



The adsorption of Cr (VI) from aqueous solution by natural materials

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Abstract

This study deals with the adsorption of chromium (VI) from the new natural materials from Morocco. The adsorbents used are characterized by different physic-chemical techniques: X-ray fluorescence spectrometry, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR). The effects of initial concentration of Cr (VI) ion, temperature, amount of adsorbent and pH of the solution on adsorption have been investigated. Optimum conditions for adsorption were determined as initial concentration of 100 mg/L, adsorbent dose=2g, and pH=2, by using the results of these experiments and an additional set of experiments was performed under these optimum conditions in order to see the change in the adsorption efficiency. Removal of chromium ion was found as highly dependent on pH and initial Cr (VI) concentration of the solution. The adsorption isotherms obey the Langmuir equation was obtained a maximum adsorption capacity of 15.67 mg/g and 14.43 mg/g, for the material KS and PN respectively. Although experimental data confirm with both Langmuir and Freundlich isotherm models. The results of this study confirm that these materials can be considered effective adsorbents for the removal of chromium (VI).

Keywords: Materials, Adsorption, Chromium (VI), Isotherm, Removal.

1. Introduction

The problem of pollution, in all forms, constitutes one of major concerns of our time, and in particular the pollution of the waste water which represents without any doubt one of the most worrying aspects of the total crisis of the environment, and arouses at the present time an private interest with the international scales [1]. Among the toxic pollutants, Chromium was the subject of many researchs and a very detailed attention in the last few years [2-4]. There exists mainly in nature in the form of derived and can be in a trivalent state (Cr^{III} chromite) or hexavalent (Cr^{VI} chromate and dichromate). Cr (VI) is very toxic but also very water soluble in this form. This solubility confers a great mobility in the ecosystems to him. He is regarded as one of the most toxic pollutants because of his carcinogenic and teratogenic properties on the human being [5-6]. It can be released in the environment by various industries, mainly the industry of the finishing of metals, the iron and steel industry and the production of inorganic chemicals [7]. The intensive use of this metal in industries involved great quantities of effluents poured in nature with raised concentrations, from where the need for a specific treatment of the rejections and a revision of the regulations concerning the contents of chromium present in water. The maximum value of chromium intended for human consumption is estimated at 0.1 mg.L⁻¹ according to U.S.EPA [8].

The traditional techniques of processing waste contaminated by chromium are numerous; one will quote in particular the techniques of membrane filtration [9], precipitation [10], the ions exchange and adsorption [11-12]. Adsorption is one of the simple, effective, economic methods and most useful for the removal of the pollutants of waste water. In this case, the solid material plays a very important part. Although, since antiquity, the development and the use of solid materials were one of the fundamental objectives of our world [1], it has

been only for a few years only that the development of new materials, in fact the porous materials, makes full great strides [13-17].

The aim of this work is to eliminate the chromium (VI) from the aqueous solutions by two natural materials: an ore “PN” of the Oriental area and clay “KS” of the Chaouia-Ouadigha area. The contact time, pH effect, initial Cr (VI) concentration, and adsorbent dose on the removal of Cr (VI) for all the adsorbate were investigated by batch experiments. The adsorption process was analysed using various kinetic and isotherm models.

2. Material and methods

2.1 Preparation of the adsorbent and methods of analysis

Before use, PN and KS materials was sieved to obtain a uniform material of <0.2mm particle size. They are used in a rough state without preliminary treatment. These materials are characterized by various physicochemical techniques: spectrometry of x-ray fluorescence [OXFORDMDX1000], diffraction of x-rays [Diffractometer X' PERT PRO on powder, of Panalytical equipped with a detector with scintillation X' Celerator High-speed, equipped with a copper anticathode ($\lambda = 1.5418 \text{ \AA}$)], IR with furrier transform [VERTEX 70]. The concentration of Cr (VI) is determined by spectrophotometry UV-screw [VR-2000].

2.2 Adsorption kinetics

An aliquot of 250 mL of Cr (VI) solution was placed in a 500 mL bottle to start the experiment. The initial metal ion concentration used in the test is 50 mg.L^{-1} . 0.5 grams of adsorbent was added to the solution and experiment was agitated with a speed of 150 rpm at a constant temperature for 6 hours.

The chromium removal (%) at any instant of time was determined by the following equation:

$$\text{Cr}(\%) = \frac{([C]_0 - [C]_t)}{[C]_0} \times 100 \quad (1)$$

Where, C_0 and C_t are the concentration of chromium at initial condition and at any instant of time, respectively. The amount of metal adsorbed at any time was calculated from:

$$q_t = \frac{([C]_0 - [C]_t)}{m} \times V \quad (2)$$

Where, q_t (mg.g^{-1}) is the adsorption capacity at time t , C_0 (mg.L^{-1}) is the initial concentration of the adsorbate; C_t (mg.L^{-1}) is the concentration of the adsorbate at time t ; V (L) is the volume of the solution; m (g) is the adsorbent mass.

2.3 Adsorption isotherms

For the determination of the adsorption isotherm, 0.1 g of the adsorbent was added into 50 mL glass flasks containing solutions of chromium concentration (50 - 250 mg L^{-1}). The time required for reaching the equilibrium condition, was estimated at regular intervals of time until equilibrium was reached (120 min). After the reaction period, the suspension was filtered through a filter paper (0.45 μm) and the supernatant was analysed for the Cr (VI) by concentration absorbance measurements in a UV-Vis spectrophotometer. The advance of the reaction was followed by the amount adsorbed at equilibrium, i.e. the adsorption capacity, q_e (mg.g^{-1}) was calculated according to the formula:

$$q_e = \frac{([C]_0 - [C]_e)}{m} \times V \quad (3)$$

Where q_e (mg.g^{-1}) is the equilibrium adsorption capacity; C_0 (mg.L^{-1}) is the initial concentration of the adsorbate; C_e (mg.L^{-1}) is the equilibrium concentration of the adsorbate; V (L) is the volume of the solution; m (g) is the adsorbent mass.

3. Results and discussion

3.1 characteristics of the adsorbents

The analyses carried out on natural materials (PN and KS), (Table 1) show that, the PN adsorbent contains significant amounts of silica (70.51%) and alumina (12.76%), but the adsorbent KS has a mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ almost is 1.

Table 1: Chemical composition of the natural materials PN and KS (%)

	Content (weight %)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI*
PN material	70,51	12,76	1,61	1,50	0,27	0,07	5,18	2,61	5,26
KS material	47,74	36,21	1,31	0,24	0,61	0,03	1,96	0,00	12,25

* Loss on Ignition at 1000 °C

Fourier Infra-Red spectrum of the two adsorbents PN and KS is given in Fig.1. The spectrum of PN material is characterized by the band at about 1004 cm⁻¹ corresponding to the stretching vibration of Si-O-Si, as well as the deformation band of Si-O located at 461 cm⁻¹.

The KS material presents the bands at 3685 and 3619 cm⁻¹ are attributed to the vibrations of silanol groups O-H, a bands about at 1114 cm⁻¹ corresponds to the vibration of Si-O, the stretching bands at 997 and 1024 cm⁻¹ are respectively attributed to symmetric and asymmetric of Si-O-Si, the vibration at 909 cm⁻¹ is attributed to the deformation of groups Al-OH, and the bands at 523 and 455 cm⁻¹ attributed respectively to the deformations of the connections Si-O-Al^{VI} and Si-O-Si [18-19].

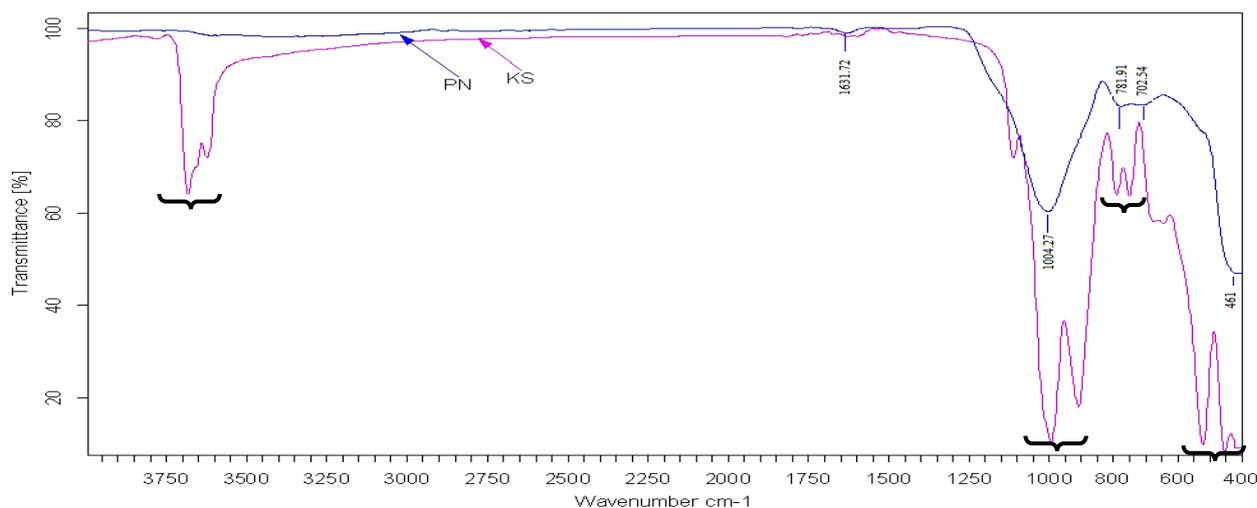


Figure1:FTIR spectra of PN and KS materials.

The XRD spectra for PN and KS materials are shown in Fig. 2. The examination of KS diagram shows that presents the characteristic peaks of kaolinite [Si₂O₅Al₂(OH)₄] at 2θ= 12.35° and 24.86° [20], the main peak of the illite [(K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)]] at 2θ = 8.84° [21] and the characteristic peaks of quartz (SiO₂) at 2θ= 26.71° [22]. But in the PN material, the spectrum appears as abroad band with a peak at 2θ = 22°, which indicates that the material is amorphous and contains pure SiO₂. [23-24].

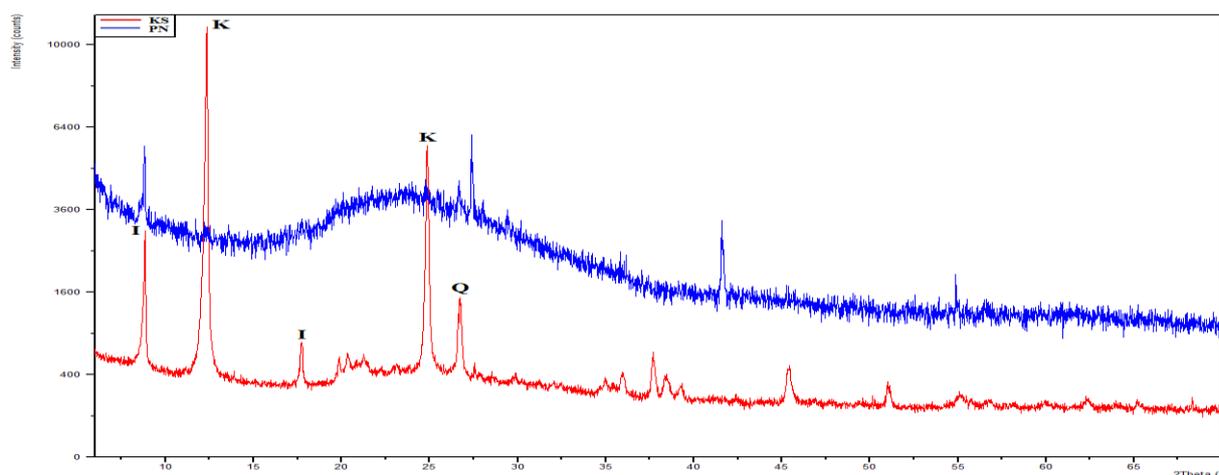


Figure2: XRD patterns of PN and KS materials (I=illite, K=kaolinite, Q=quartz).

3.2 adsorption kinetics of Cr (VI) ions by PN and KS materials

The following results of the adsorption kinetics of Cr(VI) by PN and KS are represented on the Fig. 3. They are composed on two parts, first is characterized by a slow increase in adsorption capacities of the ions of Cr (VI) during the first 120 minutes. The second part shows a stagnation signs of stabilization and saturation of material.

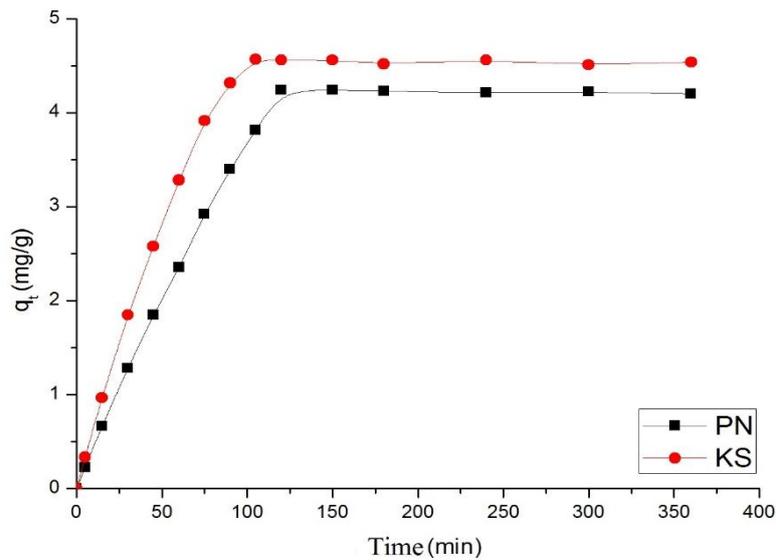


Figure3: Adsorption kinetics of Cr(VI) by PN and KS materials ($[Cr]_0 = 50 \text{ mg.L}^{-1}$, $pH_0 = 5.08$, $V = 250 \text{ mL}$, $m_{ads} = 2 \text{ g.L}^{-1}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$).

3.3 Optimum operating condition

3.3.1 Effect of adsorbent dose

The variations of dose from 0.5 g.L^{-1} to 5 g.L^{-1} for PN and KS materials are graphically represented in Fig. 4. The mass seems to exert an important influence on the adsorption process. Indeed, the adsorption capacity is strongly decreases when the mass of adsorbent increases 0.5 g.L^{-1} to 5 g.L^{-1} , this effect can be allotted to the increase in the surface of material and the active sites of adsorption [25].

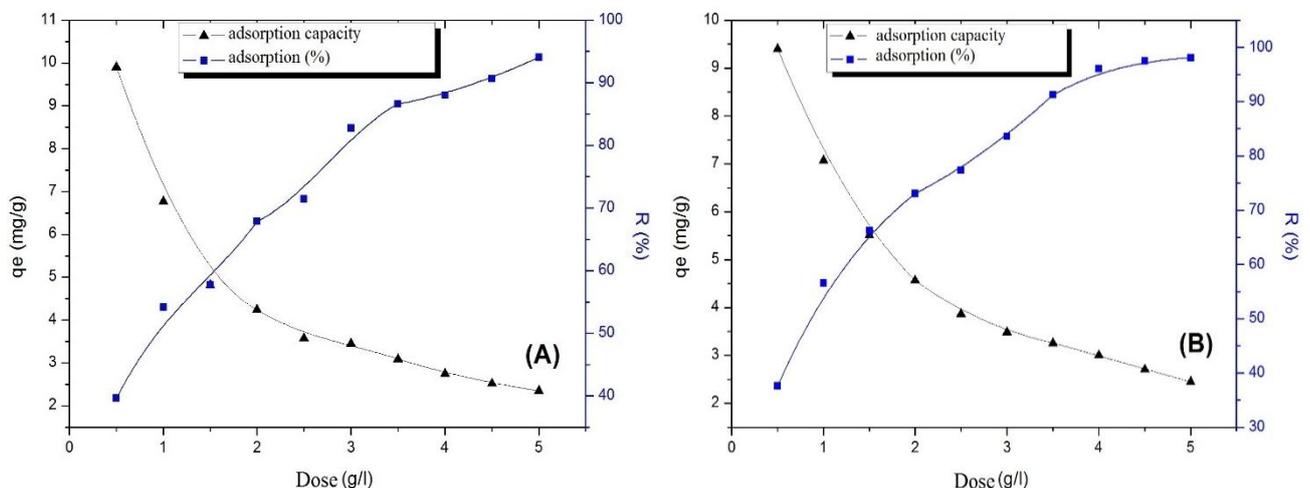


Figure4: Effect of adsorbent dose form PN (A) and KS (B) materials, ($[Cr]_0 = 50 \text{ mg.L}^{-1}$, $pH_0 = 5.08$, $t = 120 \text{ min}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$).

3.3.2 Effect of pH on Cr (VI) adsorption

The effect of the pH on the adsorption of Cr (VI) was carried out for 120 min time and 2 g.L^{-1} of dosing. The graphical representation effect of pH is shown in Fig. 5. In general, the adsorption of the metal ions on the adsorbent surface is depending the pH solution [26]. This shows that the adsorption of the Cr(VI) onto material is strongly pH dependent. The increase in Cr(VI) removal efficiency at pH 2 is due, at least in part, to the electrostatic force existing between the sorbent surface and Cr(VI) ions. A strong attraction will exist between these oxyanions of Cr(VI) i.e., HCrO_4^- and the positively charged surface of the adsorbent at low pH [27]. When the pH is increased, the adsorption capacities decrease gradually Fig. 5.

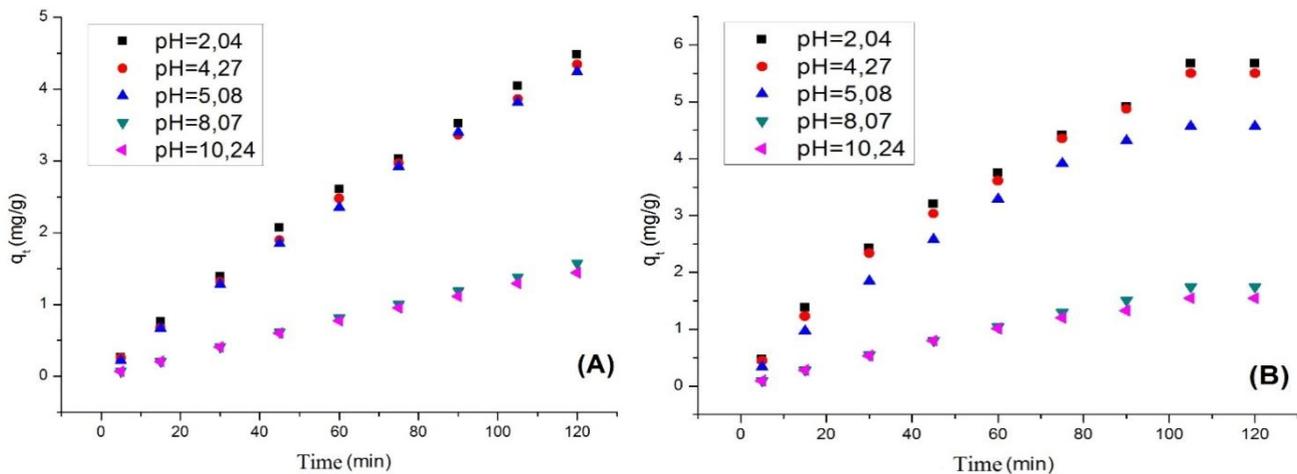


Figure 5: Effect of pH on Cr (VI) adsorption by PN (A) andKS (B) materials, ($[Cr]_0= 50 \text{ mg.L}^{-1}$, $V=250 \text{ mL}$, $m_{\text{ads}} = 2\text{g.L}^{-1}$, $T= 25\pm 2 \text{ }^\circ\text{C}$).

The Cr (VI) exists in various ionic forms in solution Fig. 6. Chromate ion (CrO_4^{2-}), dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$), hydrogen chromate ion (HCrO_4^-) or chromic acid (H_2CrO_4). The HCrO_4^- ions are most numerous in the solution compared to $\text{Cr}_2\text{O}_7^{2-}$ at $\text{pH} = 2 - 6$ and it are moreover small size [28]. At $\text{pH} < 2$, the molecular form H_2CrO_4 prevails in the solution as a species polycyclic anhydride is difficulty adsorbable by the pores of material. [29].

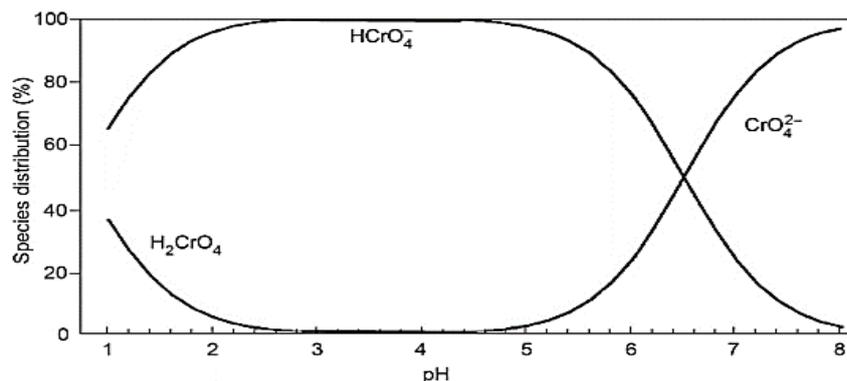


Figure 6: The distribution of the inorganic species Cr (VI) according to the pH.

Similar results were mentioned by other authors (Table 2). The maximum of adsorption capacity was obtained at $\text{pH} = 2$. We can explain this result by the electrostatic attractions between the surface of material charged positively and the HCrO_4^- ions according to the chemical reaction:



Table 2: Comparison of the pH optimum of Cr (VI) adsorption with various adsorbents

Adsorbents	pH	References
salvinia Cucullata	2	[29]
PN and KS materials	2	Our study
Alligatorweed	1	[30]
Activated exhausted clay Trichoderma	2	[31]
Lignin activated with K_2CO_3	2	[32]
Cane with sugar	2	[33]

3.3.3 Effect of the initial concentration

The initial concentration of metal has an important influence on the adsorption capacity of the solid support [34-35]. For this study, the initial concentration of Cr (VI) was varied from 25 to 250 mg.L^{-1} . The equilibrium time,

adsorbent dose and the pH were kept constant. The results of Fig. 7 show that, the concentration effect on the rate of elimination of Cr (VI) and the adsorption capacity for two adsorbents PN and KS, the elimination rate of Cr (VI) is important for the weak concentrations, it decreases by 90% to 40% while and the capacity of adsorption increases by 2 mg.g⁻¹ to 16 mg.g⁻¹ when the initial concentration increases by 25 to 250 mg.L⁻¹. This can be explained by exhaustion of all the active sites which exist on the level of the material surface. [36].

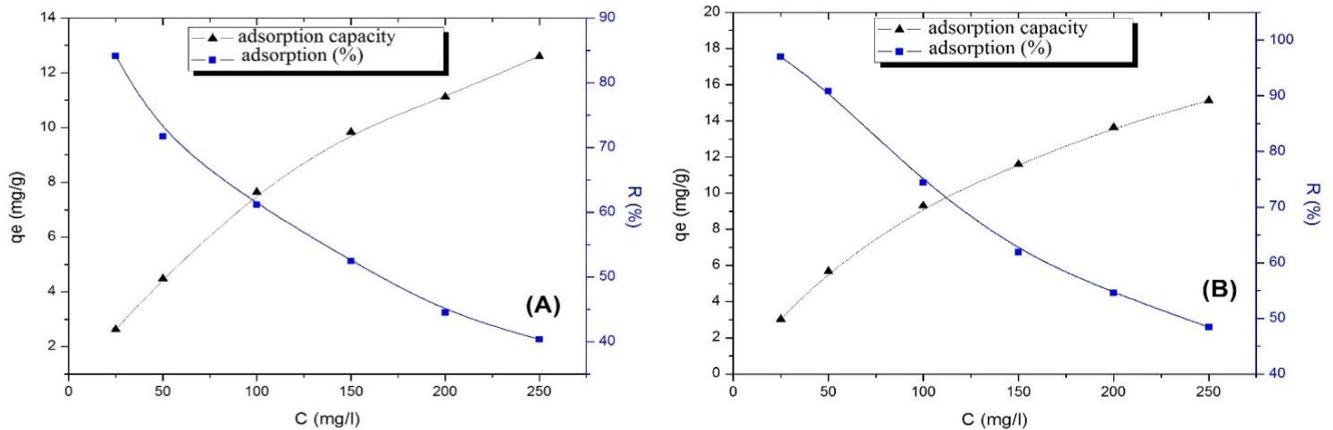


Figure 7: Effect of the initial concentration of Cr (VI) by PN (A) and KS (B) materials, ($m=2 \text{ g.L}^{-1}$, $\text{pH} = 2$, $t = 120 \text{ min}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$).

The Fig. 7 also shows that, the curves of the adsorption capacity and the elimination rate of Cr (VI) cross at a point which represents the compromise between the capacity of maximum adsorption and the maximum percentage of elimination of Cr (VI). Consequently, the initial concentration of Cr (VI) is given with approximately 100 mg.L⁻¹ to allow an optimal adsorption for these two materials.

3.3.4 Effect of the temperature

The study of the temperature effect of Cr (VI) adsorption is realized at various temperatures (25, 30, 40 and 50 °C), the all other parameters were kept constant.

The evolution of the adsorption capacity of Cr (VI) with the temperature variation Fig. 8 reveals that, the adsorption increases when the temperature increases by 25 to 50 °C. According to the literature, the adsorption capacity increases with the rise of temperature for some intervals, then decreases thereafter. An increase in the adsorption capacity with temperature can be explained by desolvation of the metal species and an increase in the particulate rate of diffusion, whereas the reduction is ascribable to a destruction of adsorption sites.

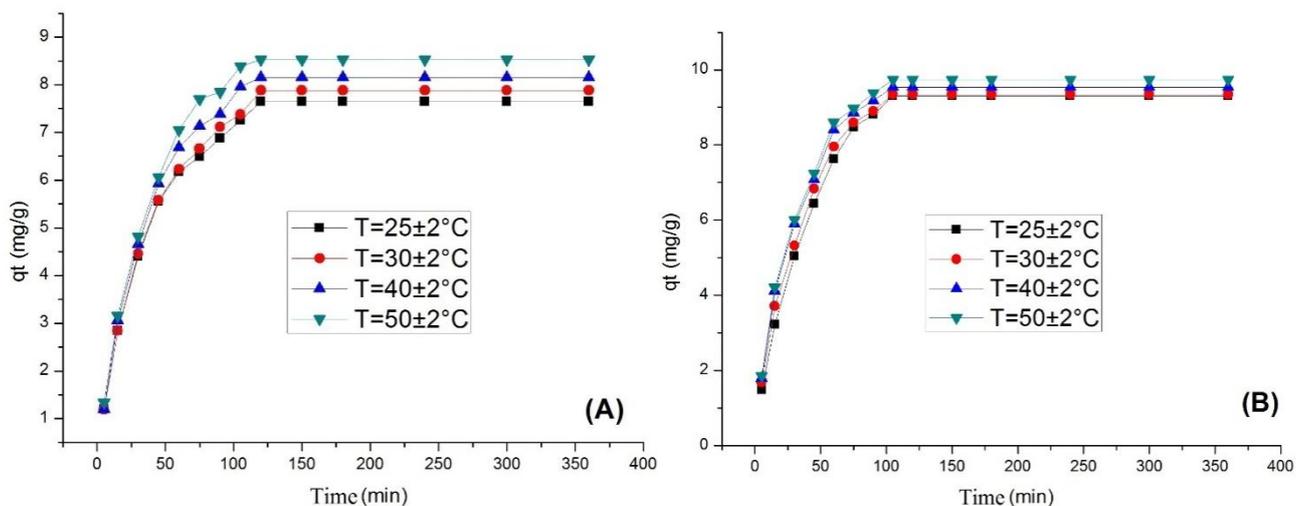


Figure 8: Effect of the temperature of Cr (VI) adsorption by PN (A) and KS (B) materials, ($[\text{Cr}]_0 = 100 \text{ mg.L}^{-1}$, $\text{pH} = 2$, $m_{\text{ads}} = 2 \text{ g.L}^{-1}$).

3.3.5 Lagergren kinetic model

3.3.5.1 First order

Lagergren showed that, the adsorption rate of aqueous solution on the adsorbent is based on the adsorption capacity and following of a first order equation [37]. The non-linear form the first order equation is given by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

Where, q_t (mg.g^{-1}) is the adsorption capacity at time t , q_e (mg.g^{-1}) is the equilibrium adsorption capacity, and k_1 (min^{-1}) is the first order constant. After integration and application of the initial condition of $q = 0$ to $t = 0$, the equation takes the following form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

The chart of the variation of $\ln(q_e - q_t)$ according to time gives the two parameters k_1 and q_e . Table 2 recapitulates the values of the kinetic parameters of the first order equation of Lagergren.

3.3.5.2 Second order

As, the kinetic model of first order gives only k_1 , the expression of the second order was used to describe the kinetics of the adsorption processes, the equation is given by the following relation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

The integration of this equation to $T = 0$ and $q_t = 0$ takes the linear form (7).

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q} \quad (7)$$

The values of k_2 and q_e were calculated from the origin and the slope of the chart of the variation t/q according to time. The constants of the second order were gathered in Table 3.

These results show that the reaction of adsorption is described better by the equation of the second order for the four temperatures 298, 303, 313 and 323K.

Table 3: Kinetic parameters of Lagergren models

Adsorbent	Temperature K	First order			Second order		
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2
KS	298	0,032	10,468	0,982	$1,811.10^{-3}$	12,898	0,993
	303	0,033	10,003	0,990	$2,411.10^{-3}$	12,208	0,995
	313	0,036	10,062	0,988	$2,834.10^{-3}$	12,077	0,997
	323	0,035	10,215	0,985	$2,794.10^{-3}$	12,310	0,997
PN	298	0,026	7,256	0,988	$2,790.10^{-3}$	9,821	0,998
	303	0,025	7,450	0,997	$2,523.10^{-3}$	10,236	0,998
	313	0,031	8,988	0,937	$2,389.10^{-3}$	10,800	0,998
	323	0,035	10,298	0,930	$2,290.10^{-3}$	11,355	0,997

3.3.6 Thermodynamic study of adsorption

The thermodynamic parameters of adsorption isotherm are the free energy (ΔG°), the enthalpy (ΔH°) and the entropy (ΔS°), which is given according to equations 9 and 10, and whose values are presented in Table 4. These parameters explain the mechanism of the process of adsorption of Cr (VI) by the PN and KS materials.

$$Kc = \frac{q_e}{C_e} \quad (8)$$

$$\Delta G^\circ = -RT \ln Kc \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

$$\ln Kc = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

K_c is the equilibrium constant, q_e ($\text{mg}\cdot\text{g}^{-1}$) is the equilibrium adsorption capacity and C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of the adsorbate. The values of ΔH° and ΔS° can be obtained from the line representing the variation of $\ln K$ according to $1/T$, where $\Delta H^\circ/R$ is the slope and $\Delta S^\circ/R$ is the ordinate of origin Fig. 9. The values of the variation of the free energy (ΔG°) are positive for PN and KS materials (Table 5). They indicate that, the adsorption process of Cr (VI) by these two adsorbents is non spontaneous, as well as the reaction is endothermic.

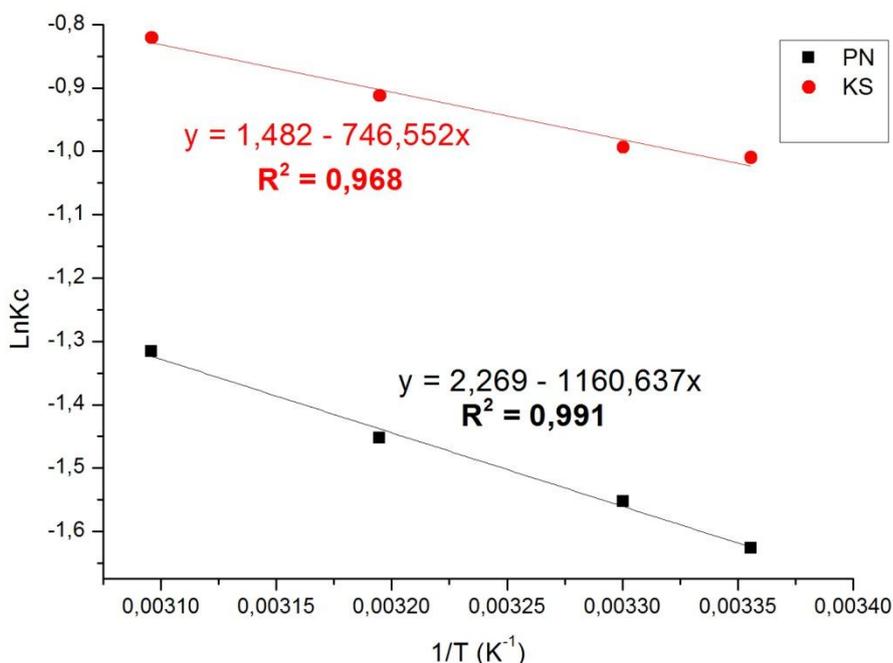


Figure9: The thermodynamic parameters of PN and KS materials

Table5: Thermodynamic parameters for the Cr(VI) adsorption onto the PN and KS materials

Adsorbent	ΔG° ($\text{kJ}\cdot\text{mol}^{-1}$)				ΔH° ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS° ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
	T=298 K	T=303 K	T=313 K	T=323 K		
KS	2,63	2,57	2,45	2,33	6,206	0,012
PN	4,285	4,195	4,015	3,835	9,649	0,018

3.3.4 Adsorption Isotherms

The adsorption isotherm represents the quantity adsorbed according to the concentration of the aqueous solution to equilibrium at a given temperature. Firstly the isotherms models of adsorption are generally used to describe the interactions between the adsorbate and the adsorbent when the process of adsorption reaches equilibrium. Secondly, they make it possible to extract the important parameters for the systems design from adsorption. The data of adsorption were analyzed by the two models of Freundlich and Langmuir. [38-39].

3.3.4.1 Freundlich Isotherm

This model gives an indication on heterogeneity to the surface of adsorbent, it was applied to measure the adsorption capacity according to the following relation:

$$q_e = K_F \cdot C_e^{1/n} \quad (12)$$

Where, K_F and $1/n$ are the constants of Freundlich connected to the adsorption capacity and the intensity of adsorption of the adsorbent respectively. The linear form of the equation of Freundlich can be written in form logarithmic curve according to the following relation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (13)$$

3.3.4.2 Langmuir Isotherm

The model of Langmuir makes it possible to determine if a monolayer is adsorbed and if there no were interactions between the adsorbed molecules. The equation of Langmuir valid for only a monolayer is adsorbed with uniform number and identical sites of adsorption energetically according to the following relation:

$$q_e = \frac{q_m \cdot b C_e}{(1 + b \cdot C_e)} \quad (14)$$

Where, b is the Langmuir constant (L.mg⁻¹). The linear form of the Langmuir equation is:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e \cdot q_m \cdot b} \quad (15)$$

The curves of the linear transforms of Freundlich and Langmuir obtained are presented in Fig. 10, and the various parameters calculated are summarized in Table 6.

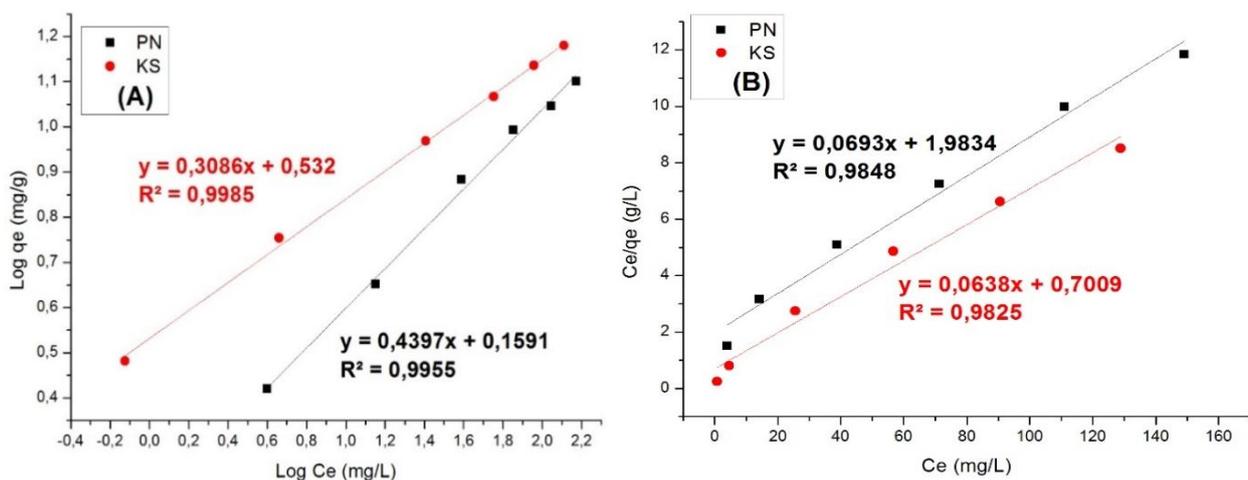


Figure 10: Linear transform of the adsorption isotherm of Cr (VI) by PN and KS materials: (A) Freundlich, (B) Langmuir

Table 6: Parameters of isotherm models for Cr (VI) adsorption onto PN and KS material

Adsorbent	Freundlich			Langmuir		
	K _F	n	R ²	q _m	b	R ²
KS	3,404	3,240	0,998	15,67	0,091	0,982
PN	1,445	2,274	0,995	14,43	0,034	0,984

The application of the linearized forms of the laws of Freundlich and Langmuir made it possible to check that these two models were applicable and that the yield of elimination of Cr (VI) vary in the same direction with the two models. It is also noted that KS has a better adsorbability of chromium VI to compare with PN, the values of the maximum capacities q_m are 15.67 mg.g⁻¹ and 14.43 mg.g⁻¹ respectively for PN and KS.

3. Conclusion

The main aim of this work was to study the elimination of Cr (VI) by the adsorption process on new local materials. A preliminary study of the influence of the various parameters was carried out in order to independently show the influence of each parameter like their dependences. The factors selected are the following: the adsorbent dose, pH, initial concentration of Cr (VI) and temperature. This study show that, the adsorption depends on the pH and the adsorbent dose put in contact for two materials PN and KS. The maximum of elimination is reached with pH= 2 and the effect of the mass made it possible to fix the optimal mass at 1.5 g/L of adsorbent. Under these conditions, one reaches 80% of elimination of chromium for initial concentrations of chromium equal to 100 mg.L⁻¹. The study of the adsorption equilibrium was carried

out at temperatures 25, 30, 40 and 50°C and the experimental results were confronted with the Freundlich and Langmuir models. These results show the existence of a remarkable potential in these two materials to eliminate chromium Cr (VI).

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