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Removal of Hexavalent Chromium Cr (VI) From an Aqueous Solution by an Industrial Waste from the Steelworks of the Algerian Steel Complex

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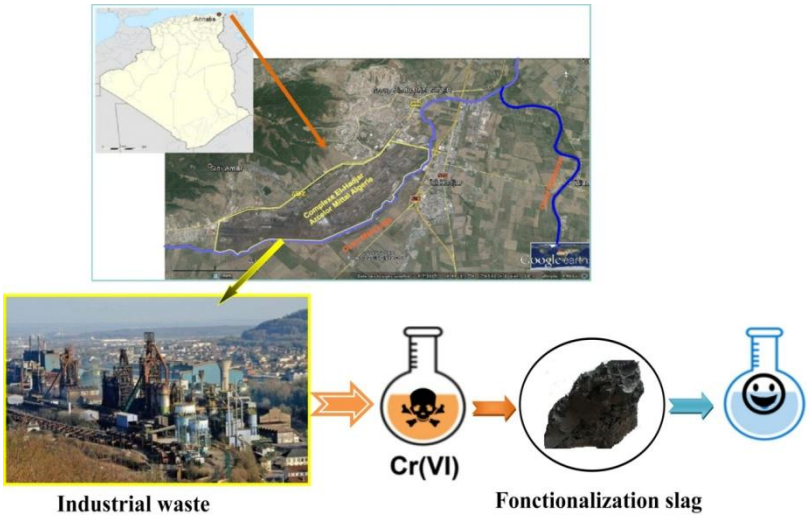
ABSTRACT

Algeria has developed a dense Industrial network, concentrating polluting and water and energy consuming sectors. Slag, a waste product of the SIDER steel complex (Annaba, Algeria), was used as an adsorbent for the removal of hexavalent chromium from artificially contaminated aqueous solutions. The experiments were carried out in static regime. The determined best parameters influencing the adsorption such as mass of adsorbant, initial concentration, stirring speed, temperature, and pH, which allowed to reach a significant efficiency rate equal to 99% were as follow: Cr(VI) concentration of 10 ppm, pH 1, contact time at equilibrium 30 min and a temperature of 40°C. Modeling of the experimental data showed that the pseudo-second order model describes the adsorption kinetics in an adequate way. Also, the adsorption isotherms are in agreement with the Freundlich model. Furthermore, the thermodynamic analysis revealed that the studied adsorption process is a favorable, endothermic, and spontaneous phenomenon.



Keywords: *Slag; Chromium-hexavalent; Waste; Adsorption, Modeling.*

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Introduction

Water is the source of life and the most important factor in achieving sustainable economic and social development. Therefore, its pollution is a critical problem for all mankind. Heavy metals are a major source of water pollution resulting from several industrial activities, including tanneries, synthetic dyes and leather industries [1, 2], and metal surface treatment [3]. Among these metals, the chromium which is in nature under several forms depending on its degree of oxidation. Of the two most stable forms, trivalent Cr and hexavalent Cr, Cr(VI) represents the greatest threat to the environment and human health, given its high toxicity and carcinogenic potential [4-6]. Several remediation processes have been developed to remove Cr(VI) from industrial effluents with the objective of environmental protection and possible reuse of water. These include chemical precipitation [7], ion exchange [8], nanoparticles [9, 10], reverse osmosis [11], electrocoagulation [12], membrane separation [13], and photocatalysis [14]. However, most of these technologies are expensive, especially when applied to high flow rate effluents. Adsorption technique [15] has been proven to be effective in the treatment of aqueous effluents especially in the removal of heavy metals from water [16], but most conventional adsorption systems use activated carbon despite its high production cost and difficulties in regeneration [17]. Recently, many researchers have focused on cheaper adsorbents for adsorption tests.
The objective of this work is the valorization of an industrial waste, the slag resulting from the operation of refining at the level of an electric steel plant of the steel complex Sider El-hadjar (Annaba, Algeria) in order to eliminate Cr(VI) in aqueous solution by adsorption in static regime. This will enable us to achieve a triple objective: to reduce pollution, to recover a waste product and to recycle water. To this end, we will study the parameters that have an influence on the adsorption equilibrium (pH, mass, agitation speed, temperatures, concentration) in order to determine the optimal conditions. A modeling of the adsorption isotherms and a thermodynamic study will also be carried out to understand the nature of the reaction mechanisms involved in the present adsorption phenomenon.

1. MATERIALS AND METHOD

1.1. Chemical products

All chemicals used in the adsorption tests such as hydrogen chloride (HCl), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), 1,5-diphenylcarbazide, and potassium dichromate ($K_2Cr_2O_7$) were purchased from Sigma-Aldrich-Fluka (Saint-Quentin, Fallavier, France).

1.2. Preparation of adsorbent

The material used was a slag from the refining operation at an electric steel mill of Sider El-hadjar (Annaba, Algeria). The sample was crushed and then sieved, only the particles with sizes between 50-125µm were used.

1.3. Caractérisations of the adsorbent

The chemical composition of the slag was determined using X-ray fluorescence spectroscopy (ARL Thermo Scientific Perform X). The surface functional groups of the sample were identified by Fourier Transform Infrared spectroscopy (FT-IR) analysis using IR^{-1} affinity in combination with a single ATR reflection. The morphology of thesample was determined using a scanning electron microscope (SEM) ((Quanta 200 FEI) combined wih scatter X-ray. The crystal structure of the material was characterized by X-ray diffraction (XRD) (Philips model PW1710) using Kα

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copper radiation (λ = 1.5460 Å) with 40 kV, 40 mA, a scan speed of 0.01 min $^{-1}$ and an angle 2θ between 0 and 90.

1.4. Adsorption kinetics of Cr (VI).

The adsorption kinetics of Cr(VI) under the different operating conditions (initial concentration, stirring speed, pH, and temperature) was carried out in a static regime. A sample mass of 12.5g.L^{-1} was mixed with a Cr(VI) solution. The suspensions were stirred with a mechanical stirrer. Over time, a constant volume of supernatant was taken and determined after centrifugation using a UV-Vis spectrophotometer (TECHCOMP 8500) at a wavelength of $\lambda_{max} = 545nm$. The removal efficiency of Cr(VI) is calculated by equation (1)[18]:

$$R\ (\%) = \frac{C_0 - C_e}{C_0} \qquad (1)$$

Where, R is the yield (%); $\boldsymbol{C_0}$ and $\boldsymbol{C_e}$are the initial and equilibrium concentration (mg.L^{-1}) respectively

The quantities of Cr (VI) adsorbed were calculated using equation (2) [18].

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (2)$$

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

1.5.Adsorption isotherm for Cr (VI)

The adsorption isotherms were carried out at different concentrations, under the optimal conditions established in the kinetic study (m = 12.5g .L-1, pH = 1, T = 25 ° C, constant stirring speed 150 rev / min, contact time 30 minutes). The suspensions, after stirring, were centrifuged and the supernatant was then analyzed.

2. Results and Discussion:

2.2 . Material Characterisation

2.2.1 Chemical Composition of Slag

The chemical composition of the slag was carried out by X-ray fluorescence. The results obtained are presented in Table 1.

Table 1.Chemical composition of slag.

Composition%	Fe	CaO	SiO_2	MgO	Al_2O_3	MnO	ZnO	P_2O_5
Scorie	12,43	32,30	31,44	7,70	2,52	16,64	0,12	0,36

According to this analysis, the slag consists of a mixture of oxides rich in (CaO, SiO_2), a low content of (MnO, Fe, MgO), and a poor content of (ZnO, P_2O_5, Al_2O_3).

2.2.2 X-ray Analysis

3 The X-ray diffraction pattern of the slag (Fig.1) shows that the sample is crystalline, with a

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very intense SiO2 peak at about 2θ= 26.46°, (JSPD 96-900-9667), peaks representing calcium oxide CaO (JSPD 96-101-1328) Lime and Calcite CaCO (JSPD 96-901-6707) as well as MnOManganosite (JSPD 96-900-6670) due to its chemical composition rich in (CaO-SiO_2-MnO) (fig.5). We can see that calcites in their different forms are the main compounds of slag.

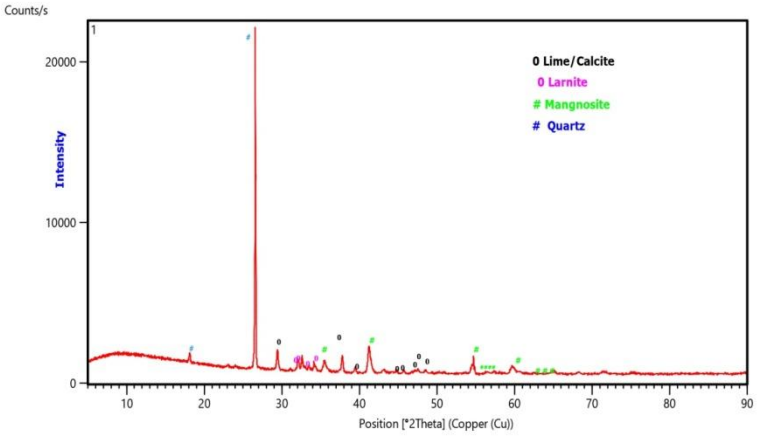

Figure.1: X-ray diffraction pattern of slag .

2.2.3. IR-TF Analysis

The IR-FT spectrum of the slag (Fig. 2) shows different peaks which are attributed to various functional groups and bands. Absorption bands at 3355-3738 cm^{-1} and 1508-1648cm^{-1} reflect the presence elongation and deformation vibrations of the O-H and H-O-H bonds of the adsorbed water molecules respectively[19,20]. Calcite phase C-O is further confirmed by presence of prominent peak at 2361,85. The absorption peaks appearing at 669 and 868 $cm^{-1}$are attributed to the elongation of the Al-O and Si-O bonds respectively [21].

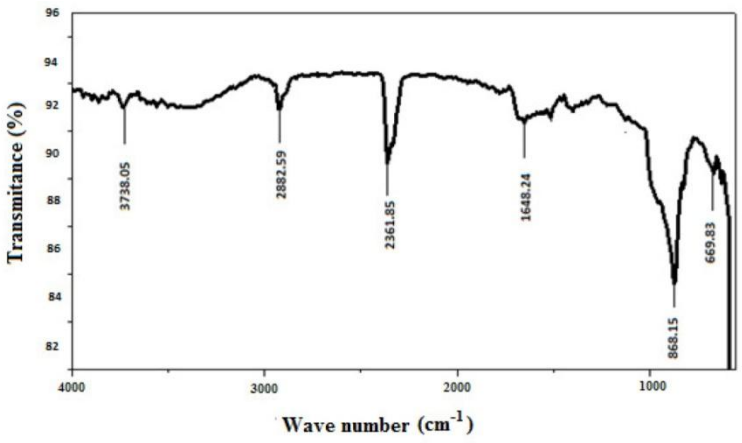

Figure.2: IR-FT of the slag.

2.2.4. SEM Analysis

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The morphological structure of the slag before and after adsorption is shown in (fig.3) at different magnifications. The (SEM) images clearly show that the wall of a slag has a large number of small holes; these holes promote the transport of chemical species in all directions through the slag, which may be suitable for the retention of pollutants.

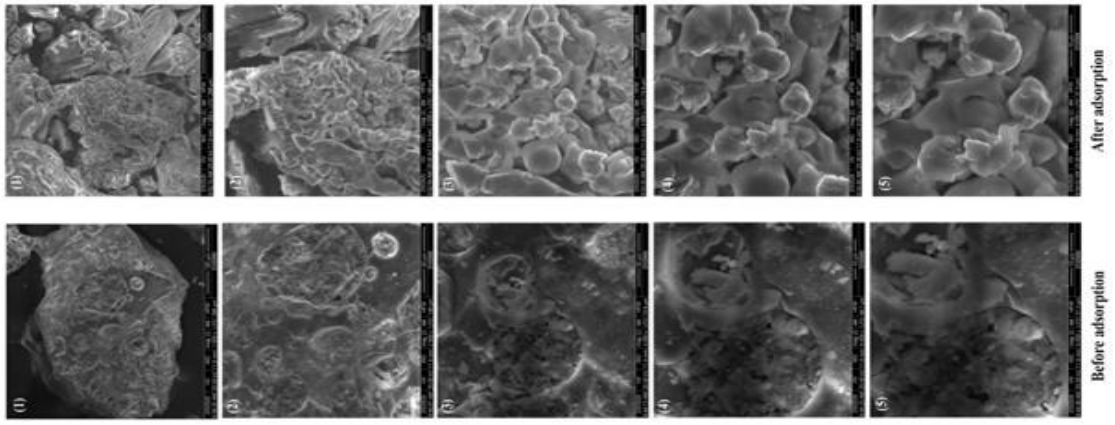

Figure. 3 SEM images before and after adsorption.

2.2.5. EDX Analyses

The atomic and mass percentage presented in (fig. 4 (a) and (b))indicate that the slag is of mineral nature. Fig. 4(b) shows the EDX profile of the slag after adsorption. We notice the appearance of a Cr(VI) peak, which confirms the fixation of Cr(VI) on the slag.

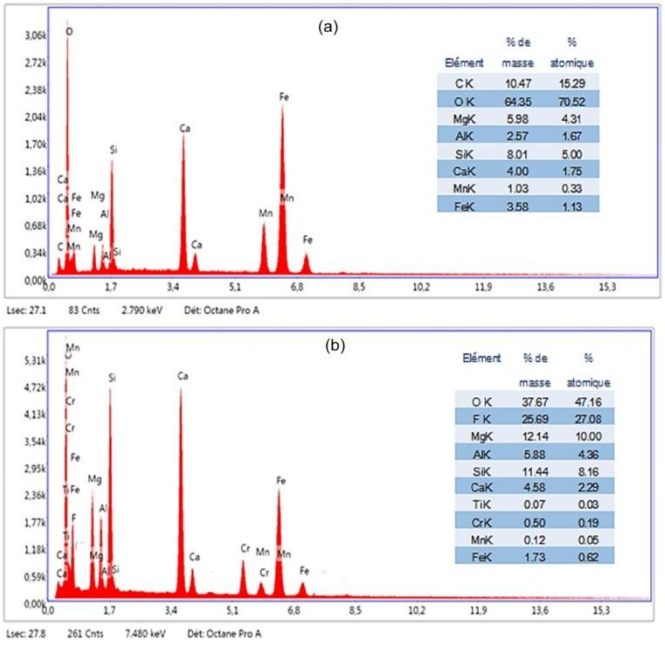

Figure .4 EDX profile of the slag (a) before and (b) after adsorption

2.3. Kinetic Study

2.3.1. pH effect

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The initial pH of the solution is an important parameter that must be considered in any adsorption study. The effect ofthis factor on the retention rate of Cr(VI) was analyzed over a pH range of 1 to 6. According to the literature the predominant forms of Cr(VI) in aqueous solution are $H_2Cr_2O_7$ at pH < 1, $HCrO_4^-$ at $1 < pH < 6$, and CrO_4^{-2}à pH > 6 [22].

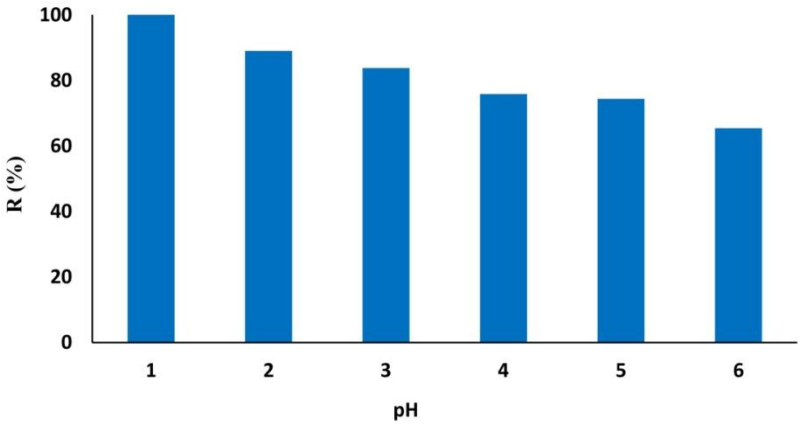

Figure.5 Effect of pH on slag adsorption yield for the removal of Cr (VI) (C_0=10mg. L^{-1} , pH=1, m=12.5g L^{-1}Va=150rmp).

The results, presented in Fig.5, showed that the maximum percentage removal of Cr(VI) occurs at pH = 1, for an initial concentration of 10 mg/L. The removal rate decreases with increasing pH of the solution, this behaviour is explained by the fact that at pH =1 the surface of the adsorbent can be strongly protonned with H^+ ions, resulting in the development of a positive electric charge on the surface of the support, this charge presents an electrostatic attraction of the $HCrO_4^-$ions and favours the adsorption of Cr (VI), which increases the percentage of removal [23]. This behavior is also explained by the fact that at pH = 1, the oxides that constitute the slag tend to form aquacomplexes that cause an increase in the positive charge density on the surface of the slag (a positively charged surface) and consequently an increase in Cr(VI) adsorption. The active functional groups on the surface of the slag might be the deprotonned (Si-O-) sites since the main constituent of the slag is SiO_2.

2.3.2 Mass Effect

Equilibrium time plays a key role in the design of wastewater treatment systems [23]. In order to determine the necessary amount of slag corresponding to maximum removal, suspensions of 20 mL of 10 ppm Cr (VI) solution were prepared in Pyrex tubes, to which masses of slag ranging from 0.1g to 0.5g were added.

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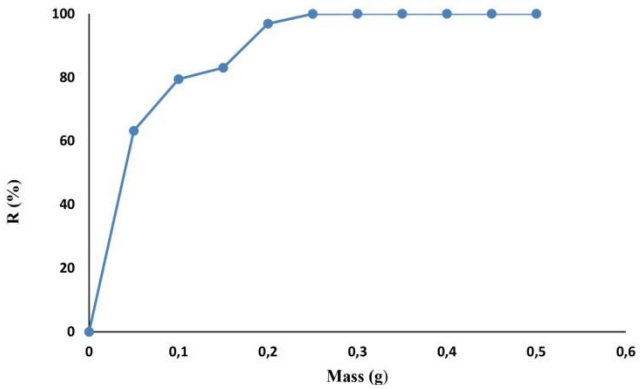

Figure.6 Effect of adsorbent mass on Cr(VI) removal by slag (C_0=10mg. L^{-1} , pH=1,Va= 50 rpm)
The results show that the percentage of Cr(VI) removal increases with increasing mass. Above a mass of 0.25g, the rate tends to stabilize and the appearance of a saturation plateau (Fig.6). This is attributed to the increase in the number of active sorption sites.

2.3.3 Effect of stirring speed

The speed of stirring is also considered as an important parameter in the adsorption process [24]. In order to study its effect on the retention process, three agitation speeds were considered: 50,100,150 rpm.

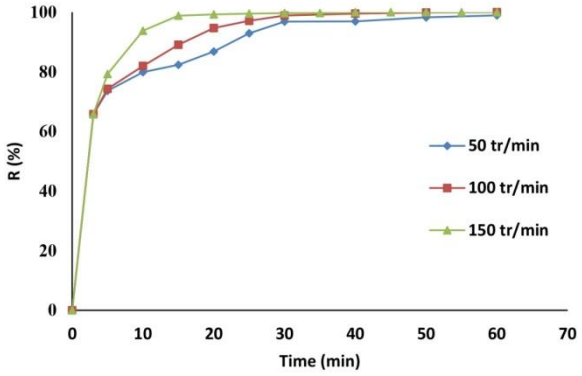

Figure.7 Effect of stirring speed on Cr (VI) removal by slag (C_0=10mg. L^{-1} , pH=1, m=12.5g. L^{-})

From (fig.7), it can be seen that high stirring speed increases the retention process. However, a very high stirring speed improves the mass transfer of Cr(VI) molecules to the solid support.

2.3.4 Effect of concentration

To study the influence of the initial hexavalent chromium concentration on the adsorption process, tests were carried out by varying the concentrations from 10 to 30mg.L^{-1}. The other parameters were kept constant.

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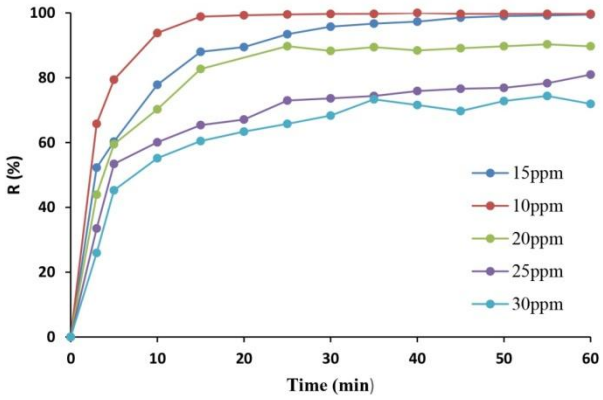

Figure. 8 Effect of initial concentration of Cr(VI) adsorption on slag (pH=1, m=12.5mg. L^{-1}, Va=150rpm)

According to (fig.8), the retention efficiency decreases with increasing concentration; this is probably due to the saturation of the surface adsorbent sites by chromium (VI).

2.3.5 Influence of temperature

In order to study the influence of temperature on the retention of Cr (VI), three different temperatures were chosen 20, 30 and 40°C. Figure.9 shows that an increase in temperature from 20 to 40 °C induces an increase in the removal rate of Cr (VI) on the slag.

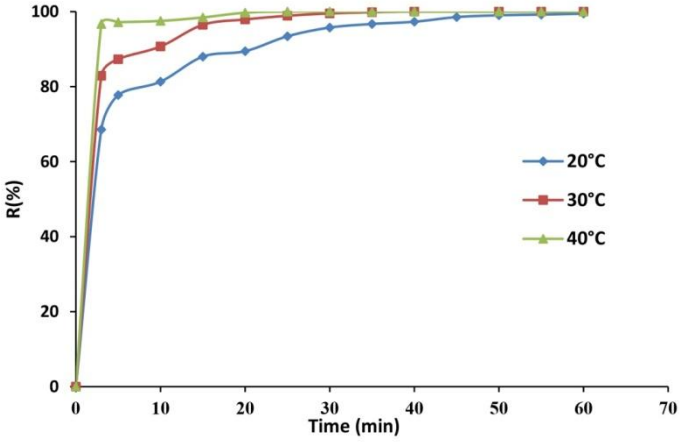

Figure.9 Effect of temperature on Cr(VI) removal by slag (C0=15mg. L^{-1} , pH=1, Va=150 rpm)

Figure.9 show that an increase in temperature from 20 to 40 ° C induces an increase in the rate of removal of Cr (VI) from the slag. This indicates that the displacement process is endothermic which may be the result of increased mobility of Cr (VI) ions with increasing temperature [25] and may be due to increased thermal energy of the adsorbent species when the temperature was increased [26].

2.3.6 Contact time effect

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The kinetic study of Cr (VI) adsorption on slag requires the knowledge of contact times, in order to reach the equilibrium between the adsorbate and the adsorbent. For this purpose, we followed the adsorption kinetics for an initial concentration of 10 $mg.L^{-1}$, with a mass of the slag of 12.5 $g.L^{-1}$.

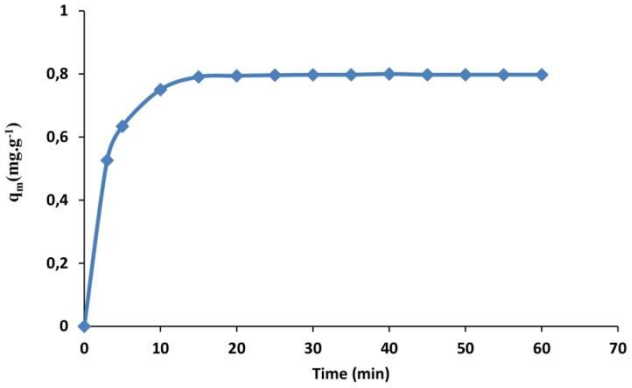

Figure.10 Adsorption kinetics of Cr (VI) on the slag (m =12.5g/L, C=10mg. L^{-1},pH=1, and T=20°C).

According to the shape of the curve (fig.10), we notice a rapid fixation of the pollutant and equilibrium is reached after 15 minutes. The speed of adsorption can be explained by the fact that at the start of adsorption the number of active sites available on the surface of the adsorbent material is much greater than the number of sites remaining aftera certain time [27]. At this level there is a pseudo-equilibrium between the rate of adsorption and desorption, the adsorption becomes relatively slower giving the impression of equilibrium. In all of the adsorption tests, we opted for a time of 30 minutes to ensure that the balance between the different phases was established

2.4 Adsorption kinetics

Several kinetic models are developed to highlight the essential parameters of the adsorption kinetics. The adsorption of Cr(VI) on slag has been modeled using the pseudo-first order Equation (3) and pseudo-second order [28] Equation (4):

$$ln(q_e - q_t\grave{}) = ln\, q_e - \mathrm{k_1 t} \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{\mathrm{k_2} q_e^2} + \frac{t}{q_e} \qquad (4)$$

Where, *t*: contact time; k_1: adsorption rate constant of pseudo-first order kinetics; k_2: adsorption rate constant of pseudo-second order kinetics; *qt*and *qe*: adsorption capacities at time *t* and equilibrium respectively.

Table 2.Summary of the results of the different kinetic models.

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Modèles			$\mathbf{q_{e\ (exp)}(mg.g^{-1})}$
PPO	$\mathbf{q_{e\ (cal)}(mg.g^{-1})}$	0.5363	0,7941
	$\mathbf{K_1}$	0.2450	
	$\mathbf{R^2}$	0,976	
PSO	$\mathbf{q_{e\ (cal)}(mg.g^{-1})}$	0.8084	
	$\mathbf{K_2}$	2.0539	
	$\mathbf{R^2}$	0.999	

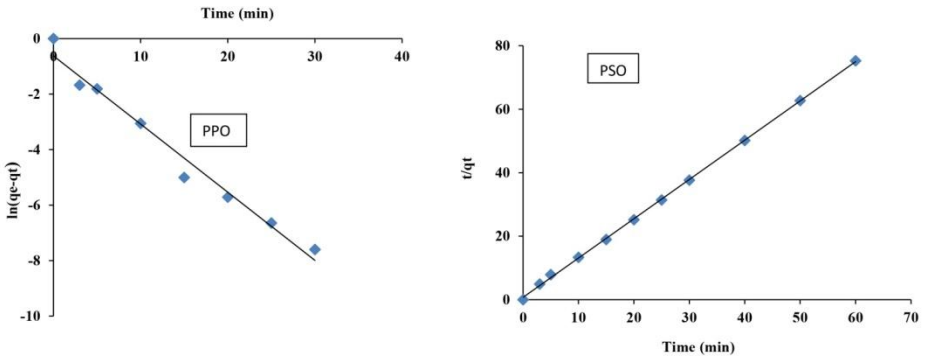

Figure.11 Linear regression of various kinetic models (a) PFO and (b) PSO (m=12.5g .L^{-1}, C=10mg. L^{-1}, pH= 1 and T=20°C).

The results of the kinetics of our adsorbent are shown by fig 11(a),(b) and gathered in Table 2. According to the value of the two correlation coefficients (R^2) the PSO kinetic model is the most convenient to describe the adsorption process of Cr (VI) on the slag. Furthermore, the theoretically calculated ($q_{e,cal}$) by this model are in good agreement with those of the experiment ($q_{e,exp}$).

2.5 Adsorption isotherm

Establishing adsorption isotherms allows us to calculate the maximum amount adsorbed by the solid and also to identify the type of adsorption. According to Gille's classification [29], the experimental results show an increase in adsorption with an increase in the adsorbate concentration indicating that the isotherm is type H (Fig. 12). The amount of chromium adsorbed at equilibrium is given by the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (5)$$

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Where ($mg.g^{-1}$) is the equilibrium adsorption capacity; C_0 and $C_e$are the initial and equilibrium concentrations ($mg.L^{-1}$) respectively; V (L) is the volume of the solution; m(g) is the mass of the adsorbent.

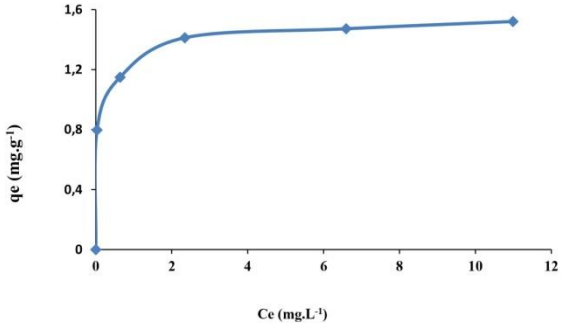

Figure.12 Adsorption isotherm of Cr (VI) on slag (m=12.5g.L^{-1}, C=10mg L^{-1}, pH= 1 and T=20°C)

2.6 Langmuir Isotherm

The Langmuir model assumes that metal ion absorption occurs on a homogeneous surface by monolayer adsorption without any interaction between the adsorbed ions [30].
The Langmuir equation in linear form is expressed by equation. (6):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L \times q_m} \times \frac{1}{C_e} \quad (6)$$

Where C_0 is the initial concentration of metal ions ($mg.L^{-1}$).

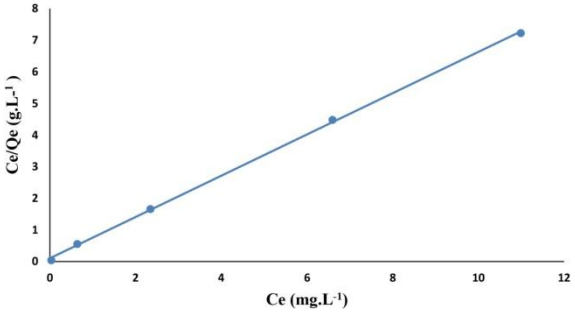

Figure.13 Langmuir linearization for Cr(VI) adsorption on slag.

Table 3. Calculated values of the separation factor R_L

C_0	10	15	20	25	30
R_L	0,01550575	0,01039087	0,00781345	0,006260543	0,005222569

From (fig.13), we notice that the linearization of adsorption isotherm of Cr(VI) on slag is satisfactory, with a value ofcalculated adsorption quantity equal to the experimental adsorption quantity and good correlation coefficient. We can say that the Langmuir model is adequate for a

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good description of this adsorption. The found values of $0 < R_L < 1$indicate a very favorable adsorption for the slag.

2.7 Freundlich Isotherm

The Freundlich equation is an empirical model based on heterogeneous adsorption on independent sites. The linear form of the Freundlich equation (7) is as follows [31]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

K_F and n are the Freundlich constants. The values of K_F and n were determined from the intercept and slope of the line graph of ln q_e versus ln Ce in (fig.14), respectively, and the results are presented in Table.4.

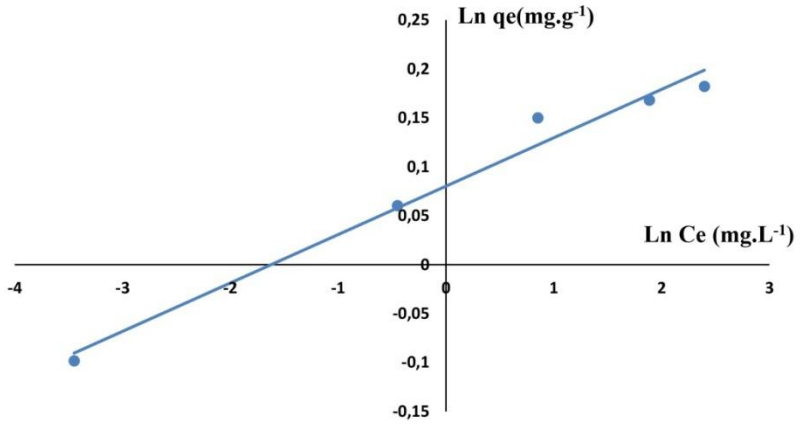

Figure.14 Freundlich linearization for Cr(VI) on slag

The intensity parameter, 1/n indicates the deviation of the adsorption isotherm from linearity. When 1/n=0, the adsorption is linear, i.e. the sites are homogeneous and there is no interaction between the adsorbed species. When 1/n<1, the adsorption is favorable, the adsorption capacity increases and new sites appear. When 1/n>1 adsorption is not favorable, the adsorption bonds become weak and the adsorption capacity decreases [32]. From the obtained results we can see that the ratio 1/n is less than 1, so the freundlich isotherm is favorable for the adsorption of Cr on the slag. A value of n between 1 and 10 represents a good adsorption [33].

2.8 Temkin isotherm

Adsorbent-adsorbate interactions are a crucial factor for this isotherm. By lifting the ultimate low and high concentration values, the model assumes that the heat of adsorption (as a function of

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temperature) of all molecules in the layer would decrease linearly rather than logarithmically in the blanket [34]. Temkin isotherm has generally been represented by the following equations(8) [35,36]:

$qe = BLnA_T + BLnC_e$ (8)

where $B = \frac{R_T}{b_T}$, b_T (J.mol-1) is the heat of adsorption, A_T is the equilibrium binding constant Lg^{-1}, RT is the adsorption constant J mol^{-1}, R is the universal gas constant 8.314 J mol^{-1} K^{-1}, T is the absolute value of temperature [298 K]. The constant parameters of the Temkin isotherm were determined from the linear curve of (qe) versus ln (Ce) fig.15.

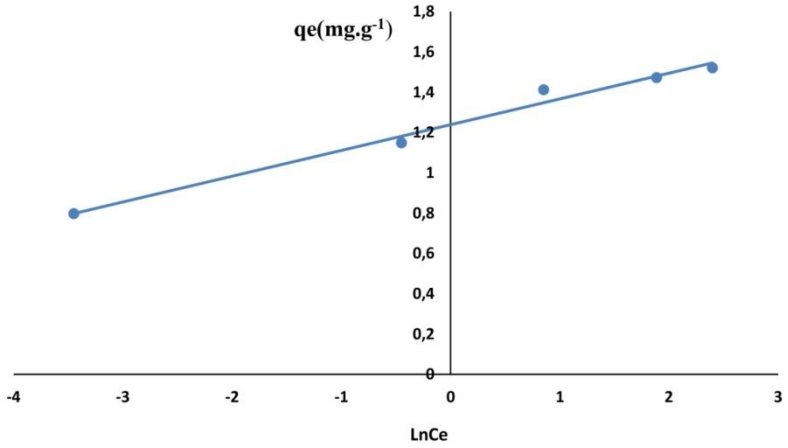

Figure.15 Temkin linearization for Cr(VI) on slag

Table 4. Langmuir, Freundlich and Temkin isotherm constants for Cr(VI) adsorption on slag.

Model		
Langmuir	$\mathbf{q_{m(exp)}(mg.g^{-1})}$	1,5209
	$\mathbf{q_{m(cal)}(mg.g^{-1})}$	1,5320
	$\mathbf{K_L(g^{-1})}$	6,3492
	$\mathbf{R^2}$	0,9995
Freundlich	**1/n**	0,0494
	$\mathbf{K_F}^{(mg1-1/nL1/ng-1)}$	1,0835
	$\mathbf{R^2}$	0,9791

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Temkin	$\Delta Q(Kj/mol)$	29,1874769
	$A(L.g^{-1})$	16220,8578
	B_1	0,1278
	R^2	0,9837

As presented in Table 4, the maximum monolayer coverage capacity (qm) of the Langmuir isotherm model was found to be 3.06 mg. g-1, K_L (Langmuir isotherm constant) is 0.078 (L mg^{-1}). The R_L values for the adsorption of Cr (VI) on slag are in the range (0.719 to 0.125) (Table 3). The value of R_L is lower than the unit, it indicates that the equilibrium sorption is favorable and the high value of the correlation coefficient R^2 (0.984) proves that the sorption data fit well with the Langmuir Isotherm model and then come the Temkin and Freundlich models. Therefore, it can be understood that, Langmuir and Temkin isotherms are the most suitable models for the sorbate-sorbent system. The variation of adsorption energy is positive with the adsorbent used, hence the adsorption of chromium by the slag is endothermic, which confirms the results obtained during the study of the temperature effect.

2.9 Determination of thermodynamic parameters

The effect of temperature on the adsorption of hexavalent chromium was studied in order to obtain the relevant thermodynamic parameters. The free energy of adsorption (ΔG°), entropy (ΔS°), and enthalpy change (ΔH°) in the adsorption process are related to the Vant Hoff equations [37]:

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

$$\ln K_C = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} \quad (10)$$

$$K_C = \frac{C_{Ae}}{C_{Se}} \quad (11)$$

Where LnKc [38] is the equilibrium constant, C_{Ae} is the amount of adsorbate on the adsorbent per volume of solution (L) at equilibrium (mg L^{-1}), C_{Se} is the equilibrium concentration of adsorbate in the aqueous solution (mg.L^{-1}), R is the gas constant 8.314 JK^{-1} mol^{-1}, and T is the temperature (K). The values of (ΔH°) and (ΔS°) were obtained from the slope and intersection of the lnKc against 1/T curve according to (fig.16).

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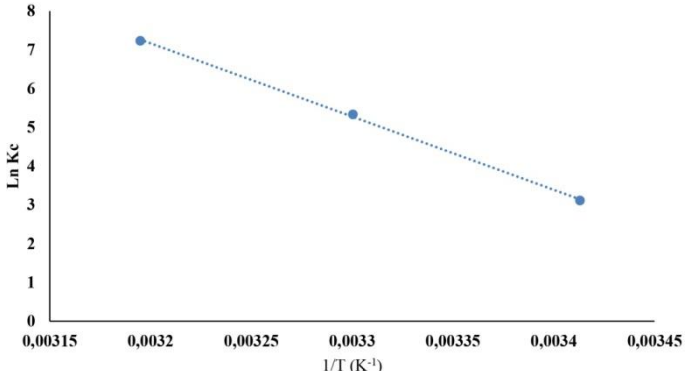

Figure.16 Determination of the enthalpy and entropy of adsorption of Cr(VI) on slag.

Table 5.Thermodynamic parameters of adsorption of chromium (VI) ions by slag at different temperatures.

T(K)	ΔH°(KJ/mol)	ΔS°(KJ/mol)	ΔG°(KJ/mol)
293			-7.58
303	157.017	0.562	-12.98
313			-17.61

From the results, it is observed that the free energy values for the different temperatures are below zero ($\Delta G^{\circ} < 0$)[39], which proves that the removal process of Cr(VI) ions is spontaneous. This shows that high temperatures, in the studied range, favor adsorption.
The positive value of the enthalpy variation ($\Delta H^{\circ} > 0$) indicates again that the adsorption of Cr (VI) by the slag is an endothermic process [40]. The positive value of entropy ($\Delta S^{\circ} > 0$) indicates the increase of the disorder at the adsorbate-adsorbent interface during the adsorption of chromium on the surface [41-44].

3. Conclusion

This work showed that slag could be used for the removal of Cr(VI) from aqueous effluents. The study of the influence of the parameters (pH, mass, initial concentration, agitation speed and temperature), allowed the determination of the optimal conditions.
The adsorption kinetics is best described by the pseudo-second order model. According to the Gilles classification, the experimental results showed that the isotherm shape is H-type. The adsorption isotherms of our adsorbent obey to the Langmuir model indicating a homogeneous monolayer adsorption. The study of the thermodynamic parameters (ΔH°, ΔG° and ΔS°) showed that the fixation process of Cr(VI) ions on the slag is endothermic and spontaneous

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