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Hexavalent chromium removal from aqueous solution by adsorbent prepared from Moroccan oil shale of Timahdit

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ABSTRACT

Removal of Cr (VI) from aqueous solution using new adsorbent starting from the Moroccan oil shale of Timahdit (layer Y) by a chemical activation with sulfuric acid H_2SO_4 under different experimental conditions was investigated in this study. The effects of agitation time, pH on the removal of Cr (VI) were studied. In order to investigate the adsorption isotherm, two equilibrium models, Langmuir, and Freundlich isotherm models, were analyzed. The effect of solution pH on the adsorption onto this adsorbent was studied in the pH range 2.1-7.89. Adsorption of Cr (VI) is highly pH dependent and the results indicate that the optimum pH for the removal was found to be 2.1 for this adsorbent.

Keywords: Oil shale, Activation, Sulfuric acid, Chromium removal, Adsorption isotherms.

INTRODUCTION

Industrial progress has made life more comfortable and easy. But at the same time the natural environment had suffered from the unfavorable effects of pollution. Heavy metals are unpleasantly affecting our ecosystem due to their toxicological and physiological effects in environment. These metals, if present beyond certain concentration can be a serious health hazard which can leads to many disorders in normal functioning of human beings and animals [1]. The main reason for heavy metal pollution is due to metal-plating facilities, battery manufacturing processes, mining and metallurgical engineering, dyeing operations, electroplating, nuclear power plants, aerospace industries, the production of paints and pigments and glass production industries [2]. The main heavy metals which cause metal ion pollution are Th, Cd, Pb, Cr, As, Hg, Cu and Ni. Unlike most organic pollutants, heavy metals are generally refractory and cannot be degraded or readily detoxified biologically [2].

Chromium is one of the most toxic pollutants which cause severe environmental and public health problems. When accumulated at high levels, chromium can generate serious problems and when concentration reaches 0.1 mg/g body weight, it can ultimately become lethal [3]. The most common forms of chromium are Cr (0), Cr (III), and Cr (VI). Hexavalent form is more toxic than trivalent and requires more concern. Strong exposure to Cr (VI) causes cancer in the digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [4].

In aqueous solution, Cr (VI) exists in the form viz. - chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$ and hydrogen chromate $HCrO_4^-$. CrO_4^{2-} is predominant in basic solutions, $HCrO_4^-$ is predominant at pH < 1 while $HCrO_4^-$ and $Cr_2O_7^{2-}$ are predominant at pH 2-6. The removal of toxic metals from waste water has been achieved by several processes such as ion exchange [5], sedimentation [6], electrochemical processes [7,8], cementation [9], biological operations [10], coagulation/flocculation [11], filtration and membrane processes [12,13], chemical precipitation, adsorption [14] and solvent extraction [15,16]. Most of these methods suffer from drawbacks like high capital and operational cost and there are problems in disposal of residual metal sludge [17]. In contrast, the adsorption technique has become one of the most preferred methods for the removal of heavy metals due to its high efficiency and low cost.

Many agricultural wastes had directly been used as sorbents for heavy metal adsorption from wastewater which included soybean hull [18], olive cake [19], wheat straw [20], maize cob [21], rice husk [22], barley straw [23], bagasse pith [24], coconut husk [25], cocoa shells [26], tea leaves [27], spent coffee grounds and pomelo skin [28], almond shell [29], orange peel and banana peel [30]. Activated carbons are more effective in the removal of heavy metals due to some specific characteristics that enhance the use of activated carbon for the removal of contaminants including heavy metals from water supplies and wastewater [31]. Many studies have used different type of activated carbon to remove Cr (VI) by adsorption.

Coconut shell activated carbon [32], wood and dust coal activated carbons [33], hazelnut activated carbon [34], sawdust and used tyre activated carbon [35] were used for Cr (VI) uptake.

The present paper is concerned with the synthesis of activated carbons derived from Moroccan oil shale of Timahdit (layer Y) by chemical activation with H_2SO_4 and the removal of hexavalent chromium from aqueous solution. In order to enhance local materials and not expensive, we used as a precursor decarbonated of Moroccan oil shale obtained by elimination of the carbonates in the native rock, was mixed with sulfuric acid and treated in different conditions [36]. The kinetics and isotherms about the sorption of Cr (VI) on the prepared samples were studied. The influence of several operating parameters, such as pH and contact time of adsorbate on the adsorption capacity, were also investigated.

MATERIALS AND METHODS

Preparation of adsorbents

Preparation of the precursor YH

The raw material used in this work is Moroccan oil shale of Timahdit (layer Y). This material is composed from the organic matter chemically linked to the mineral matter essentially formed by calcite, dolomite, silicate and clays (table 1) [36, 37].

Table 1. Mineralogical composition of the Timahdit oil shale.

Constituent	Calcite	Dolomite	Clays	Silicate	Organic matter
Wt. (%)	15.16	12.33	26.87	21.75	23.89

The naturally oil shale was crushed and ground to 100-200 µm and the resulting product was attacked with 6N HCl. This attack was continued until there was no more CO_2 release. After filtration, the residue was washed by distilled water to eliminate excess acid. The product obtained, referred to as YH, was used as the precursor for preparing the adsorbents. Elemental analysis of this precursor (Table 2) shows the presence of C, O, H, S, Si, Mg and other minorities' elements [36].

Table 2. Chemical composition of the precursor YH.

Element	C	O	Si	S	Mg	P
Atomic %	50.00	35.60	8.12	1.87	0.95	0.07

Activation of the precursor and characterization of the product

The precursor YH, a particle size of 80-100µm in diameter, was mixed with the sulfuric acid at 80%, with a weight ratio H_2SO_4/precursor = 3. The choice of the activating agent and the weight ratio was dictated by results obtained after many studies trials in the laboratory and according to our previous studies [36, 37]. The activation experiments were performed under various conditions to obtain the optimal condition for activation.

The mixture was heated in furnace under oxidant atmosphere gaze (air) at different temperatures bitewing 200 and 450°C, after preprocessing at 120°C in oven under air [36]. Thermally treated product, referred by YHS, was washed with distilled water in a Soxhlet extractor, to eliminate excess acid (H_2SO_4) and soluble matter then dried at 110°C. The general procedure of the activation process of this study is described below an dis schematically outlined in figure 1.

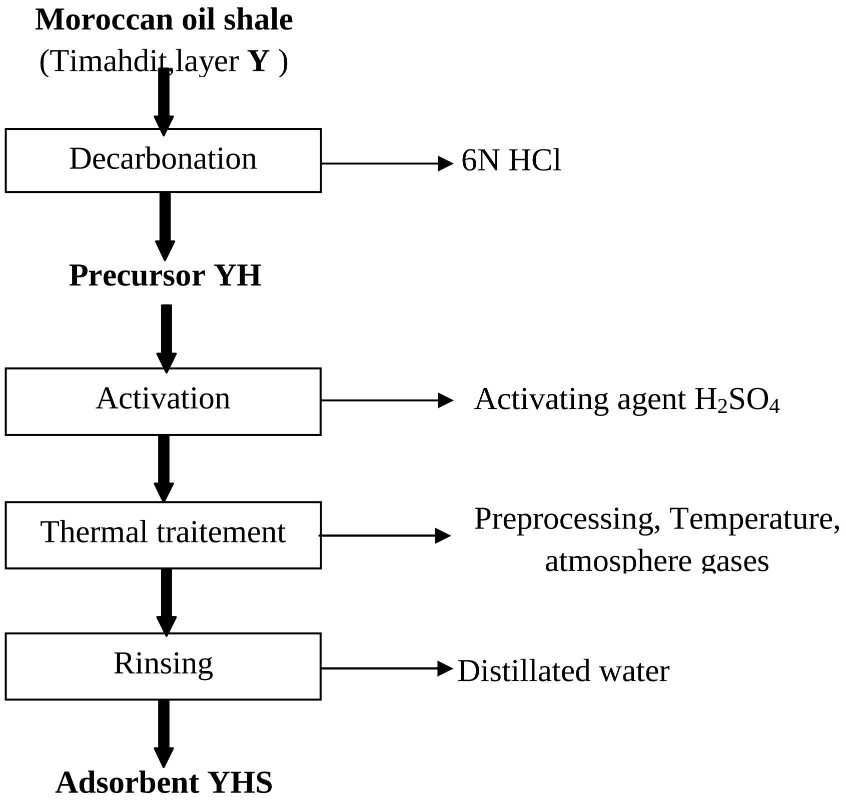

Figure 1. Flow diagram for activation process.

Before used in adsorption tests the adsorbent was sieved, more 95% of the final particles had an average diameter than of 100 mm, and characterized by different analytical methods.

The performance of a prepared adsorbent was evaluated by determination of the maximum adsorption capacity of potassium dichromate, the specific area (S_{BET}).

Preparation of potassium dichromate solution

The stock solutions of Cr(VI) of concentration 1 g/L was prepared by dissolving 2.8 grams of analytical grade of $K_2Cr_2O_7$ in 1 L of distilled water. The stock solution was further diluted with distilled water to desired concentration for obtaining the standard solutions for absorbance measurement. The initial pH of the test solutions was adjusted to the desired value by using dilute solutions of HCl and NaOH. The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

Experimental procedure

The adsorption tests were carried out in batch method. Indeed, a mass of 80 mg of each adsorbent is emerged in 400 mL of a potassium dichromate (PDC) solution concentration to 10 mg / L. The mixture is subjected to constant agitation and samples were taken at different time intervals. To determine the maximum adsorption capacity of Cr (VI), we adopted the method known as “the bottle point method”. For this purpose, various weights between 20 and 80 mg of each adsorbent are emerged in a volume of 200 mL of a solution of dichromate concentration of 30 mg / L. In late each experiment: The measurement of the concentration of non adsorbed Cr (VI) was carried out according to standard colorimetric method in different time. The amount of adsorption at equilibrium, Q_e (mg/g) was calculated by the following mass balance equation.

$$Q_e = \frac{V\left(C_0 - C_e\right)}{m_{ads}} \tag{1}$$

Where Co and Ce (mg/L) are the liquid phase concentrations of PDC at initial and equilibrium respectively .V (L) is the volume of the solution. m_{ads} (g) is the mass of dry adsorbent used. The DC removal percentage can be calculated as follows

$$\mathrm{Re}\,moval\% = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

Theory of Adsorption isotherm

To quantify the adsorption capacity of the absorbent for the removal of Cr (IV), the most commonly used isotherm, namely Freundlich and Langmuir have been adopted.

Freundlich isotherm.

The linear form of freundlich isotherm [38] is represented by the equation

$$Lnq_e = LnK_f + \frac{1}{n} LnC_e \tag{3}$$

Where qe is the amount of dyes adsorbed per unit weight of the adsorbent, (mg/L), K_f is (mg/g (L/mg)) measure of adsorption capacity and 1 / n is the adsorption intensity. In general K_f value increases the adsorption capacity for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of n > 1 represents favorable adsorption condition [39, 40] (or) the value of 1 / n are lying in the range of 1 to 10 confirms the favorable condition for adsorption. The linear plot of Ln q_e against the Ln C_e (figure is given) shows that the adsorption obeys the Freundlich model.

Langmuir isotherm

Langmuir isotherm model [41] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$C_e / q_e = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{4}$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent; q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. q_m is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption (or rate of adsorption). The linear plot of specific adsorption capacity against the equilibrium concentration (C_e) (figure is given) shows that the adsorption obeys the Langmuir model. The Langmuir constant q_m and b were determined from the slope and intercept of the plot and are presented in table 1. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L [42, 43] by the equation

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

$R_L > 1$	Unfavorable adsorption
$0 < R_L < 1$	Favorable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	Linear adsorption

The R_L values lies between 0 to 1 indicate the process is favorable adsorption.

RESULTS AND DISCUSSION

Properties of a prepared adsorbent

The elementary analysis of the decarbonated rock YH and the best adsorbent YHS by X-ray fluorescence (Table 1), revealed that both samples contain mostly oxygen, carbon, silicon and sulfur. And other elements with low amounts (Iron, sodium and phosphorus). We also note that the content of oxygen, carbon, silica and sulfur increases slightly, and those of phosphorus, iron, decrease in the adsorbent YHS comparing the precursor YH.

Table 1. Results of chemical analysis for YH and YHS (%wt).

Element	YH	YHS
O (%)	60.4	63.1
S (%)	2.46	3.758
C (%)	12.3	14.02
Si (%)	16.5	18.01
Fe (%)	1.92	0.45
Al (%)	3.86	0.000
Na (%)	0.292	0.100
P (%)	0.000	0.000
Mg (%)	0.354	0.000
Ca (%)	0.189	0.102

The BET surface area was calculated by the Brunauer, Emmett, and Teller (BET) method using the adsorption isotherms [44]. The results of analyzes specific surface S_{BET} of the product YHS compared to the precursor YH are summarized in Table 2.

Table 2. Specific surface obtained by the BET method.

Sample	YH	YHS
S_{BET} (m^2/g)	24	180

This table shows that the total surface area of the adsorbent YHS is higher than that obtained by the precursor YH which allows that chemical activation with sulfuric acid causes an increase in the surface.

The morphology of the samples YH and YHS was examined by scanning electron microscope (SEM) (Fig 2). The examination of this figure shows a significant effect of chemical activation with sulfuric acid on the development of porosity within the adsorbent YHS compared to YH.

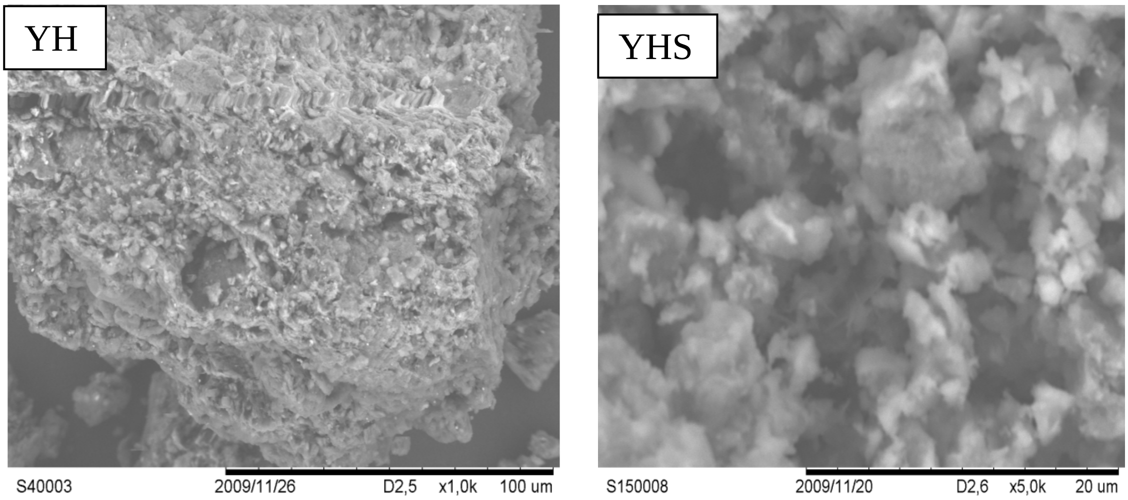

Figure 2. SEM of precursor YH and prepared adsorbent YHS.

Fourier transform infrared spectroscopy results (Fig. 3), enabled us to highlight the structural changes of the material during the chemical activation with sulfuric acid. The comparison between the spectra of the two samples YH and YHS has enabled us to identify the following points:

❖The disappearance of the bands situated towards 2927 and 2860 cm^{-1} characteristic of CH elongations groups CH_3, CH_2 and CH.

❖The disappearance of the very fine bands situated towards 872 cm^{-1} characteristic groups C = CH_2 and HC = CH_2, the alkanes.
❖An increase in the intensity of the band at towards 3635 cm^{-1} characteristic of OH elongations.

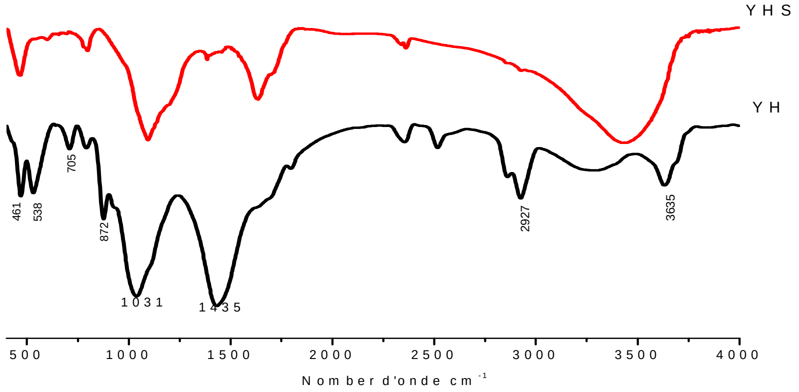

Figure 3. Infrared spectra (FTIR) of the adsorbent YHS200°C1/2h.

Effect of pH value

The pH value, associated with the adsorption mechanism, is one of important parameters in controlling the adsorption of Cr(VI). It causes the change of surface charge of the sorbent, conversion of the chromium species and other ions present in the solution, and extent of dissociation of functional groups on the active sites of the adsorbent. For chromium aqueous, the distribution of Cr(VI) species is dependent on both the total concentration of Cr(VI) and pH value of the equilibrium solution. The Cr(VI) may exist in the aqueous phase in several anionic forms, such as chromate CrO_4^{2-} (pH > 6.0), dichromate $Cr_2O_7^{2-}$ and $HCrO_4^-$ (1.0-6.0) or H_2CrO_4 (pH < 1.0) [45]. In this work, Cr(VI) adsorption onto YHS as a function of pH ranging from 2.1 to 7.89 was shown in Fig. 4. It can be seen from Fig. 4 that the adsorption abilities of Cr(VI) on this adsorbent was sharply decreased with the increase in pH from 2.1 to 7.89. Cr(VI) adsorption was superior at low pH as observed by several workers [46-53]. In order to understand this effect it is necessary to examine the adsorbate and the adsorbent surface at different pH. Cr(VI) exists as hydrogen chromate anions ($HCrO_4^-$) between pH 1.0 and pH 6.5 and it exists as chromate ions (CrO_4^{2-}) at pH≈8 according to the following equations:

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \quad 0.80 \qquad (6)$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^- \quad 6.50 \qquad (7)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad 1.52 \qquad (8)$$

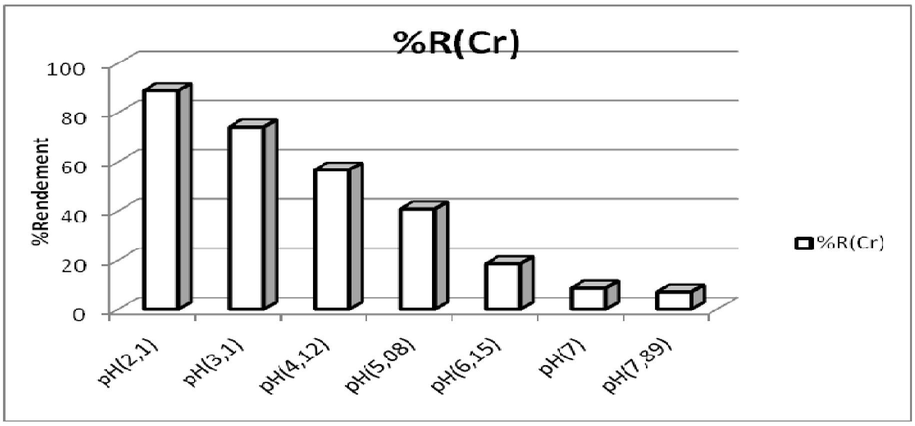

Figure 4. Cr(VI) removal percentage at different pH.

The percentage of Cr(VI) removal was higher in the lower pH ranges due to high electrostatic force of attraction. As the number of H^+ ions increased with lowering the solution pH, which neutralized the negative charge on adsorbent surface and thereby increased the diffusion of chromate ions into the bulk of the adsorbent [54]. The decrease in the adsorption with increase in pH may be due to the increased number of OH^- ions in the bulk which retarded the diffusion of chromate ions. The decrease in adsorption at higher pH may be due to the competitiveness of the oxyanions of chromium.

Effect of contact time

The amount of Cr(VI) adsorbed on YH and YHS carbons was studied as a function of shaking time at 10 mg/L) of Cr(VI) at 200°C, 80 mg of each adsorbent and desired pH. The results are given in Fig. 5. It is evident from this figure that the adsorption of Cr(VI) increased with increase in contact time from 0 min to 300 min, then became slow up to 100 min and the saturation is almost reached in 100 min for YHS, per it is against the order of 50 min for adsorbent YH. The plot reveals that the rate of percent removal of chromium is higher at the beginning. This is probably due to availability of more adsorption sites for the adsorption of chromium ions for both adsorbents. We also note that the removal rate of Cr adsorbed by YH is higher than that obtained by YHS. Moreover, it should be noted that the removal rate of Cr(VI) by YHS equal to 84.68%.

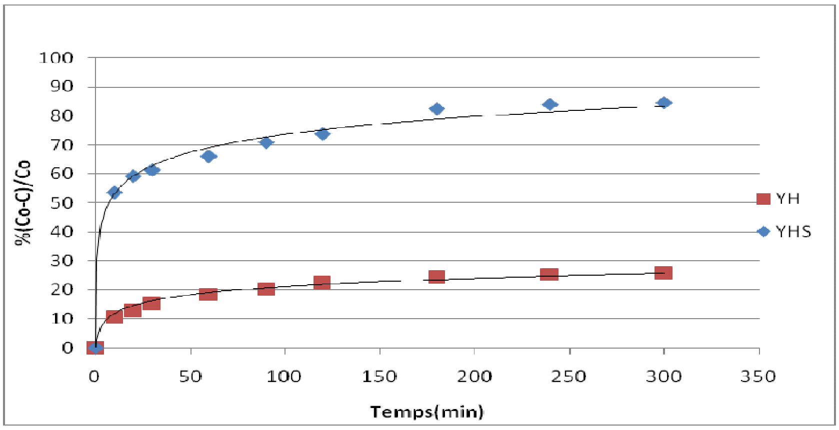

Figure 5. Percentage removal of chromium ion using YH and YHS at different time intervals.

Adsorption isotherms

Equilibrium data, commonly known as adsorption isotherms, are important in the basic design of adsorption systems, and are critical in optimizing the use of adsorbents. To optimize the design of an adsorption system for removing Cr(VI) from solutions, it is essential to establish the most appropriate correlation for the equilibrium curves. Several isotherm equations are available and two important isotherms were applied to fit the equilibrium data in this study: the Langmuir and Freundlich isotherms. The adsorption isotherms and fitting results are shown in Figs. 6 and 7 and Table 3. Linear regression allowed us to determine the parameters of adsorption such as Q °, b, n and K_f of the ion $Cr_2O_7^{2-}$.

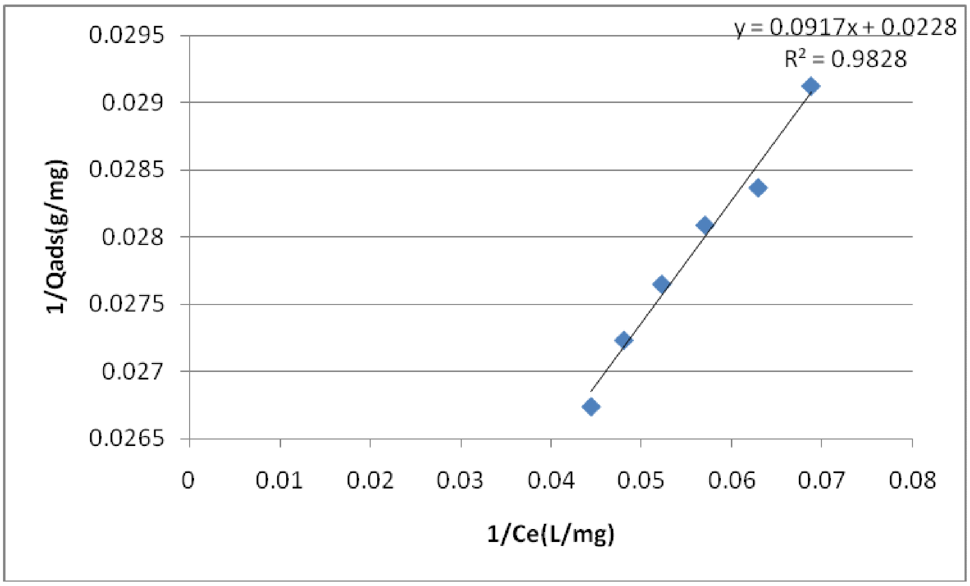

Figure 6. Langmuir isotherm plots of $Cr_2O_7^{2-}$ adsorption on YHS.

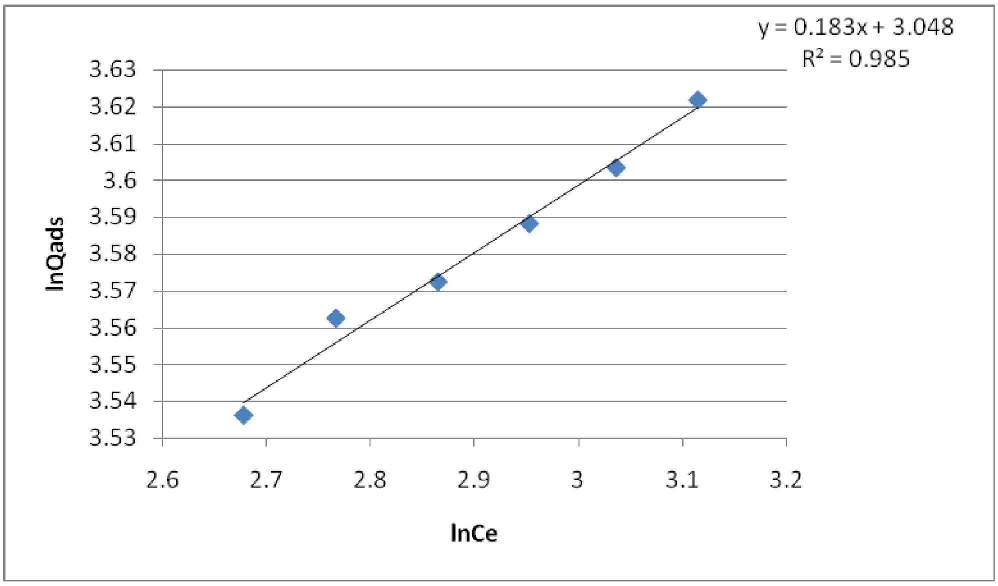

Figure 7. Freundlich isotherm plots $Cr_2O_7^{2-}$ adsorption on YHS.

Table 3. Isotherm parameters obtained for the adsorption of Cr(VI) ion onto YHS.

Isotherm models	Langmuir				Freundlich			
Adsorption parameters	Q_o(mg/g)	b_1	R_L	R^2	K_f	n	1/n	R^2
	43.85	0.2	0.1	0.983	21.07	0.1	5.46	0.985

We note that the correlation coefficients are close to unity, which allowed us to infer that the adsorption of Cr(IV) is dominated by surface adsorption which translates as the Langmuir model by building a monomolecular layer of adsorbate on the surface of the adsorbent [55,56]. The Freundlich adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir isotherm assumes that the adsorption occurs in a monolayer, or the adsorption may only occur at a fixed number of localized sites on a surface on which all adsorption sites are identical and energetically equivalent. The higher correlation coefficient (R^2) for the Freundlich isotherm indicated that the data fitted satisfactorily the Freundlich isotherm. This leads further support to the conclusion that the surface of the YHS investigated in this work is likely made up of small heterogeneous adsorption patches, which are dissimilar to each other in respect of adsorption phenomenon. Dimensionless separation factor, R_L, shows that the adsorption onto YHS is favorable (Table 3). The values of maximal adsorption capacity, of the Cr(IV) ion, obtained from Langmuir and Freundlich models are 43.85 and 21.07 mg/g, respectively.

CONCLUSION

This work shows that adsorbent materials prepared from Moroccan oil shale of Timahdit (layer Y), is an efficient sorbent for the removal of Cr (VI) from aqueous solution. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. Adsorption of Cr(VI) was highly pH-dependent, reaching a maximum (84.68%) at pH 2.1. Comparing the regression coefficient (R^2) for the two isotherms, it was found that Freundlich is the best with average R^2 value of 0.985 followed by Langmuir with average R^2 value of 0.983. The maximum value of monolayer adsprption capacity is 43.85 mg/g.

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