

Adsorption of Cr (VI) Onto Clay Modified by Sodium Chloride and Clay Modified by Aluminum Hydroxide of Karewa (North Cameroon)

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Abstract— In this study, removal of Cr (VI) from aqueous solutions by adsorption onto clay modified by sodium chloride and clay modified by aluminum hydroxide was investigated as a function of pH, contact time, adsorbent dosage, initial metal concentration and temperature. Time-dependent experimental studies showed that the adsorption quantity of Cr (VI) increases with initial concentration and decreasing adsorbent dosage. The equilibrium time of 10 and 40 min was observed clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) and maximum adsorption was favored at pH 3. The Cr (VI) removal using 0.1 g of adsorbent was more than 90%. This dosage (0.1 g) was considered as the optimum dosage to remove Cr (VI) aqueous solutions. Experimental data were investigated by two adsorption isotherms models (Langmuir and Freundlich). Applicability of isotherm equation to describe the adsorption process was analysed by the correlation coefficients values, R^2 . Langmuir and Freundlich models show best fit with R^2 values superior of 0.95. The mechanism of adsorption of Cr (VI) is therefore based on the assumption of the kinetic model of pseudo-second order in two steps. Thermodynamic parameters such as ΔH° , ΔG° and ΔS° demonstrated that adsorption mechanism of Cr (VI) onto clay modified by sodium chloride and clay modified by aluminum hydroxide, physisorption, spontaneous and exothermic in the ranges of temperature of 203-333K.

Keywords— Adsorption, clay, exothermic, isotherms models, kinetic model, physisorption.

I. INTRODUCTION

Hexavalent chromium is a solid oxidizing specialist that is water-dissolvable in its anionic form. Due to its solvency, it is highly mobile in soil and aquatic environments and readily penetrates plant and animal epidermis where it irritates the tissues (Kubota; 2009). Mining activities, tanneries, textile coloring, electroplating, and metal finishing industries (Wang *et al.*, 2009). Several treatment processes, including chemical precipitation, phytoextraction, reverse osmosis, electro dialysis, ion exchange and membrane filtration or adsorption, have been developed to remove heavy metals from industrial wastewater (Domga *et al.*, 2015; Domga *et al.*, 2016; Béné *et al.* 2016; Domga *et al.*, 2018 ;Tcheka *et al.*, 2018). However, most of these methods have some disadvantages such as complicated process, high cost and high energy consumption. The main disadvantage of adsorption treatment method is the high cost of the adsorbents. Therefore, it is necessary to find new adsorbents with low cost and high

efficiency for the treatment of wastewater. Thus, new ways to remove Cr (VI) from wastewater in a single step would be advantageous. In this work, we focus attention on new ways to remove Cr (VI) from aqueous solutions using inorganic materials.

Clay is mineral composed of alumina and silica that usually includes bound water. Clays exhibit large surface areas and are capable of adsorbing cationic, anionic, and neutral metal species. The high specific surface areas, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), have made clays excellent adsorbent materials (Li *et al.*, 2010). The adsorption of Cr (VI) from aqueous solution by observed clay modified by sodium chloride and clay modified by aluminum hydroxide are investigated in the present study.

II. MATERIALS AND METHODS

2.1. Physico-Chemical Characteristics of Clays

The clay used for this work was taken from Karewa's deposit in the Djeboa Sub-Division, North Region of Cameroon. Karewa is a village located at 30 km in the south-east of Garoua, center of the area of Cameroun North. It is located between 9°16' and 9°54' of Northern latitude, 3°52' and 14° of longitude. Administratively, the village is in the district of Tchéboa, department of Bénoué. The soil, with a surface of 16 km², under the traditional authority of the lamidat of the district. The natural clay (rough) used in this work is a montmorillonite, of white color, taken layer of karewa located at the North of Cameroun.

2.2. Preparation and Modification of Clay

The extraction of the clay fraction less than 2 μm was collected by sedimentation after 8 hours (depth $x = 10$ cm) after application of the Stokes law, then dried at 105 °C in the oven for 24 hours. The fraction is sprayed in an Agate mortar. The product obtained is treated with sulfuric acid (2M), washed during 30 minutes with distilled water until the pH is close to neutral and then dried at 105 °C. (oven). The sample thus purified is then treated by stirring in a solution of sodium chloride (1N). The collected sodium clay is dried at 105 °C in an oven for 24 hours and milled, then stored in a closed jar. The bridging of our material is from a bridging solution of

aluminum hydroxide (prepared from 0.2M AlCl₃.6H₂O and 0.2M NaOH) and calcined at 400 ° C for 3 hours.

2.3. Batch Adsorption Experiments

Cr(VI) solution (1000 mg.L⁻¹) was prepared by mixing 2.827 g of K₂Cr₂O₇ in 1 L of de-ionized water. Adsorption capacity of adsorbent was determined by contacting 0.1g with 50 ml metal solutions of known concentration (20–100 mg L⁻¹) in 250 ml Erlenmeyer flasks, shaken on an orbital shaker at 120 rpm for 60 min at room temperature (25 ±2 °C), followed by centrifugation at 5000 rpm for 5 min to separate clay modified by sodium chloride and clay modified by aluminum hydroxide from the Cr (VI) solution. Residual Cr (VI) concentration in the supernatant Cr (VI) solutions was determined by UV-visible spectrophotometry analysis. Rate of Cr (VI) adsorption by clay modified by sodium chloride and clay modified by aluminum hydroxide was determined by analyzing residual Cr (VI) ions in the supernatant after contact periods of 10, 20, 30, 40, 50 and 60 min and the solid phase mass is 0,1g. For determining the effect of pH on Cr (VI) adsorption by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) , initial pH of Cr (VI) solution was adjusted to the desired value (3–10) using 0.1 M HCl or 0.1M NaOH. Final pH of the adsorbate–adsorbent adsorption mixture was measured at adsorption equilibrium. All the experiments were performed in triplicate. Adsorption capacities were obtained using a mass balance equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

The adsorption percentage is determined as below:

$$\text{Adsorption percentage}(\%) = 100 \times \frac{C_0 - C_e}{C_0} \tag{2}$$

Where *q_e* is the equilibrium adsorption capacity per gram dry weight of the adsorbent (mg/g), *C₀* is the initial concentration of Cr (VI) in the solution (mg/L), *C_e* is the final or equilibrium concentration of Cr (VI) in the solution (mg/L), *V* is the volume of the solution (L), and *m* is the dry weight of the adsorbent (g).

III. RESULTS AND DISCUSSION

3.1. Physicochemical Characteristics of Natural Clay

The natural (raw) clay is taken from the Karewa deposit (Garoua) in northern Cameroon. The physicochemical characteristics are mentioned in the following table 1:

TABLE 1. Some Characteristics of Karewa Natural Clay

Parameters	H (%)	IG (%)	D	C (%)	Ph	PAF
Values	22.40	98.83	1.13	95.75	6.83	4.35

H: GI: swelling index, d: density, c: colloidal, PAF: loss on ignition. It is found that the humidity is important (22.40%). This explains the hygroscopic nature of montmorillonite. This water corresponds to the free water of hydration which evaporates at 100 °C (Roller and Bouaziz, 1972). The quantity of this water in most of the time corresponds to that of the intermediate layers between the sheets of silicates, and depends on the nature of the adsorbed ions. The loss on

ignition being low, this shows that the clay contains less calcium salts and metal oxides. The low value of the moisture content of the clay suggests that the clay has a microporous structure because the micropores adsorb very little water and cause low humidity. The colloidal and swelling index values (95.75% and 98.83%).

3.2. Particle Size Analysis

The results from particle size analysis of Karewa clay are shown in Table 2:

TABLE 2. Particle size analysis of Karewa raw clay (Mohamadou, 2011).

Fraction (µm)	< 2	2-20	20-50	50-200
Percentage (%)	40.60	27.59	19.26	12.55

It is found that the clay fraction, characterized by a diameter of less than 2 µm constitutes 40.60% of the mass of the clay sample. The remainder of the sample consists of 27.59% fine silt, 19.26% coarse silt and 12.55% sand.

Many other characteristics concerning natural clay are determined by means of different analysis techniques and the results will be presented and commented on in what follows.

3.3. Determination of Cation Exchange Capacity (CEC)

The following tables 3 and 4 give respectively the cation exchange capacity and the exchangeable bases of the clay fraction and the mineralogical characteristics of our sample:

TABLE 3. CEC and exchangeable bases of the clay fraction of Karewa raw clay (Mohamadou, 2011)

Clay	CEC (meq/100g)	Bases exchangeable in meq / 100g			
		Cu ²⁺	Mg ²⁺	Na ⁺	K ⁺
Karewa	36.80	0.24	18.80	0.13	0.06

TABLE 4. Mineralogical Characteristics of Karewa Clay

Montmorionite	Quartz	Kaolinite	Feldspaths	Amphiboles
++++	+			

+ represents the quantity of elements in our clay

The high CEC value (36.80 meq / 100g of sample) could be due to the abundance of so-called swelling soils mainly montmorillonites (Nguetnkam et al., 2005) which belongs to the smectite family. Montmorillonite is indeed one of the main clays of vertisols in northern Cameroon (Nguetnkam et al., 2005).

The macroscopic appearance of our sample collected between 0-30 cm is a dark gray horizon, silty-clayey, has many roots: it is a porous horizon, plastic, sticky in wet state, friable in the dry state, abundant drying slots (Mohamadou, 2011). The results from the physico-chemical analysis of our adsorbent are shown in Table 5.

TABLE 5. Physico-chemical characters of Karewa clay (Mahamadou, 2011)

Organic matter (%)			pH		Phosphorus assimilable
CO	MO	NT	H ₂ O	KCl	
4.60	2.30	0.73	6.59	4.62	0.84

The physico-chemical analysis showed a total organic matter content of 4.60 with organic carbon and total nitrogen

proportions of 2.30% and 0.73% respectively. It is a weakly acidic horizon on the surface with a pH of 6.59 and 0.84% of assimilable phosphorus. The acidity of the Karewa soil may be due to the presence of acidic salts such as KCl and other acidic salts that generally form part of clays (Mohamadou, 2011). The presence of organic matter can be explained by the presence of organic manure and the chemical fertilizers dumped by farmers.

3.4. Effect of Contact Time

In fact, it can be seen that the Cr (VI) fixation curves by clay modified by sodium hydroxide and clay modified by aluminum hydroxide (CSC and CAH) can be divided into two parts: the first part of the kinetics corresponding to one phase very short, where the fixation of Cr (VI) is very fast, it is carried out in the first minutes of the adsorption and a second phase of medium speed where the adsorbed quantity evolves

more slowly and the adsorption rate is relatively low. The latter is well represented by sites saturation. This phenomenon can be explained by the existence of a first step of adsorption of Cr (VI) by clay modified by sodium hydroxide and clay modified by aluminum hydroxide (CSC and CAH) on easily accessible sites and probably localized on surfaces CSC and CAH solid supports, followed by molecular diffusion of Cr (VI) to less accessible adsorption sites such as the CSC and CAH interface spaces, or within the organic matter before achieve an adsorption equilibrium where all sites become occupied. The rapid fixation is explained by the high affinity of the supports for the retention of Cr (VI) and by a better diffusion of the substrate through the pores of these adsorbents. The equilibrium time is almost identical for the two kinetics carried out, it is 10 min for the CSC and CAH.

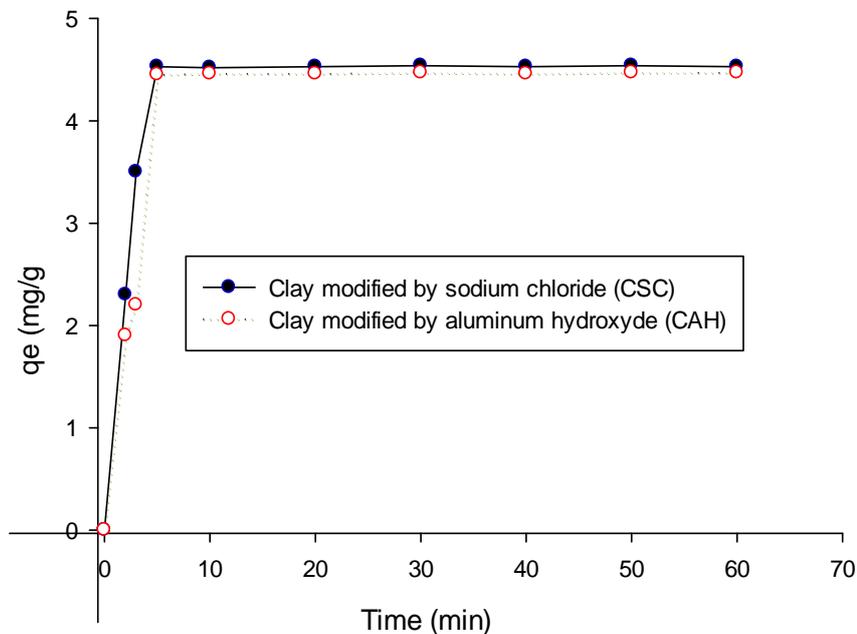


Fig. 1. Influence of stirring time on the amount of Cr (VI) adsorbed by clay modified by sodium hydroxide and modified by aluminum hydroxide (CSC and CAH).

3.5. Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter for the determining of the adsorbability of adsorbent at a given initial condition. The influences of clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) the adsorption of Cr (VI) is shown in Fig. 2. The results obtained at equilibrium and presented in Fig. 2 show that the increase in the mass of the adsorbent in the reaction medium decreases on the adsorption capacity and consequently the adsorbed amount of Cr (VI). In other words, a decrease in the mass of the animal activated carbon to an improvement in the fixation efficiency (Domga et al., 2018). This can be explained by the fact that by increasing the mass of adsorbent, there is a decrease in the number of active adsorption sites due

to the superposition of the adsorbent particles on the surface of the solid and the adsorbed amount of Cr (VI) caused by the increase in adsorbent mass. Indeed, the adsorbed amount is maximum for a mass of 0.1 g of adsorbent. These results are in agreement with the work done by Harouna et al., 2016 adsorption of Cu²⁺, Mn²⁺ and PO₄³⁻ ions from aqueous solution onto aluminum pillared clay from Karewa (North-Cameroon) .

3.6. Effect of Solution pH

The solution pH is another important parameter and it has a strong effect on the adsorption of metal ions on the surface of the clay. The effect of pH on the adsorption of Cr(VI) is investigated in the pH range of 3–10, and the results are shown in Fig. 3.

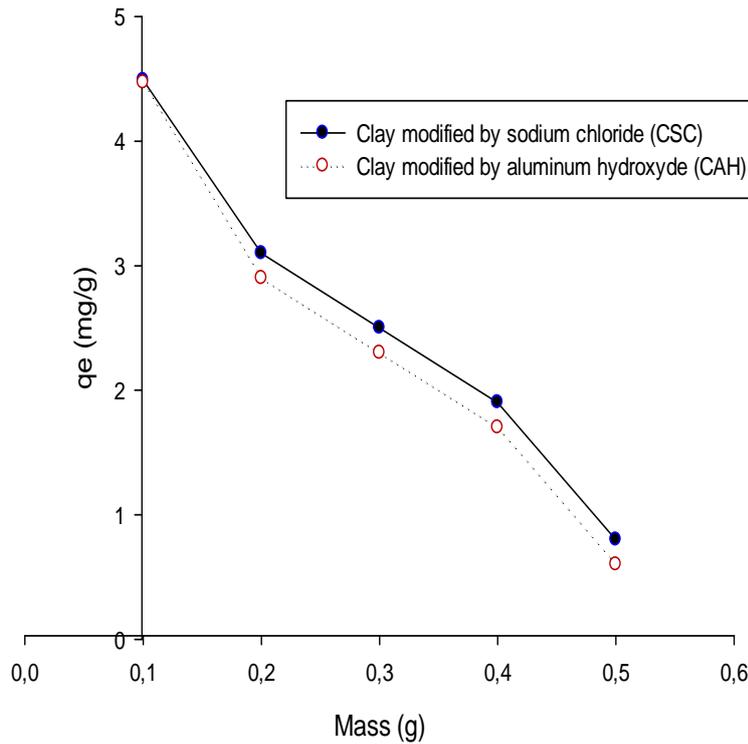


Fig. 2. Influence of the mass on the quantity of Cr (VI) adsorbed by clay modified by sodium hydroxide and clay modified by aluminum hydroxide (CSC and CAH).

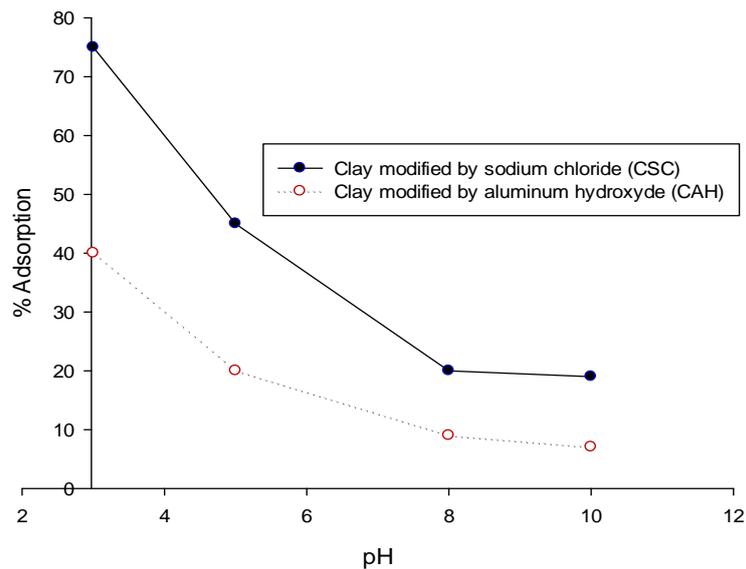


Fig. 3. Influence of the pH of the solution on the amount of Cr (VI) adsorbed by clay modified by sodium hydroxide and clay modified by aluminum hydroxide (CSC and CAH).

Figure 3 indicates the effect of solution pH on Cr (VI) removal by using clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH). The removal performance decreased from 75-19 % (CSC) to 40-7% (CAH) as the pH elevated from 3 to 10; but, the performance modifications were no longer dramatic in range

of 6 - 10. Solution pH had an important function within the adsorption process. In acidic environment, the principle chromium species were HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and H_2CrO_4 , whilst in alkaline medium CrO_4^{2-} predominated. In an acidic condition, the adsorbent surface was protonated to a high quantity. Thus the attraction among anionic species HCrO_4^-

and $\text{Cr}_2\text{O}_7^{2-}$ with a positively charged adsorbent surface strongly increased. Increasing the pH of the solution decreased the extent of positive charge on adsorbent main to weak bonding of negatively charged species on adsorbent surface. In an alkaline solution, other negative ions such as OH^- need to compete with the major anion, CrO_4^{2-} ion, for the sorption sites on the adsorbent. Since better chromium removal happened at acidic pH and because the actual chromium samples had acidic pH in nature, there has been no need to decrease the pH (Kalhori et al., 2013). This result was in agreement with the reports by Zhao and et al. (2013) and Chen et al. (2010).

3.7. Effect of Initial Concentration

Figure 4 shows the effect of initial concentration on Cr (VI) removal by of clay modified by sodium chloride and clay

modified by aluminum hydroxide (CSC and CAH). we find that the increase in the initial concentration of Cr (VI), causes an increase in the amount adsorbed on the surface of the various adsorbents used. In this case, the results obtained suggest that if the initial concentration of Cr (VI) in the solution is low, they adsorb only at the surface to form a monolayer for a very short time (Al-Ghouti et al., 2003 and when the initial concentration is high, there will consequently be more molecules that will diffuse toward the surface of the adsorbent particle sites than the retention becomes larger (Garg et al., 2003, Kadirvelu et al., 2005). It is obvious that for the concentration used, the different adsorbents used adsorb Cr (VI) almost with the same capacities.

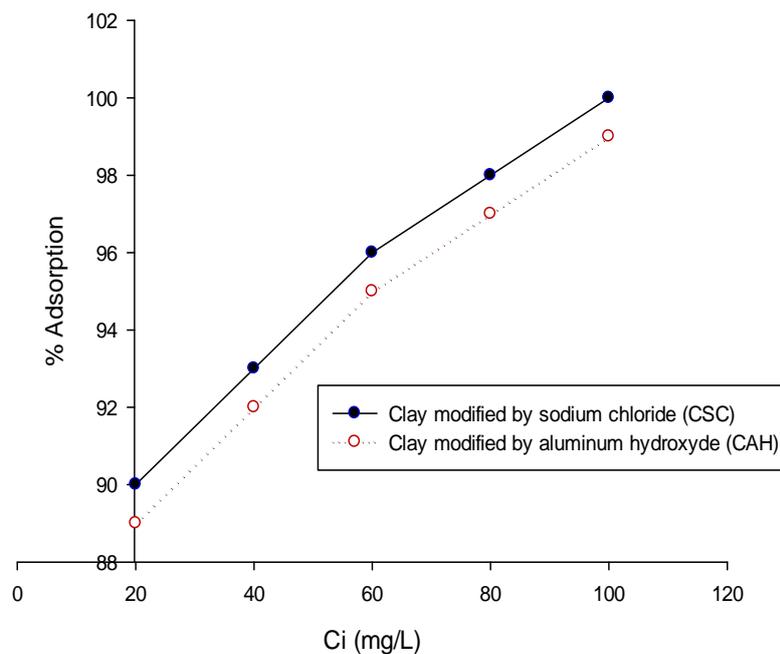


Fig. 4. Adsorption percentage influence on the concentration of Cr (VI) adsorbed by clay modified by sodium hydroxide and modified by aluminum hydroxide (CSC and CAH).

3.8. Effect of Temperature

Figure 5 shows the effect of temperature on Cr (VI) removal by of clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH). Temperature is a very important parameter in the adsorption process. It has two important effects (Hamdi et al., 2010). It increases the diffusion rate of the adsorbate molecules through the outer boundary layer and inside the pores of the adsorbent particles by decreasing the viscosity of the solution. It also increases the solubility of the adsorbate. We find that the increase in temperature in the range studied causes a slight decrease in adsorption capacity on both adsorbents. The clay adsorption modified by sodium chloride (4.86 mg / g for CSC) is more important than clay modified by aluminum hydroxide (4.77 mg / g for CAH) which could

explain the process adsorption is physical and exothermic. These results are contrary to those of Domga et al., (2018).

3.9. Study of the Adsorption Isotherm

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Analysis of equilibrium adsorption data by fitting different linear isotherm models is an important step to find the suitable model that can be used for design purposes (Haghsereht and Lu, 1998). The studies of adsorption isotherms are carried out on two well-known isotherms, the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of

adsorbate in the plane of surface. While, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a

function of the surface coverage (Weng *et al.*, 2013). The applicability of the isotherm equation is compared by judging the correlation coefficients R^2 .

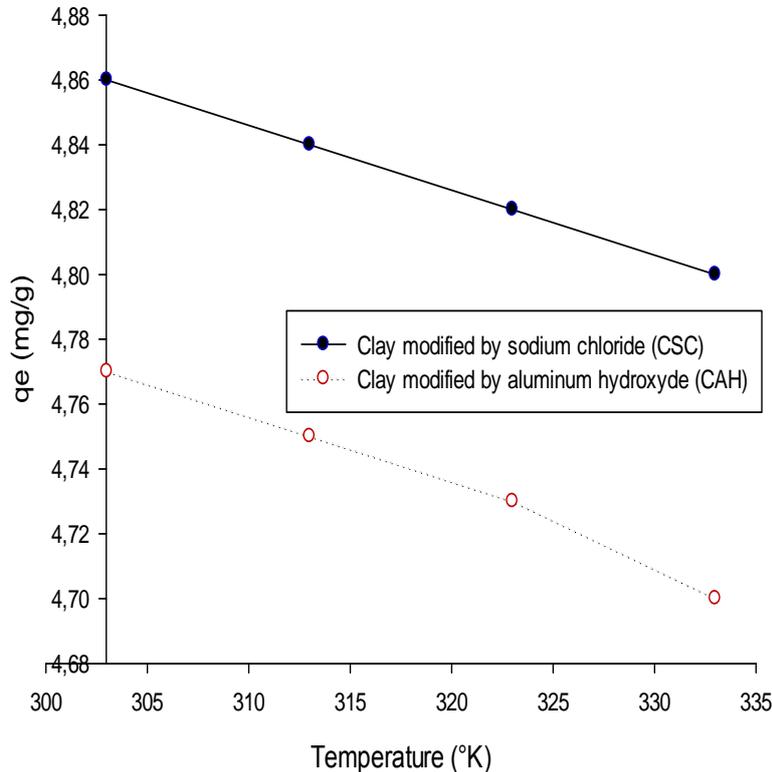


Fig. 5. Influence of temperature on the amount of Cr (VI) adsorbed by clay modified by sodium hydroxide and modified by aluminum hydroxide (CSC and CAH).

Langmuir and Freundlich isotherm models are applied to establish the relationship between the adsorption density of Cr (VI) on modified clay and its equilibrium concentration in aqueous solution.

The experimental data conform to the linear form of Langmuir model expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_e} \quad (1)$$

Where C_e is equilibrium concentration of the Cr (VI) (mg L^{-1}), q_e is the adsorption density of Cr (VI) (mg/g). q_m and K_L are the Langmuir constants which relate to the adsorption density (mg g^{-1}) and the energy of adsorption (L g^{-1}), respectively. q_m and K_L constants are obtained from the slope and intercept of the linear plot of C_e/q_e vs C_e , respectively. The adsorption equilibrium data are also applied to the Freundlich model in logarithmic form given as follows (Ali *et al.*, 2013):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

Where K_F (mg g^{-1}) and n are the constants of Freundlich which are related to adsorption density and adsorption intensity, respectively. K_F and $1/n$ are determined from the intercept and slope of linear plot of $\log q_e$ vs $\log C_e$, respectively.

The isotherm constants and correlation coefficients are calculated from the linear Langmuir and Freundlich plots by the plotting C_e/q_e vs C_e and $\log q_e$ vs $\log C_e$ and are represented in Table 1.

The adsorption pattern of Cr (VI) on tailings is well fitted by both Langmuir and Freundlich models with R^2 of 0.97–0.99. Both models are equally applicable.

The K_F value of the Freundlich equation (Table 1) indicates that the modified clay have a very high adsorption density for Cr (VI) ions in aqueous solutions. With high n values (between 1 and 10), the modification is beneficial to the adsorptions of metal ions (Ali *et al.*, 2013).

The adsorption parameters according to the Freundlich and Langmuir equations are summarized in Table 6 below.

TABLE 6. Freundlich and Langmuir adsorption model constants.

Models	Langmuir			Freundlich		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F	$1/n_f$	R^2
CSC	6.390	8.020	0.986	8.050	0.920	0.992
CAH	5.450	7.840	0.973	8.380	0.983	0.995

The results obtained show that the Freundlich model better describes the phenomenon of adsorption of Cr (VI) on the surface of the clay because they are close to unity. The values of $1/n$ of the Freundlich model are less than 1. This shows that the adsorption is done with a great intensity characterized

by heterogeneity between the surface of our clay and that of the molecules of ions and highlights a high adsorption capacity of clay (Li et al., 2010). Moreover, the Freundlich k_F constant reflects the adsorption capacity of a pollutant considered by the solid (Ali et al., 2013). The value of k_F is directly proportional to the amount of adsorbed pollutant. In other words, the higher the value of k_F , the greater the quantity retained. In our case, the results obtained from k_F vary between 8.05 and 8.38 in Cr (VI) respectively representing sodium clay and bridged clay. These data thus make it possible to classify the various adsorbents studied according to the adsorption capacity. In descending order, we have: bridged clay > sodium clay. Regarding the results of the Langmuir model, we have a homogeneous distribution of adsorption sites on the surface of our clay. The Langmuir isotherm is the separation factor defined by Equation 3 (Langmuir, 1918). The R_L values obtained ($0 \leq RL \leq 1$) indicate that the adsorption is all the more favorable.

$$R_L = 1 / (1 + K_L C_0) \quad (3)$$

3.10. Study of Adsorption Kinetics

Adsorption kinetics, the solute uptake rate, is one of the most important characteristics that represent the adsorption

efficiency of the modified clay. The adsorption rates of Cr (VI) on the modified clay in the first time, and then reaches equilibrium gradually at about 10 min respectively. In order to analyze the adsorption rate of Cr (VI) on modified clay, the pseudo first-order equation of Lagergren (4), the pseudo-second-order rate equation (5) and the intraparticle diffusion model (6) are evaluated based on the experimental data (Ho and Llow, 1998; Ho, 2004):

$$\ln(q_e - q_t) = k_1 t + \ln q_e \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

$$q_t = k_{int} t^{0.5} + X_i \quad (6)$$

Where k_1 is the Lagergren adsorption rate constant (h^{-1}) and k_2 is the pseudo-second-order adsorption rate constant ($g\ mg^{-1}\ h^{-1}$). q_e and q_t are the amounts of metal ions absorbed ($mg\ g^{-1}$) at equilibrium and at time t , respectively. Plots of $\log(q_e)/(q_e - q_t)$ vs t and $t/(q_t)$ vs t (mg/g) is the amount adsorbed at time t and K_{int} is the intraparticle rate constant. The different linear correlation coefficients R^2 and the speed constants deduced from each kinetic model are reported in Table 7.

TABLE 7. Parameters Characterizing the Adsorption Kinetics of Cr (VI).

Models	Pseudo first - order			Pseudo second - order			Intraparticle diffusion		
	q_e (mg/g)	K_1 (min ⁻¹)	R^2	q_e (mg/g)	K_2 (g.mg ⁻¹ .min ⁻¹)	R^2	X_i (m ² .s ⁻¹)	K_{int} (mg.L.min ⁻¹)	R^2
CSC	0.018	0.007	0.027	4.530	4.870	0.999	157.040	33.350	0.208
CAH	0.045	0.016	0.228	4.490	5.380	0.999	100.260	23.620	0.081

Clearly, it can be seen from table. 2 that the pseudo-second-order kinetic model provides a good correlation for the adsorption of Cr (VI) on modified clay in contrast to the pseudo-first-order model and the intraparticle diffusion model. In addition, the correlation coefficient of the pseudo second-order kinetic model is bigger than that of the pseudo-first order kinetic model and the intraparticle diffusion model (see Table 2). However, the R^2 value coefficient greater than 0.95 of the pseudo-second-order model shows that the latter is applicable to our experimental data. This model reflects the existence of strong interactions between the clay surface and the adsorbate molecules. This indicates that the adsorption is done in 2 steps. The first step is the diffusion of the Cr (VI) molecules towards the clay surface and the interaction of the Cr (VI) molecules on the clay surface.

3.11. Thermodynamic Study

Thermodynamic parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role to determine spontaneity and heat change of the adsorption

process. Thermodynamic parameters were calculated using the following relations (Karagoz, et al., 1999):

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

The equilibrium constant K_c was calculated using the ratio:

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

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Where; K_c is the equilibrium constant, q_e and C_e are amount adsorbed (mg/g) and concentration of solution (mg/L) at equilibrium respectively. R is the universal gas constant ($8.314J/mol/K$) and T is the temperature (K). ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot $\ln K_c$ vs. $1/T$, respectively (From equation 9), ΔG° were determined using $\ln K_c$ values for different temperatures. The Results were summarized in Table 8.

TABLE 8. Thermodynamic parameters of Cr (VI) adsorption clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH).

	ΔG° (kJ mol ⁻¹)				ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
	Temperature (°C)					
	30	40	50	60		
CSC	-11.370	11.780	-12.160	-12.540	-0.110	0.038
CAH	-54.400	-55.100	-55.800	-56.500	-33.650	0.068

The thermodynamic parameters, the standard Gibbs energy (ΔG°), standard enthalpy (ΔH°) and entropy (ΔS°) for Cr (VI) at various temperatures are shown in Table 3. As shown in Table 3, the negative values of the standard Gibbs energy (ΔG°) Cr (VI) indicate that the adsorption is possible and thermodynamically spontaneous. We note also that, for clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH), ΔG° decreases with increasing temperature of the solution. This can be explained by the fact that adsorption becomes easier, thus indicating the presence of a high drive strength. The value of the standard enthalpy (ΔH°) is negative, and this indicates that the adsorption of clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) is exothermic. Furthermore, examination of the values of the standard enthalpy of adsorption (<40 kJ/mol) shows that it is a physisorption (Gherbi, 2008). The positive value of standard entropy (ΔS°) shows decreasing appearance at the solid/liquid interface during the adsorption of Cr (VI).

IV. CONCLUSION

This study revealed that the clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) could be used as an effective adsorbent material for the treatment of Cr (VI) in waste water. It also shows that the adsorption of Cr (VI) on clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) depends on the contact time, initial concentration, pH, temperature and adsorbent dose. In the study of the adsorption kinetics, the model of pseudo-second order allows a better or relation between the adsorption data model of pseudo-first order; this suggests that the rate limiting step may be a physical adsorption rather than diffusion. Modeling the adsorption process mounted it in all the cases studied follows the model of pseudo-second order, the time that the isotherm follows the Langmuir and Freundlich models. The adsorption of clay modified by sodium chloride and clay modified by aluminum hydroxide (CSC and CAH) is possible, thermodynamically spontaneous, exothermic and physisorption. The clay is economic in the treatment of waste water containing Cr (VI).

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