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Preparation and Development of a Novel Activated Carbon based on Moroccan Oil Shale Using Activation Process

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Abstract The objective of this study is the optimization of experimental conditions and the identification of various parameters influencing the preparation of the activated carbon using activation process. The results obtained throughout this work confirm good adsorption capacity of the activated carbon based on Moroccan oil shale. The (SEM) and (FTIR) analysis were used to confirm the adsorption performance of activated carbon from oil shale. Moreover, the Langmuir isotherm showed the best fit with experimental data, the maximum adsorption capacity of cadmium (II) ions was determined to be 55.87 mg/g. The kinetics analysis illustrates that the adsorption processes can be described by the pseudo-first order model.

Keywords Moroccan Oil shale, Activated carbon, Activation process, Equilibrium and kinetics study

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1. Introduction

In the context of the valorization of natural resources, we proceeded to transformation of the Moroccan oil shale to activated carbon. The aim of this work is to optimize the conditions for the preparation of activated carbon using activation process. During the first step, we prepared the rock of Moroccan oil shale, our choice was on the Timahdit deposit especially the Y-layer. The oil shale rock is composed of carbonates, the elimination of which is relatively simple. Indeed, the presence of organic matter and clays in oil shale encouraged us to prepare the activated carbon by physical or chemical activation based on Moroccan oil shale (Table 1). The activated carbon from the oil shale is intended for applications in the field of sewage water treatment. Oil shale is a sedimentary rock drowned of organic matter called kerogen [1, 2]. It is essentially an immature geological form of oil [3]. It is estimated that there are at least 8 trillion barrels of oil shale resources around the world [4].

Table 1. Composition of oil shale (Y-layer)

Constituent	Organic mater	Calcite	Dolomite	Silicate	Clays
Wt. (%)	23.87	15.16	12.33	21.75	26.87

Morocco has large reserves of oil shale, which allows it to be ranked the sixth country regarding its oil shale reserves, estimated to produce some 50 billion barrels of oil shale [5, 6]. It is endowed with a large resource of oil shale and at least 10 distinct oil shale deposits (Figure 1) [7]. The two deposits that have been explored most extensively are the Timahdit and the Tarfaya deposits [8, 9]. The Timahdit deposit is located about 250 kilometres southeast of Rabat [10]. It underlies an area about 70 kilometres long and 4 to 10 kilometres wide. The thickness of the oil shale ranges from 80 to 170 meters [11].

There is a growing interest in using oil shale as activated carbon for removal of heavy metal from aqueous solutions. The aim of the present work is to evaluate the potential of oil shales as a potential source of activated carbon for heavy metal retention. For this objective, a set of experiments at various conditions of activation were performed. The results of the cadmium (II) adsorption test are very encouraging and show that oil shale can be used as activated carbon.

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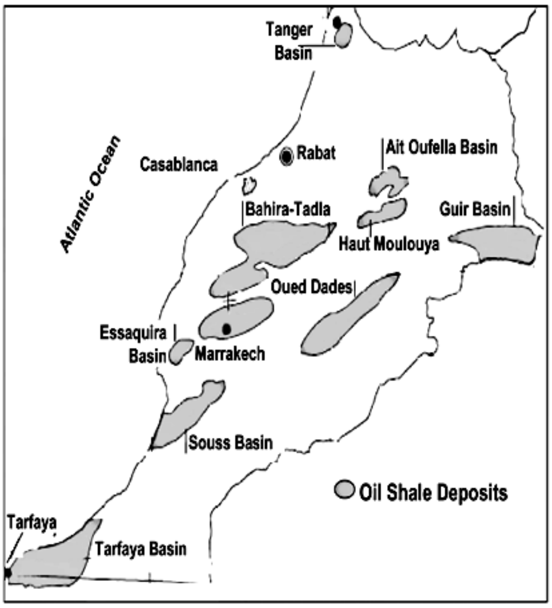


Figure 1. Map of Moroccan resources [7]

2. Materials and Methods

2.1. Preparation of Activated Carbon Based on Oil Shale

The raw material used is Moroccan oil shale (Y-layer). This material is composed from the organic matter and the mineral matter [12]. The raw rock (Y) there was crushed, and then ground. At a mass of the powder (Y) was lixiviate with hydrochloric acid, to obtain the concentrated oil shale to be named (YC). The precursor (YC) was mixed with the sulfuric acid different ratio m_{H2SO4}/m_{YC}.

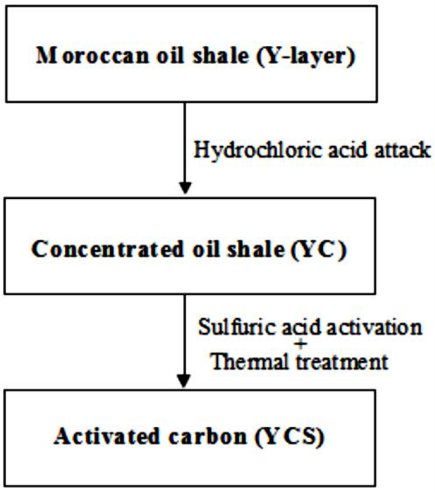


Figure 2. Scheme for elaboration of activated carbon (YCS)

The mixture was heated in electric furnace under oxidant atmosphere gaze at different temperatures, after preprocessing at 140℃ in oven under air. The (YCS) precursor are subjected to extensive washing with distilled water in a soxhlet apparatus for 72 h, to eliminate excess acid (H_2SO_4) then dried at 80℃ (Figure 2).

3. Results and Discussion

3.1. Experimental Response

3.1.1. Yield Char

The yield char or activation yield of the prepared activated carbon is determined from the mass of the concentrated rock initially used. It is given by the following formula (Eq. (1)) [13]:

$$R(\%) = \frac{m_{YCS}}{m_{YC}} * 100 \qquad (1)$$

With R: yield char, m_{YCS}: mass of activated carbon prepared and m_{YC}: the mass of the concentrated rock initially used.

3.1.2. Maximum Adsorption Capacity

This method provides several equilibrium points at one time under similar experimental conditions. We adopted to determine maximum adsorption capacity of cadmium (II) ions by activated carbon, the adsorption of cadmium on the activated carbon has been realized on the solution from cadmium chloride. A solution of cadmium (II) ions of concentration 30 mg/L was prepared by dissolving 50 mg of $CdCl_2$ in a 1000 mL volumetric flask. This solution was stirred on a magnetic stirrer for one hour to obtain homogeneity. The pH of the mixture was adjusted either with 0.1 N HCl or 0.1 N NaOH. The cadmium concentration was determined using atomic absorption spectroscopy (AAS). At the end of each series of experiments, the equilibrium concentration in cadmium was determined by atomic absorption spectroscopy and the mass of cadmium adsorbed per gram of activated carbon. The amount of cadmium (II) ions adsorbed per unit mass of activated carbon (Q_{max}) was calculated using the following formula (Eq. (2)) [14]:

$$Q_{max}\,(\mathrm{mg/g}) = \frac{(C_0 - C_e) * V}{m_{YCS}} \qquad (2)$$

With: Q_{max}: amount adsorbed at the equilibrium per activated carbon unit mass (mg/g), V: volume of the solution of cadmium (L), C_0: initial concentration of cadmium (mg /L), C_e: equilibrium concentration of cadmium (mg /L) and m_{YCS}: mass of the sample put into of solution (g).

3.2. Concentration of the Organic Matter

We studied the influence of concentration in the organic matter by the hydrochloric acid with the maximum capacity of adsorption of cadmium (II) ions. The quantity of oil shale powder (Y) was added under agitation to a solution of HCl (1 mol /L) until the complete release of carbon dioxide. The concentrated oil shale will be named (YC).

From the histogram in Figure 3, we see that the maximum adsorption capacity of Cd (II) ions depends on the concentration of organic matter by the hydrochloric acid. Indeed, when hydrochloric acid is present, the maximum adsorption capacity of Cd (II) ions increase at 58.33 (mg/g) while the concentration of organic matter by the hydrochloric acid increase the maximum adsorption capacity for Cd (II) ions up to six times. This can be explained by the elimination of mineral matter (carbonate) of oil shale by the hydrochloric acid.

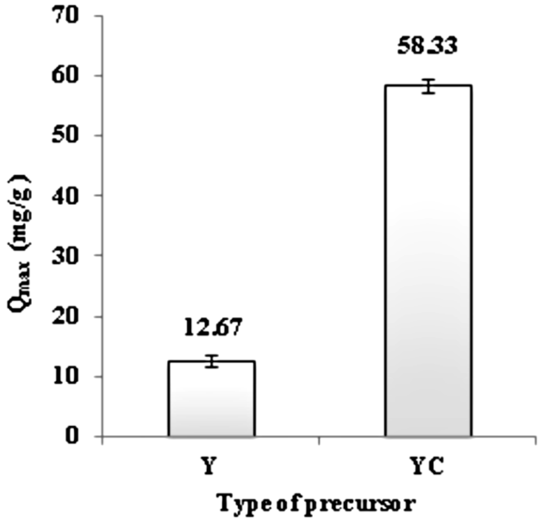


Figure 3. Effect of the concentration of organic matter on adsorption capacity of Cd (II) ions

3.3. Activation Process

Activation with sulfuric acid has become a widespread method for the manufacturer of activated carbon [15]. The use of sulfuric acid has some environmental benefits such as easy recovery and low cost of energy [16]. The sulfuric acid acts as a catalyst to promote bond cleavage, dehydration, and may operate as a template because the volume occupied by sulfuric acid to the interior of the activated carbon is coincident with the micropore volume of the activated carbon obtained [17]. The precursor (YC) was activated by the sulfuric acid H_2SO_4. The product obtained, referenced by (YCS) where "S" designates the activation with sulfuric acid H_2SO_4.

3.3.1. Effect of Massic Ratio (m_{H2SO4} /m_{YC})

The sulfuric acid impregnation stage plays a key role in the activation process. To start with, we set the objective by determining at what range does the optimal acid massic ratio (weight of acid/ weight of YC) stand. We have systematically used the Cd (II) ions, an inorganic compound commonly used for tracer studies in water research on the activated carbon based on oil shale as performance indicators for all products obtained for this purpose. The precursor (YC) was activated by the sulfuric acid H_2SO_4 at 300°C temperature for 1 hour. The sulfuric acid concentration 18 mol/L has been used for these series of tests. The adsorption of cadmium (II) ions tests showed that the preferable massic ratio expressed in (kg of acid/kg of YC) should be between 2 and 2.5 for sulfuric acid. The rates of cadmium adsorption are also higher in these two ranges of values (Figure 4).

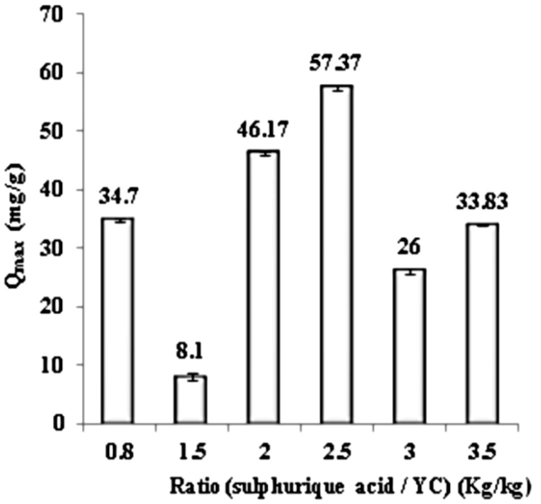


Figure 4. Evaluation of the massic ratio on maximum adsorption capacity of Cd (II) ions

The cadmium adsorption rate is obtained from one single experiment.

3.3.2. Concentration, Quantity and Consumption of Sulfuric Acid

To define the concentration and the required amount of the acid for the production of the activated carbon (YCS), we have varied the concentration of sulfuric acid for each massic ratio within the respective range. The cadmium metal may represent inorganic compound to be absorbed. This result is important because it tells us that we can act at the level of operating conditions for the preparation of specific adsorbent.

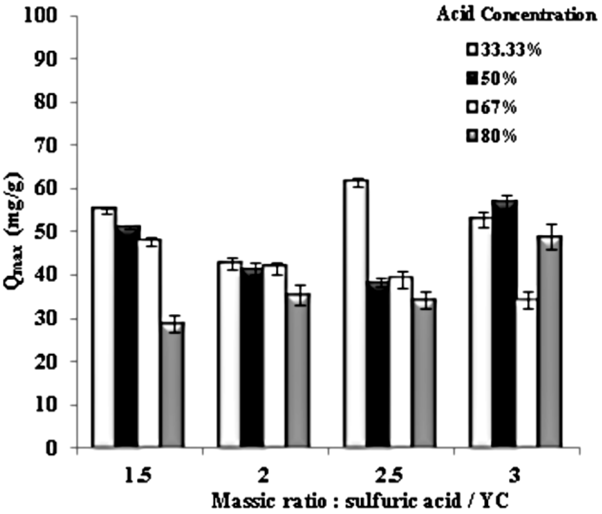


Figure 5. Evaluation of concentration and quantity of sulfuric acid

From the result in Figure 5, the acid requirement was determined by the use of the (YCS). The preparation of (YCS) requires 33.33(%) in the amount of sulfuric acid for the removal of Cd (II) ions.

3.3.3. Effect of Activation Temperature

The activation temperature for (YCS) was determined at 33.33(%) of sulfuric acid. The curve plotted below according to the capacities of adsorption Cd (II) ions clearly shows that the treatment temperature (YCS) optimum is around 240°C. From the results presented in Table 2, the acid sulfuric requirement was determined by the use of (YCS).

Table 2. Determination of optimal activation temperature according to cadmium adsorption

Temperature of activation (°C)	Yields char R (%)	Maximum adsorption capacity Q_{max} (mg /g)
160	99.8	35.60
180	98.5	33.57
200	91.7	37.30
220	91.6	49.10
240	81	62.90
260	80.4	51.27
280	80	46.13

3.3.4. Effect of Activation Time

The last activation parameter investigated was the activation time. To determine the effect of activation time on the maximum adsorption capacity of Cd (II) ions, adsorption experiments have been conducted by varying the activation time from 30 min to 120 min. The effect of the activation time is shown in Figure 6. The optimum activation time was found to be 30 min.

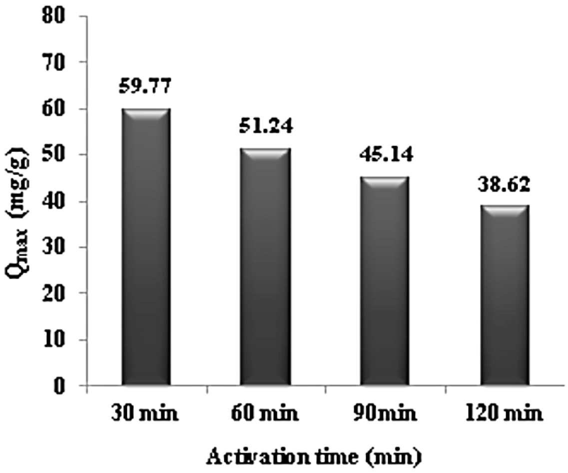


Figure 6. Evaluation of the activation time on maximum adsorption capacity of Cd (II) ions

3.4. Characterization

3.4.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transform Infrared (FTIR) Spectroscopy is one of the important techniques which base its functionality on the principle that almost all molecules absorb infrared light. The FTIR spectrum of the (Y) and (YCS) prepared for oil shale is shown in the following plots.

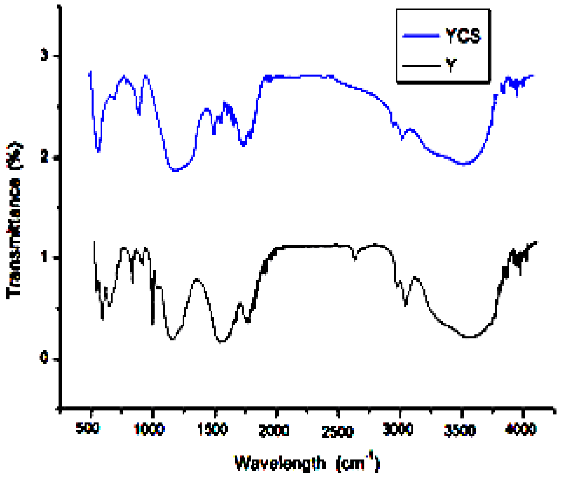


Figure 7. Fourier transform infrared (FTIR) spectra plots of (Y) and (YCS)

From Figure 7, we can observe the FTIR analysis of (Y) and (YCS) prepared based on oil shale. The sharp peaks are noted at a wavelength of 520 cm^{-1}, 950 cm^{-1}, 1260 cm^{-1}, 1425 cm^{-1} which is due to the presence of alkyl halides (C-Br Stretch), carboxylic acids (O-H bend), Ethers (C-O Stretch) and nitro (N=O Stretch) groups respectively.

The presence of alkanes (H-C-H bend), is observed at the wavelength of 1500 cm^{-1}. the sharp peaks, however, are observed at wavelengths 1600 cm^{-1} which is due to the presence of alkenes (C-C=C Symmetric Stretch). The ketones (C=O Stretch) groups are also observed at wavelength 1725 cm^{-1}. The sharp peaks are observed at a wavelength of 2960 cm^{-1} which is due to the presence of alkanes (H-C-H asymmetric and symmetric stretch). In the figure above, a peak is observed at a wave of 3500cm^{-1} which is due to the presence of alkenyl (C-H Stretch).

3.4.2. Scanning Electron Microscope (SEM) Analysis

The images of the (Y) and (YCS) surface are obtained from scanning electron microscope (SEM). Scanning Electron Microscope (SEM) analysis revealed the surface structure of the samples. (SEM) images of concentrated oil shale and activated carbon were presented in Figure 8. In all the cases the well-developed porous surface was apparent.

The scanning electron microscopy (SEM) was carried out for the activated carbon (YCS) before and after activation in order to evaluate changes on their microstructures. The (SEM) analysis was executed in the Centre National de Recherche Scientifique et Technique (CNRST). In figure 8, it was noted that the activated carbon (YCS) has a rough texture with heterogeneous surface and variety of randomly distributed pore size. Comparing the two images, we can confer that high porous surface can be observed for the activated carbon. The (SEM) image of activated carbon based on oil shale (YCS) clearly indicates surface alterations when compared to the rock of oil shale (Y), which may be due to oxidation of the organic matter existing in the (YC). The (SEM) photograph of the activated carbon based on oil shale (YCS) demonstrates the catalytic role of the sulfuric acid in the chemical activation of oil shale and the development of microstructure.

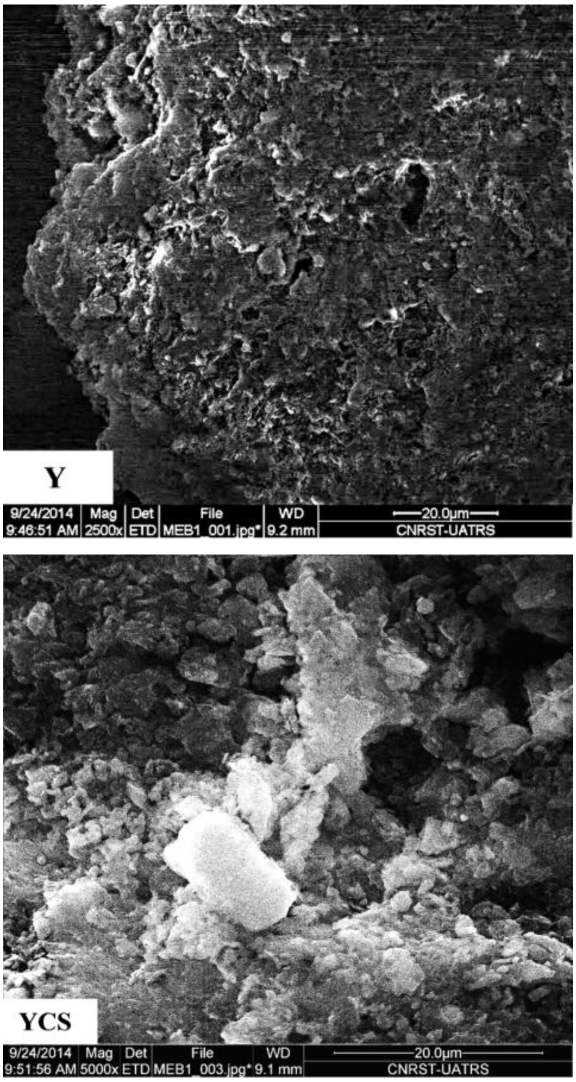


Figure 8. SEM images of (Y) and (YCS)

3.5. Adsorption Equilibrium

The Adsorption equilibrium was applied to discuss the equilibrium of the adsorption process for Cd (II) on activated carbon based on oil shale (YCS).

3.5.1. Langmuir Isotherm

The Langmuir isotherm is valid for single-layer adsorption on a surface containing a finite number of identical sites. The linear Langmuir isotherm represented the following equation [18]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_m} \tag{3}$$

Where C_e is the concentration of the Cd (II) ions (mg/L), Q_e is the number of adsorbed solute (mol/g), Q_{max} is the maximum adsorption and K_L is constant of Langmuir (L/mg). The plot of Langmuir ($1/C_e$ by report to $1/Q_e$) gives a straight line and the values of the constant Q_{max} and K_L for this model are presented in Table 3 and Figure 9 (a). The correlation coefficient is linear ($R^2 = 0.98$), showing that adsorption can be described with the Langmuir model. To confirm this result, the favorable or unfavorable adsorption was evaluated on the Langmuir model by calculating the separation factor (R_L) as follows [19]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

Where K_L (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial concentration. If the R_L value is between 0 and 1, the adsorption will be favorable. The calculated value R_L was found in the range of 0-1, indicating that the process of adsorption was favorable for the removal Cd (II) ions.

3.5.2. Freundlich Isotherm

Freundlich isotherm is one of the first empirical equations. The Freundlich Isotherm takes the form of [20]:

$$Log\, Q_e = Log\, K_F + \frac{1}{n} Log\, C_e \tag{5}$$

Where K_F (mg/g) and n are constants of isotherm, the factor of 1/n also signifies heterogeneity factor and varies between 0 and 1 [21]. The value of K_F and n was obtained from the interception and the intercept and slope of the line has been obtained by plotting log Q_e versus log C_e and their values are given in Table 3 and Figure 9 (b).

3.5.3. Temkin Isotherm

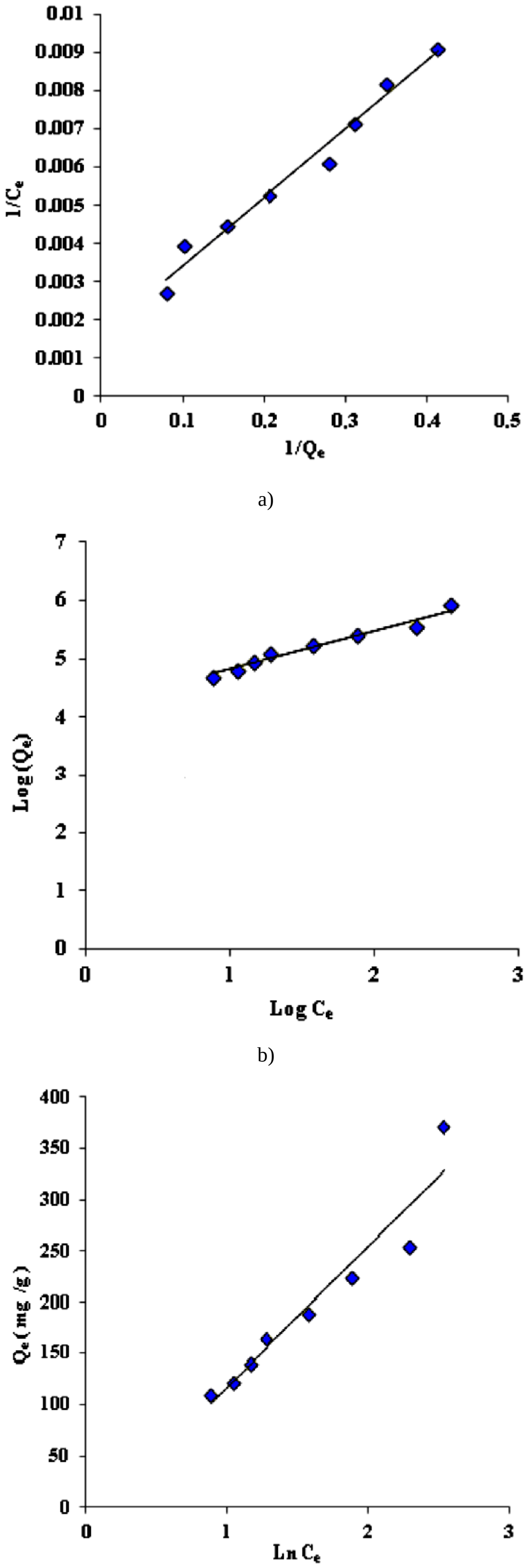
Temkin is one of the isotherms that assume the heat of adsorption decreases linearly with an increasing coverage. The Temkin isotherm model is as follows [22]:

$$Q_e = B_T \ln K_T + B_T \ln C_e \tag{6}$$

Where BT = RT/b, T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), K_T is the Temkin isotherm equilibrium constant (L/mg) and B_T is the constant related to heat of sorption (J/mol). The values of B_T and K_T were calculated from the plot of Q_e versus lnC_e (Table 3). As exposed in Table 3 and Figure 9(c), the low R^2 value of this model shows its inapplicability for interpretation of experimental data.

Table 3. Isotherm parameters correlation coefficients calculated by various adsorption models on to 1g of activated carbon based on oil shale (YCS), 20 mg/l of Cd (II) ions, pH 10, and room temperature

Adsorption kinetic	Parameters	
Pseudo-first order model	k_1 (min^{-1})	2.51
	R^2	0.399
Pseudo-second order model	k_2 (g/mg min)	0.22
	R^2	0.999
	Q_e(mg/g)	18.55



a)

b)

(c)

Figure 9. (a) Langmuir isotherm for adsorption of Cd (II) ions, (b). Freundlich isotherm for adsorption of Cd (II) ions, (c). Temkin isotherm for adsorption of Cd (II) ions

3.6. Adsorption Kinetics

The experimental kinetics data of removal of Cd (II) ions assessed by conventional models, namely the pseudo-first and second order, in order to study of the mechanism of the adsorption process. Kinetics properties and constant of model are presented in Table 4 at the initial Cd (II) ions concentration of 20 mg/L using 0.1g of activated carbon based on oil shale (YCS).

3.6.1. Model of Pseudo-first Order

The pseudo-first order model presented in Eq. (7), by plotting the values of log (Q_e - Q_t) versus t, the k_1 and Q_e values can be determined from its slope and the intersection.

$$Log(Q_e - Q_t) = \log Q_e - \frac{k1}{2.303} \tag{7}$$

Where Q_e and Q_t (mg/g) are the quantities of Cd (II) and to the balance of ions adsorbed at time t (min), respectively, and k_1 (min^{-1}) is the constant of the pseudo-first-order model [23]. As we can see in Table 4, the distance of the experimental value of the intercepts and Q_e the low correlation coefficient show the insufficiency of this model to explain the experimental data and thus, the adsorption process does not follow this equation. Figure 10(a) shows the pseudo-first order model the kinetic of Cd (II) ions.

3.6.2. Model of Pseudo-second Order

The model of pseudo-second order may be described in a linear form as:

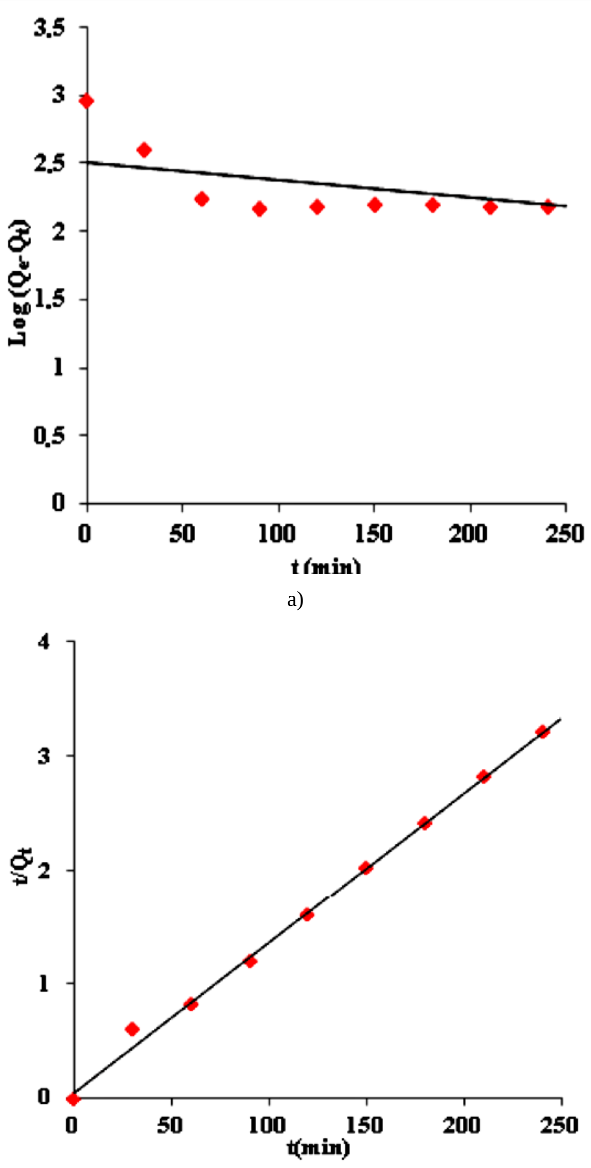
$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \tag{8}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{9}$$

Where k_2 is the rate constant (g /mg min). We have plotted (t/Q_t) in terms of t, the values Q_e and k_2 can be determined experimentally [24]. From Table 4 and Figure 10 (b), the agreement of calculated and experimental Q_e value and the high R^2 value confirm the suitability of this model. The result was presented in Table 4.

Table 4. Adsorption kinetic parameters at pH 10, and Cd (II) ions concentration of 20 mg/l

Isotherm	Parameters	
Langmuir	Q_{max}(mg/g)	55.87
	K_L(L/mg)	11.19
	R^2	0.98
Freundlich	(1/n)	0.67
	K_F(L/mg)	63.69
	R^2	0.97
Tmkin	B_T	138.33
	K_T(L/mg)	0.86
	R^2	0.93



a)

b)

Figure 10. (a) Plots of pseudo-first order kinetic for Cd (II) ions, (b) plots of pseudo-second order kinetic for Cd (II) ions

4. Conclusions

The study that was carried allowed for the determination of the optimum preparation conditions of activated carbon, in particular the activation parameters. This study shows that the optimum conditions for the preparation of the activated carbon by activation process is 240°C, massic ratio of 2.5 and 33% of sulfuric acid. The adsorption kinetic and equilibrium were found to be in good agreement with pseudo-second order and Langmuir model, respectively. The maximum adsorption capacity of cadmium by (YCS) achieved was 55.87 mg/g, which is very encouraging and we remain highly confident in light of the results produced in this study.

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