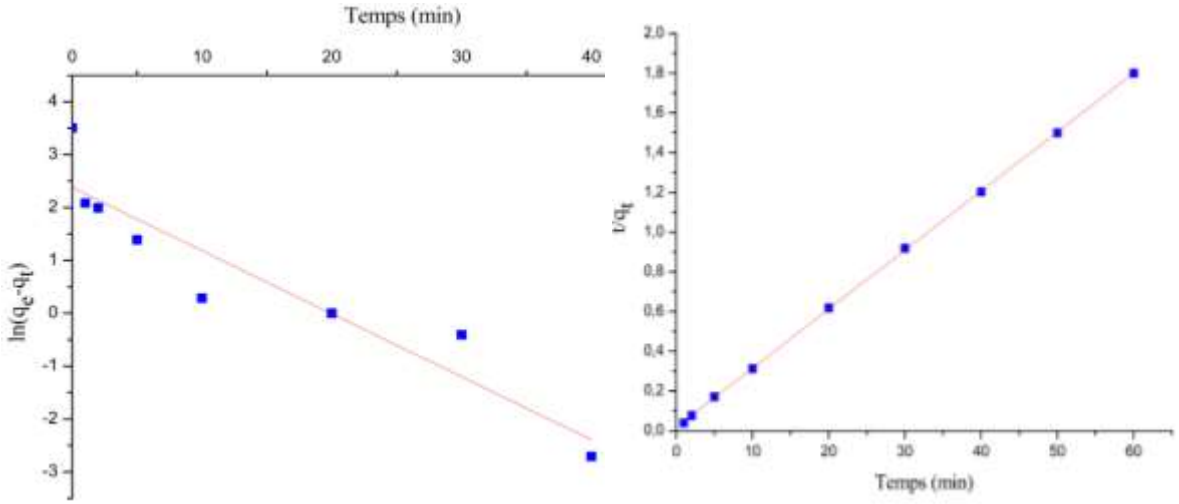

Figure 9: Pseudo-first-order kinetics and Pseudo second-order of bio-reduction of Cr(VI) by Punica granatum leaves

Table 1
Parameters of pseudo-first order and pseudo-second-order models of Cr(VI) bio-reduction by Punica granatum leaves

Pseudo first order					Pseudo second order		
C_0 ($mg \cdot L^{-1}$)	q_e théorique ($mg \cdot g^{-1}$)	q_e expérimentale ($mg \cdot g^{-1}$)	K_1 (min^{-1})	R^2	qe expérimentale ($mg \cdot g^{-1}$)	K_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2
100	33.33333	2.37747	0.11927	0.86117	33.65870	0.049339	0.99992

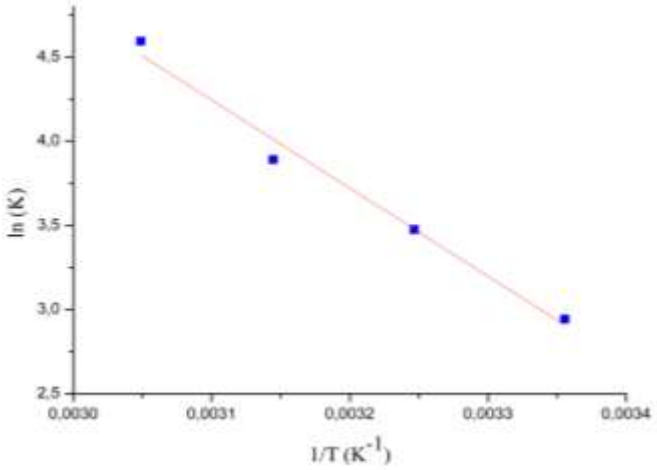

Figure 10: Van't Hoff plot for the bio-reduction of Cr(VI) by *Punica granatum* leaves

Table 2
Thermodynamic parameters of the bio-reduction of Cr(VI) by *Punica granatum* leaves

T(K)	Ln(K)	ΔH^0(kJ·mol^{-1})	ΔS^0(J·mol^{-1}·K^{-1})	ΔG^0(kJ·mol^{-1})
298	3.944438979	43.50695082	170,1627211	-50.66498395
308	3.47609869			-52.36661116
318	3.891820298			-54.06823837
328	4.59511985			-55.76986558

Conclusion

The results obtained following the various bio-reduction tests of Cr(VI) by Punica granatum leaves are very interesting; very appreciable yields of up to 100% were observed after one hour of contact with the Cr(VI) solution. All the parameters that may interfere with the yield of Cr(VI) bio-reduction have been studied and it has been shown that a strongly acidic pH and a temperature of 55°C promotes the reduction process. A mass of 0.150 g of *Punica granatum* leaves allows a total reduction of 50 ml of a 100 mg.L^{-1} Cr(VI) solution after one hour of contact time.

The thermodynamic study shows that Cr(VI) bio-reduction by *Punica granatum* leaves is thermodynamically favourable, endothermic, spontaneous and is accompanied by a decrease in Gibbs energy when the temperature increases. The possible follow-up of this work could consist of directing the research towards other selected components of the material.

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