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Research Article

MODELING AND OPTIMIZATION OF THE ACTIVATION PROCESS OF OIL SHALE FOR REMOVAL OF Cd (II) USING THE RESPONSE SURFACE METHODOLOGY

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ABSTRACT

This study for the first time designed to modeling and optimize of activation process for removal of cadmium (II) ions by adsorption on oil shale using the response surface methodology. The optimal activation parameters selection was carried out on the basis of three factors by central composite design (CCD). The factors that have been identified are: activation temperature, activation time and massic ratio (m_{H2SO4}/m_{YC}). The capacity of adsorption of the cadmium (II) ions ($Q_{ads}(mgg^{-1})$) , was chosen as a response. The measured parameters were found in accordance with the predicted values with a coefficient of determination (R^2) of 0.92. The model has been confirmed by experimental tests to validate the results obtained. Based on the equation of the model and the desirability function, the activation temperature and activation time significantly affect of the adsorption capacity of Cd (II) ions. According to optimal activation conditions obtained using prediction profiler, the powder of oil shale mixed with H_2SO_4 at 213.8°C during 30 min in a massic ratio of 1.76, the adsorption capacity of Cd (II) ions is 68.38 (mgg^{-1}). Subsequently, the impact of various influential variables such as pH, contact time and dose of activated oil shale were examined. The kinetic, isotherm and thermodynamic studies were found to be in good agreement with pseudo-second order and Langmuir model, respectively. The activated oil shale prepared under optimal activation conditions has a maximal capacity of adsorption equal to 68.02 mgg^{-1} according to model of Langmuir with BET surface area of 181.35 (m^2g^{-1}). The values of thermodynamic parameters (ΔH°, ΔS°, ΔG°) affirm that the removal of Cd (II) ions on the activated oil shale (YCS) is an endothermic process. The (YCS) has great potential for adsorption of Cd(II) ions with regeneration efficiency more than 70% .

INTRODUCTION

Industrial wastewater containing cadmium is a threat to public health, due to its accumulation in aquatic life. It is a heavy metal of considerable toxicity with a destructive effect on most organ systems, this pollutant originating from the metallurgical alloying, industrial operations. The principal sources of contamination are welding contaminated food and beverages (Ding *et al*., 2015).

The conventional processes for removing cadmium from aqueous solution include chemical precipitation, ion exchange, membranes and adsorption technologies (Mohapatra *et al*., 2009). Among these different physicochemical processes, adsorption has shown to be the best prospects owing to its economic feasibility (Tan *et al*., 2010). Today the oil shale has received increasing interest in the removal of heavy metals. The oil shale is a sedimentary rock contained the organic and the mineral matter (Tan *et al*., 2016); it is essentially an immature form of petroleum. Morocco has a great resource of the oil shale. The deposits that have been explored are the Timahdit and Tarfaya deposits, the Timahdit deposit is located about 250 kilometers southeast of rabat. The average sulfur

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content is two percent (Knaus *et al*., 2010). The deposits that have been strongly explored are the Timahdit and Tarfaya deposits. The total content from Moroccan oil shale is evaluated 86 billion tons (Elhammoudi *et al*., 2017).

The objective of the present study is to optimize and modeling of activation conditions of oil shale for removal of cadmium (II) ions using response surface methodology. Therefore, various parameters impacting the removal of cadmium (II) ions such as pH, contact time and dose of activated oil shale (YCS) were evaluated. The kinetic, isotherm and thermodynamic studies were examined and discussed. The response surface methodology is one of statistical method to optimize of the parameters, and reducing the number of experimental trials (Goupy *et al*., 1990). The initial step in planning the response surface design was to determine the activation parameters that have an influence on the removal of cadmium (II) ions (Rao and Subbarao, 2012).

The second step was the modeling of the response; it consists of selecting the appropriate plan, and validating the model. For this reason, we employed a central composite design, to optimize of activation conditions of oil shale for removal of cadmium (II) ions. The final step was the optimization of the conditions for the working of the activation process (Tinsson, 2010). The factors studied including, the activation temperature (X_1), activation time (X_2) and massic ratio (X_3). The response measured, it is the adsorption capacity of Cd(II) ions: Qads(mgg-1). Various parameters impacting the removal of cadmium (II) ions such as pH, contact time and dose of activated oil shale (YCS) were evaluated. The kinetic, isotherm and thermodynamic studies of the adsorption of cadmium (II) ions by the activated oil shale (YCS) were examined and discussed.

MATERIALS AND METHODS

Materials

This material is composed of the organic and the mineral material essentially formed by calcite, dolomite, silicate and clay. The choice of the Moroccan oil shale for this application was eluted by two factors, the estimated reserve and its composition rich in organic matter constituted a carbon source.

Preparation of the activated oil shale

The oil shale (Y) is crushed then ground until we get a fine powder (Kribii *et al*., 2001). At a mass of the oil shale was leached with hydrochloric acid, to obtain the concentrated oil shale to be named (YC). The precursor (YC) was mixed with different ratio (m_{H2SO4}/m_{YC}) of the sulfuric acid. The mixture was heated in electric furnace under oxidant atmosphere gaze at different temperatures, after preprocessing at 140°C in oven under air. The product obtained (YCS) is thoroughly washed with distilled water in a soxhlet apparatus, to remove excess sulfuric acid (H_2SO_4) and to extract any soluble material, and then to dry at 80°C.

Experimental response

The measured response in this study was the adsorption capacity of Cd (II) ions. The removal of cadmium (II) ions on the activated oil shale (YCS) has been realized on the synthetic solution from cadmium chloride $CdCl_2$. A solution of Cd (II) ions of concentration 20 mg L^{-1} was prepared by dissolving 32.62 mg of cadmium chloride $CdCl_2$ in a 1000 mL. The pH of solution from cadmium chloride $CdCl_2$ was adjusted with 0.1N HCl or 0.1 N NaOH. In each adsorption test, 200 ml of cadmium solution of 20 mg L^{-1} was mixed with a 20 mg mass of activated oil shale (YCS), and then the mixture is stirred during 24 hours. The equilibrium concentration in Cd (II) ions was determined by atomic absorption spectroscopy (AAS), the quantity of Cd (II) ions adsorbed per unit mass of the activated oil shale (YCS) was calculated using the following form (Eq. (1)):

$$Q_{ads}\ ((mgg^{-1}))=((C_0-C_e)*V)/m_{YCS} \qquad (1)$$

Where Q_{ads} is the adsorption capacity of Cd (II) ions $Q_{ads}(mgg^{-1})$. V: volume of the solution of Cd (II) ions (L), C_0: initial concentration of Cd (II) ions (mg L^{-1}), C_e: equilibrium concentration of Cd (II) ions (mg L^{-1}) and m_{YCS}: mass of the activated oil shale (g).

Response surface methodology

Response surface methodology is a combination of mathematical and statistical techniques used to develop and optimize processes and to determine the relative significance and interaction of all variables, response surface methodology step followed by determination of the optimal region (Elharti *et al*., 2012). One of the most popular response surface methods is the Central Composite Design (CCD). The CCD was used to examine the influence of the activation parameters on the response (Roosta *et al*., 2015; Alansi *et al*., 2018). In the central composite design step, experiments were randomly planned to minimize the effect of uncontrolled variables as shown in Table 1.

Table 1 Experimental factors and levels in the central composite design.

Factors	Levels		
	Low (-1)	Central (0)	High (+1)
(X_1)	160°C	210 °C	260 °C
(X_2)	15 min	30 min	45 min
(X_3)	1.5	2	2.5

A central composite design was used to determine the pertinence of the three factors: the activation temperature (X_1), activation time (X_2) and massic ratio (X_3). The first step of this study is the choice of appropriate plan that suits us ideas to optimize the experimental conditions (Saeed *et al*., 2015). We have chosen to work with the composite plan on three factors with three levels. The chosen allows studying the influence of these factors on response. The plan consists of three parts: factorial design helps in optimizing the activation parameters (Ahmad *et al*., 2015), whose factors are two levels -1 and +1, experimental point in the center of the study area 0 and axial points on the axes of each factor. For three variables (n = 3) and two levels (low (-) and high (+)), the total number of experiments was 16 determined by the expression: (2n (2^3 = 8: full factor points) + 2n (2* 3 = 6: axial points) + 2 (center points)) (Table 2). The response measured was the adsorption capacity of Cd (II) ions, the design consisted of 16 experiments point carried out in random order. The suggested model for the quadratic model of the response variable, according to the independent variables (Tuzen *et al*., 2018), the mathematical relationship between the independent variables can be approximated by the second order polynomial model (Eq. (2)):

$$R=a_0+ a_1X_1+a_2X_2+a_3X_3+a_{11}X_1^2+a_{22}X_2^2+a_{33}X_3^2 + a_{12}X_1X_2+ a_{13}X_1X_3 + a_{23}X_2X_3 \quad (2)$$

Where R is the predicted response: adsorption capacity of Cd (II) ions. X_{is} are the independent variables, (Activation temperature (X_1), activation time (X_2) and massic ratio (X_3)), the parameter a_0 is the model constant, a_1, a_2, a_3 are the linear coefficients, a_{11}, a_{22} and a_{33} are the quadratic coefficients and a_{12}, a_{13} and a_{23} are the interaction effect (Asadollahzadeh *et al.*, 2014). The modeling is performed adjusting polynomial equation obtained by analysis of variance (ANOVA) (Elatharasan and Kumar, 2012).

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Table 2 Experimental design in coded and reels variables for central composite design

	Matrix of the coded factors			Matrix of the reels factors			Comment	Experimental Value of Q_{ads}
1	-1	-1	-1	160	15	1.5	Full factorial	75.1
2	1	-1	-1	260	15	1.5	Full factorial	63.12
3	-1	1	-1	160	45	1.5	Full factorial	50.61
4	1	1	-1	260	45	1.5	Full factorial	62.74
5	-1	-1	1	160	15	2.5	Full factorial	76.99
6	1	-1	1	260	15	2.5	Full factorial	72.69
7	-1	1	1	160	45	2.5	Full factorial	62.74
8	1	1	1	260	45	2.5	Full factorial	16.52
9	0	0	-1	210	30	1.5	Axial point	62.73
10	1	0	0	260	30	2	Axial point	62.74
11	0	1	0	210	45	2	Axial point	45.23
12	0	0	1	210	30	2.5	Axial point	38.68
13	0	-1	0	210	15	2	Axial point	90.91
14	-1	0	0	160	30	2	Axial point	82.74
15	0	0	0	210	30	2	Center point	98.61
16	0	0	0	210	30	2	Center point	87.41

Each experiment was repeated three times

RESULTS AND DISCUSSION

Acid attack of oil shale

The powder of oil shale (Y-layer) was added, with stirring a solution of hydrochloric acid HCl (1 mol L^{-1}) until the complete release of carbon dioxide (Sahu *et al.*, 2016), according to the following equations.

$$2\,HCl + CaCO_3 \longrightarrow CaCl_2 + CO_2 + OH_2$$

$$CaMg(CO_3)_2 + 4\,HCl \longrightarrow CaCl_2 + MgCl_2 + 2\,CO_2 + 2H_2O$$

Activation process of oil shale

Activation processes can be classified into physical and chemical activation. During physical activation, the oil shale may undergo gasification produced during carbonization (Aboulkas *et al.*, 2009). On the other hand, chemical activation consists of impregnating with chemicals such as $ZnCl_2$, H_3PO_4, HNO_3 or H_2SO_4 (Li *et al.*, 2016; Namane *et al.*, 2005). The concentrated oil shale (YC) was activated by sulfuric acid H_2SO_4 at the temperature 300°C for 1 hour. The product obtained, referenced by (YCS) where "S" denotes the activation with sulfuric acid H_2SO_4. The activation with sulfuric acid H_2SO_4 has become a widespread method for the manufacture of activated carbon. The use of sulfuric acid (H_2SO_4) has some environmental advantages such as easy recovery, low energy cost, plays two roles during the preparation of activated oil shale (YCS), acts as an acid catalyst to promote bond cleavage, dehydration, and may function as a template because the volume occupied by sulfuric acid in the interior of the activated is coincident with the micropore volume of the activated oil shale obtained (Mui *et al.*, 2010).

Optimization using the response surface methodology

The variables studied are: the activation temperature (X_1), activation time (X_2) and massic ratio (X_3) and the measured response was the adsorption capacity of Cd (II) ions (Q_{ads}(mg g^{-1})). After choosing the response and the variables, we have sought to optimize and modeling of the activation process for removal of Cd (II) ions by oil shale using the response surface methodology. The central composite design to three levels was conducted to evaluate the influence of experimental factors on the adsorption capacity of Cd (II) ions. We realized an adsorption test of the 16 experiments. The experimental data have been reproduced three times to evaluate the statistical quality of the results (Table 2).

Evaluation of the quality of the model

The coefficient of adjusted regression R^2 for the adsorption capacity was equal to 0.92. This indicated that more than 92% of the variation observed was explained by the direct effects of the factors. Therefore, the choice of quadratic model to modeling of activation process was best. The result of this test is shown in Fig 1 and Table 3.

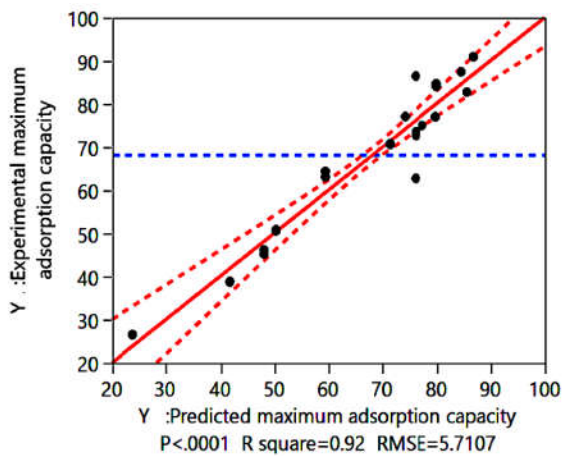


Figure 1 Graphical representation of observed values as a function of predicted values.

Table 3 Quality of quadratic model chosen to model the activation conditions for removal of Cd(II) ions.

	Variable studied	Adsorption capacity of Cd (II)
Regression analysis	R square (R^2)	0.92
	Adjusted R square (R_A^2)	0.91
ANOVA test	F value	50.82
	p-value	<.0001*
Validation model	F value	3.101
	p-value	<.0001*

* Significant at the level 95%.

Test of variance (ANOVA)

The validation quadratic model for the removal of Cd (II) ions on activated oil shale (YCS) was performed using the model analysis of variance (ANOVA) and the method of the absence of adjustment analysis, also called analysis bias. ANOVA was used to assess the variance of the model established in relation to the variance of the residue, using the test "Fisher Snedecor", the result was considered significant if ($F_{exp} >> F_{\alpha}, \nu_{mod}, \nu_{res}$),where $\alpha = 0.05$ (Myers *et al.*, 2009). According to the result of ANOVA test, analysis of experimental give a factor F_{exp} = 50.82. The theoretical values determined according to the table of Fisher Snedecor (for $\nu_{model} = 9$, $\nu_{residue} = 38$ and confidence level = 95%) was $F_{\alpha}, \nu_{mod}, \nu_{res}$ = F 0.05, 9, 38 = 2.19.

This theoretical factor was much lower than the experimental factor, $F_{exp} = 50.82 >> F_{theo} = 2.19$. The results of the lack of adjustment of analysis indicate that the p-value was largely experimental factor less than 0.05, these analyses were determined using the JMP12 software, shown in Table 3. The results of ANOVA test and the lack of adjustment showed that the quadratic model established was validated.

Equation of the model

The significance of each coefficient was determined using the F-test and p-value given by JMP 12 software. A p-value less than 0.05 indicate the significance of an effect at 95% confidence level (Khuri *et al.*, 2010).The significant effects and their coefficients are shown in Table 4.The effects coefficients of model showed that the adsorption capacity of Cd (II) ions was significantly affected by the quadratic term of activation temperature (X_1) and massic ratio (X_3), the antagonistic effect of activation time and massic ratio (X_{23}), was not significantly, p-value larger than 0.05, we can neglect this coefficient from the equation of the adsorption capacity of Cd (II) ions. The fitted quadratic model for removal of Cd(II) ions given by equation (3).

$$Q_{ads}\ (mg\ g^{-1}) = 76.15 - 15.95*X_1 - 4.76*X_2 + 10.19*X_3 - 5.69*X_{12} + 4.51*X_{13} - 12.07*X_1^2 + 5.95*X_2^2 - 6.50*X_3^2 \quad \text{Eq. (3)}$$

Table 4 Significant effects coefficients of established equation model for removal of Cd(II) ions

Term	Estimation	Standard deviation	t value	t value	Prob.>|t|	Comment
X_1	-15.95	1.043	15.30		<.0001*	Significant
X_3	10.189	1.04	9.77		<.0001*	Significant
X_1*X_1	-12.07	2.03	-5.94		<.0001*	Significant
X_1*X_2	-5.69	1.16	-4.88		<.0001*	Significant
X_2	-4.76	1.04	-4.56		<.0001*	Significant
X_1*X_3	4.51	1.16	3.870		0.0004*	Significant
X_3*X_3	-6.50	2.03	-3.20		0.0028*	Significant
X_2*X_2	5.95	2.03	2.931		0.0057*	Significant
X_2*X_3	-1.46	1.16	-1.260		0.217	Not Significant

* Significant at the level 95%.

Desirability function

After validation of the quadratic model, the optimal conditions of the activation process for removal of Cd (II) ions by oil shale were determined using the desirability function. The function of desirability established to discover the optimal conditions based globally on the function of the desirability of Derringer (Z *et al.*, 2012). The main advantage of the function of desirability is the ability to obtain answers by a simple processing and rapid response. First and foremost, the response is converted to a function of a particular desirability in the range of 0-1. The value equal to 0 shows a minimum applicability (Gadhe *et al.*, 2013). The prediction plot showing the effects of various parameters, the factors that appear to be more influential are the activation temperature and activation time, allows to conclude that its factors affect the response Q_{ads}(mg g^{-1}). It is clear that an increase of the activation temperature and activation time causes an increase in the adsorption capacity of the activated oil shale (YCS).

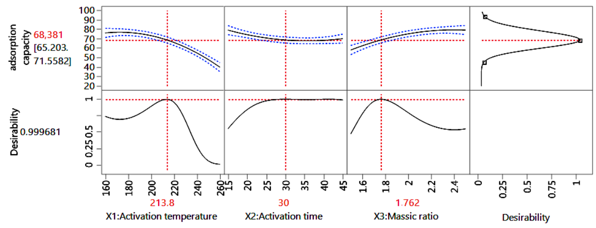


Figure 2 Prediction plot show the effect of parameters: activation temperature (X_1), activation time (X_2) and massic ratio (X_3) on the adsorption capacity of Cd (II) ions.

The optimal condition determined using JMP 12 Software was represented in Fig.2. On the other hand, the result indicated the highest adsorption capacity of Cd (II) ions of 68.381 mg g^{-1} was obtained to 213.8°C, during 30 min with 1.76 of massic ratio. Depending on the results presented in Fig. 2, we can conclude that the desirability function permitted to reduce activation temperature, activation time and massic ratio (m_{H2SO4} /m_{YC}) for a high adsorption capacity

Three-dimensional response surface

Three-dimensional (3D) for the measured response, was formed based on the model polynomial functions, to assess the change of the response surface (Divsar *et al.*, 2015), also the relationship between the variables can be further understood (Bezerra *et al.*, 2008), it is method to visualize the relationship between responses and experimental levels of each variable and the type of interactions between variables (Lin *et al.*, 2015). The validated model can be plotted in a three-dimensional graph and generate a surface response that corresponds to response function used for determination of the best conditions for response. Since the model has three factors, one factor was held constant for each diagram. The plot of response surface (3D) presented by Fig.3, show the effect of activation temperature (X_1) and activation time (X_2) on the response Q_{ads}(mg g^{-1}) .According to the plot (3D), an increase of activation temperature reduces adsorption capacity values. Further, as can be observed, the continuing increment of activation time, promotes a marked increase in adsorption capacity values. The quadratic effect of activation temperature and activation time can be observed in plot moreover their interaction was also significant ($p < 0.05$).

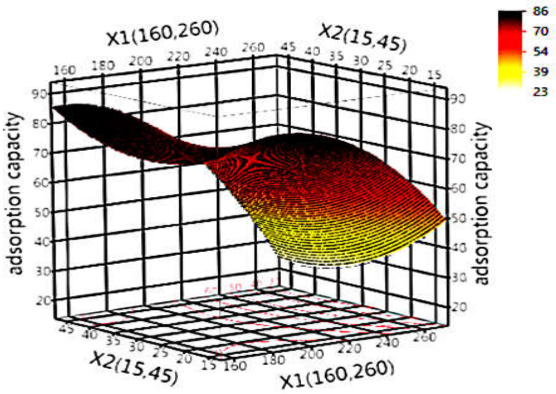


Figure 3 Response surface result of quadratic model (3D) show the effect of the various factors on the removal of cadmium (II) ions.

Experimental validation

To confirm the quality of the results determined by experimental data, experimental tests have been realized to validate the results obtained. The values of the confirmation experiment trials present the same values compared to the optimal conditions for removal of Cd(II) ions on activated oil shale (YCS) obtained using the response surface methodology, no significant difference was observed between the experimental and predicted values, the results of this test are presented in the Table 5.

Table 5 Confirmation experiment of optimal activation process for removal of Cd(II) ions

Response	Activation conditions	Experimental results	Result of (RSM)
Adsorption capacity of Cd (II) ions (mg g^{-1})	(X_1)= 213.8°C; (X_2)= 30 min; (X_3)= 1.76	68.73 ±0.96	68.38
	(X_1)=160°C ; (X_2)= 25 min ; (X_3)= 1.5	66.58 ±1.77	67.71
	(X_1)= 200°C ; (X_2)= 40 min ; (X_3)= 1.7	68.37 ±0.24	70.94

Adsorption studies

Effect of pH.

The effect of pH on the Cd (II) ions adsorption for pH between 2.0 and 8.0 is presented in Fig. 4. The removal of the Cd (II) ions has rapidly increased with the increase of the pH values of 2 to 8. We can see that the removal efficiency increases with increasing pH .The optimal pH for the removal of Cd (II) ions by activated oil shale (YCS) has been optimized to 5. The result is shown in Fig. 4.

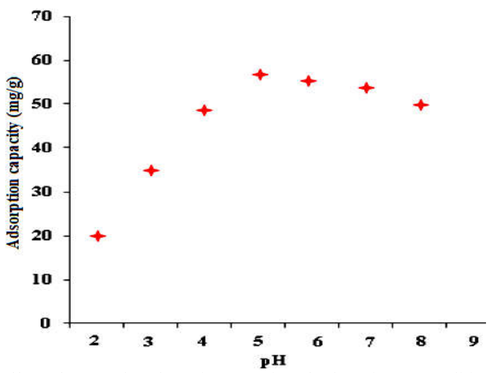


Figure 4 Effect of pH on the adsorption capacity of Cd (II) ions, [Conditions: initial concentration of Cd(II) ions 20 mg L^{-1}, room temperature, (YCS) dose 0.02g, contact time 24 h].

Effect of contact time

The effect of contact time on the removal of cadmium (II) by the activated oil shale (YCS) is shown in Fig. 5. The adsorption of Cd (II) increases with an increase of the contact time and that most of the Cd (II) ions are adsorbed in 60 min. After 60 min, the amounts of the adsorption of ions Cd (II) achieved respectively 72.77 and 75.42 mg g^{-1}. Therefore, 60 min is the appropriate contact time for the removal of Cd (II) ions.

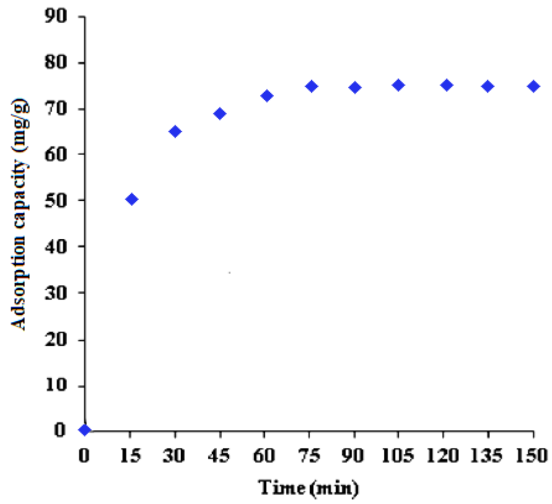


Figure 5 Effect of contact time on the removal of Cd (II) ions, [Conditions: pH 5, initial concentration of Cd (II) ions 20 mg L^{-1}, room temperature, (YCS) dose 0.02g].

Effect of the dose (YCS)

The adsorption of Cd (II) on activated oil shale (YCS) has been studied using different dose of (YCS) in the range of 0.02-0.16 g, at Cd (II) ions concentration of 20 mg L^{-1}. It is evident in Fig. 6, that Cd (II) ions adsorption decreases significantly with rising the dose of (YCS). As this figure shows, the removal rate increased with increasing the dose of (YCS). This may be due to the availability of specific surfaces of the activated oil shale (YCS). Therefore, 0.06 g was chosen as the optimum activated oil shale dose for further experiments.

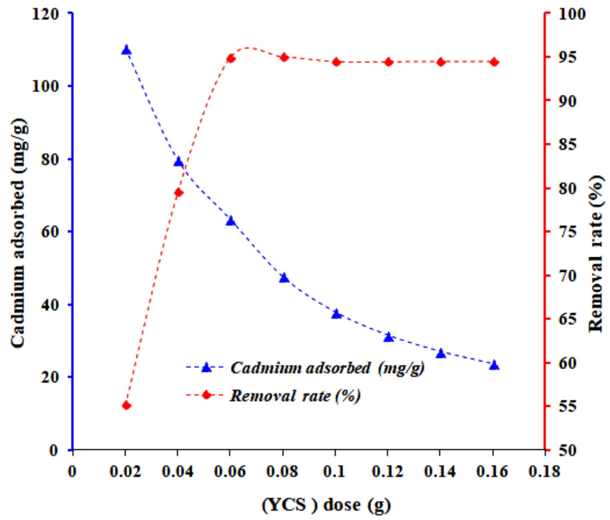


Figure 6 Effect of activated oil shale (YCS) dosage on the removal rate and the adsorption capacity of Cd (II) ions, [Conditions: contact time 60 min , pH 5, room temperature, initial concentration of Cd (II) ions 20 mg L^{-1}].

Adsorption equilibrium

In this study, four non-linear isotherms, Langmuir, Freundlich and Temkin were applied to discuss the equilibrium of the adsorption process for the cadmium (II) on activated oil shale (YCS). The Langmuir isotherm is valid for single-layer adsorption on a surface containing a finite number of identical sites (Marrakchi *et al*., 2016). Non-linear form of the Langmuir represented the following equation:

$$Q_e=(K_L*C_e)/((1+K_L*C_e))=(Q_m*K_LC_e)/((1+K_LC_e)) \quad (4)$$

Where C_e is the concentration of the Cd(II) ions (mg L^{-1}), Q_e is the number of adsorbed solute per unit weight at the concentration (mol g^{-1}) ,Q_m is the maximum adsorption and K_L constant of Langmuir (L mg^{-1}). The plot of Langmuir (Q_e by report to C_e) and the values of the constant Q_m and K_L for this model are presented in Table 6 and Fig.7. To confirm this result, the favorable or unfavorable adsorption was evaluated on the Langmuir model by calculating the separation factor (R_L) as follows (Sun *et al*., 2013):

$$R_L=1/(1+ K_L*C_0) \quad (5)$$

When K_L (L mg^{-1}) is the Langmuir constant and C_0 (mg L^{-1}) 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. The R_L value obtained were 0.051 indicate that the adsorption is a favorable process. The Freundlich isotherm model is commonly used to describe the adsorption characteristics for the heterogeneous surface (Shamsizadeh *et al*., 2014). The non-linear form of the Freundlich Isotherm takes the form of:

$$Q_e=K_F\, C_e^{\,1/n} \quad (6)$$

Where, Q_e (mg g^{-1}) is the equilibrium concentration, C_e (mg L^{-1}) is the equilibrium concentration, and K_F (L mg^{-1}) and n are constants of the isotherm, the factor of 1/n also signifies heterogeneity factor and varies between 0 and 1.The graph has obtained by plotting Q_e versus C_e (Khan *et al*., 2015). The isotherm of Temkin is one of the isotherms assumes that the heat of adsorption decreases with an increasing coverage. The non-linear Temkin form is as follows (Dehghani *et al*., 2016):

$$Q_e= B_T \ln((K_T\, C_e) \quad (7)$$

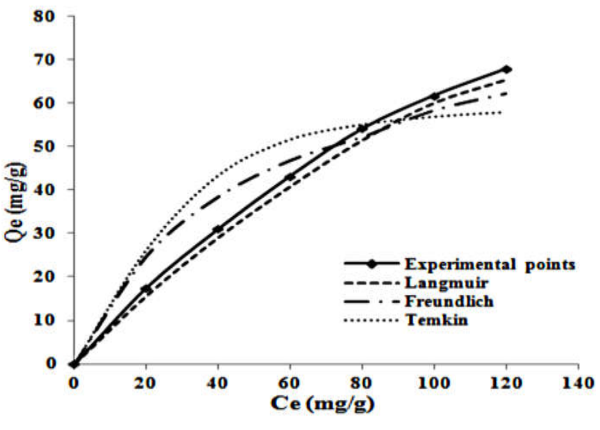


Figure 7 Isotherms obtained using the non-linear method for adsorption of Cd (II) ions onto activated oil shale (YCS), [Conditions: 0.06g of (YCS) , pH 5, room temperature, initial concentration of Cd (II) ions 20 mg L^{-1}].

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 Temkin isotherm equilibrium constant (L mg^{-1}), B_T is constant related to heat of sorption (J mol^{-1}). The graphical representations of these three models are presented in Figure 7.

In Table 6 and Figure 7, the high coefficients of determination are obtained by the Langmuir isotherm (R^2= 0.999) and the Freundlich isotherm (R^2=0.985), relative to the Temkin isotherm (R^2=0.959). These suggest that the Langmuir isotherm and the Freundlich isotherm can generate a satisfactory fit to the experimental data. As indicated, the value of the maximum adsorption capacity determined using the Langmuir model was 68.017mg g^{-1}.

Table 6 Isotherm parameters correlation coefficients calculated by various adsorption models onto 0.06 g of activated oil shale (YCS), 20 mg L^{-1} of Cd (II) ions, pH 5, and room temperature.

Isotherm	Parameters	
Langmuir	Q_m (mg g^{-1})	68.017
	K_L (L mg^{-1})	0.828
	R^2	0.999
	Std .error	0.037
Freundlich	(1/n)	1.008
	K_F (L mg^{-1})	17.814
	R^2	0.985
	Std .error	0.064
Tmkin	B_T	1.246
	K_T (L mg^{-1})	25.43
	R^2	0.959
	Std .error	0.208

This value is close to the experimental value of adsorption capacity and corresponds to the adsorption isotherm, which indicates that the Langmuir modeling for adsorption is acceptable. From Table 6, it is found that the following isotherms in the order: Langmuir > Freundlich > Temkin. The correlation coefficient showed that the Langmuir isotherm and the Freundlich isotherm can describe the experimental results. The experimental result with Temkin is rather low compared to the Langmuir and the Freundlich isotherm.

Adsorption kinetic

The experimental kinetic data of removal of Cd (II) ions assessed by the non-linear forms of the pseudo-first order and pseudo-second order equations to study of the mechanism of adsorption process. Kinetic properties and constant of model are presented in Table 7 at the initial Cd (II) concentration of 20 mg L^{-1} using 0.06 g of activated oil shale (YCS). The non-linear form of pseudo-first order presented in Eq. (8) by plotting the values of Q_t versus t.

$$Q_t=Q_e\,(1- e^{k1t}) \quad (8)$$

Where Q_e and Q_t(mg g^{-1}) 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. As we can see in Table 7, the correlation coefficient low shows the insufficiency of this model to explain the experimental data and the adsorption process do not follow this equation. The model of pseudo-second order may be described in a non-linear form as:

$$dQ/dt=k_2(Q_e-Q_t)^2 \quad (9)$$

$$Q_t=k_2\, Q_t^2\, t/1+K_2\, Q_e\, t \quad (10)$$

Where k_2 is the rate constant (gm g^{-1} min^{-1}), we have been plotting (Q_t) in terms of t (Guaracho *et al.*, 2009). From on Table 7 and Fig.8, the agreement of calculated and experimental Q_e value and the high R^2 value confirm the suitability of this model. According to Table 7, the pseudo-second order kinetic model was more representative than the pseudo first-order kinetic model.

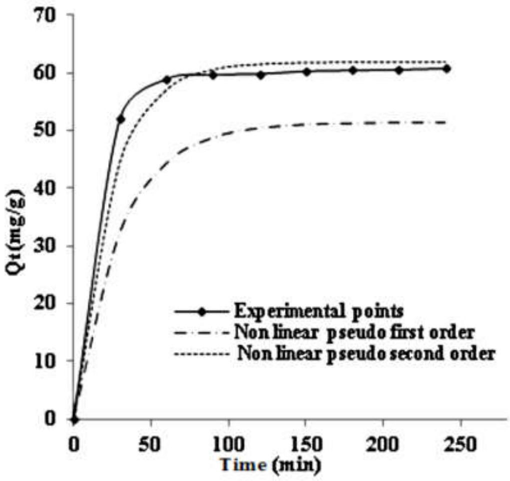


Figure 8 Non-linear plots of pseudo-first order and pseudo-second order kinetic models for the adsorption of Cd (II) ions onto activated oil shale (YCS) , [Conditions: 0.06g of (YCS), pH 5, room temperature, initial concentration of Cd (II) ions 20 mg L^{-1}].

increase in the randomness at the solid/solution interaction during the adsorption of Cd (II) ions.

N_2 adsorption-desorption

The surface area of the oil shale (Y), concentrated oil shale (YC) and activated oil shale (YCS) are obtained by the BET method (N_2 adsorption in gaseous phase).

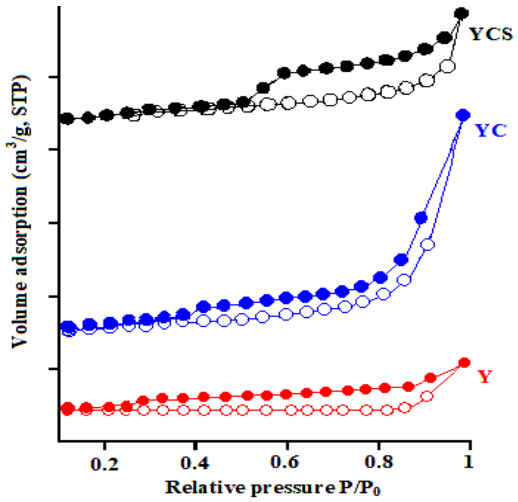


Figure 9 N_2 adsorption–desorption isotherms of oil shale (Y), concentrated oil shale (YC) and activated oil shale (YCS).

Table 7 Determined parameters for non-linear kinetic models for the adsorption of Cd (II) ions onto activated oil shale (YCS) at pH 5, and Cd (II) ions concentration of 20 mgL^{-1}.

Pseudo-first order model				Pseudo-second order model				
k_1 (min^{-1})	R^2	Q_e(cal) (mgg^{-1})	Std .error	Q_e(exp) (mgg^{-1})	k_2 (gmg^{-1} min^{-1})	R^2	Q_e(cal) (mgg^{-1})	Std .error
0.033	0.569	48.525	0.0164	60.821	0.052	0.997	58.752	0.0185

Adsorption thermodynamics

To estimate the spontaneous of the removal of cadmium (II) ions, thermodynamic parameters such as free energy change, enthalpy change and entropy were studied. Thermodynamic constants can be obtained from the following equations:

$$\Delta G° = -RT \ln K_D \quad (11)$$

$$\Delta G° = \Delta H° - T \Delta S° \quad (12)$$

Where ΔG° , ΔH° ,ΔS°, R, K_D, T, are the Gibbs free energy (kJ mol-1), enthalpy (kJ mol-1), entropy (kJ $mol^{-1}K^{-1}$), universal gas constant (8,314 $Jmol^{-1}$ K), thermodynamic equilibrium constant and the absolute temperature (K) respectively , K_D is the equilibrium partition constant. The values of other parameters such as the change of enthalpy (ΔH°) and the entropy change (ΔS°) can be determined from the Van't Hoff equation (Eq. (13)) (Scheufele *et al.*, 2016):

$$\ln K_D = (\Delta S°/R) - (\Delta H°/R) 1/T \quad (13)$$

The experiment was performed with 20mg L^{-1} of Cd (II) concentration. The thermodynamic parameters ΔG° values were between -2.548 to -118.114 (kJ mol_{-1}) over the temperature (298.15-338.15 K).

The negative values of energy ΔG° growing with increasing the temperature suggest that the adsorption was spontaneous. The data show positive value of ΔH° = 71.209 (kJ mol^{-1}) that indicate the endothermic nature of the adsorption while the positive value of ΔS° = 245.346 (kJ $mol^{-1}K^{-1}$) suggested an

The Nitrogen adsorption and desorption isotherms of the precursors are given in Figure 9 and Table 8 respectively.

Table 8 Specific surface obtained by the BET method

Sample	Y	YC	YCS
S_{BET}(m^2g^{-1})	7.14	23.92	181.35

The BET surface area of the (Y), (YC) and (YCS) materials were calculated and found to be 7.14 m^2 g^{-1}, 23.92 m^2 g^{-1} and 181.35 m^2 g^{-1} respectively. The results of analyzes specific surface SBET are summarized in Table 8. This table shows that the total surface area of the activated oil shale (YCS) is higher than that obtained by the two precursors (YC) and (Y) which allows that chemical activation with sulfuric acid causes an increase in the surface.

SEM analysis

The scanning electron microscopy (SEM) was carried out for the activated oil shale (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). As can be observed in Fig. 10, the rock of oil shale (Y) untreated and the concentrated oil shale (YC) present a rigid and very compact morphology, without any apparent porous structure, while the activated oil shale (YCS) has a porosity much developed compared to the rock of oil shale (Y) of departure where the grains are not consistent with the virtual absence of porosity. The SEM image of activated oil shale (YCS) clearly indicates surface alterations when compared to the rock of oil shale (Y) and the concentrated oil shale (YC), which may be due to oxidation of the organic matter existing in the (YC). The SEM photograph of the activated oil shale (YCS), demonstrate the catalytic role of the sulfuric acid in the chemical activation of oil shale and the development of microstructure.

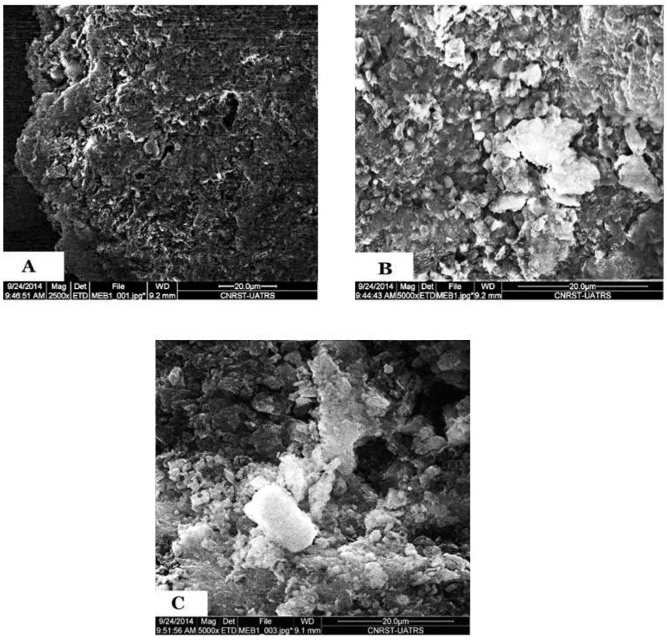
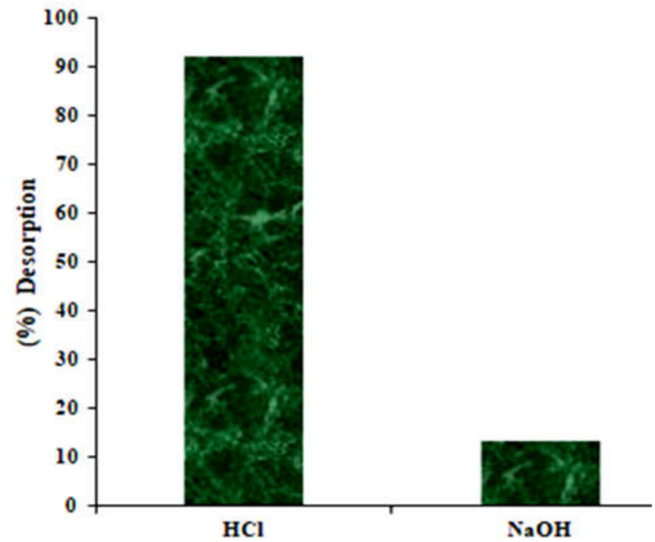


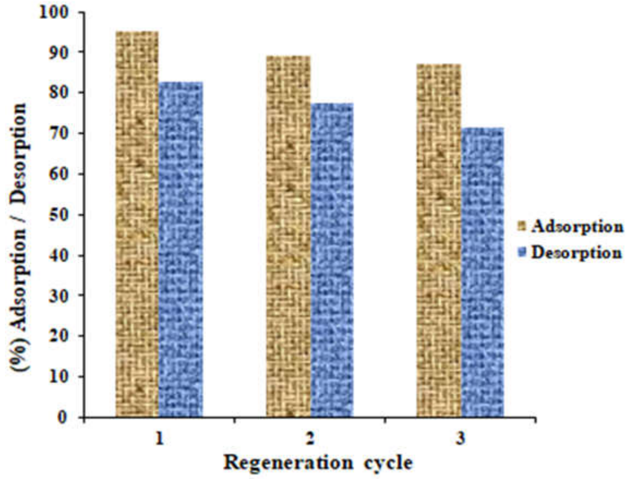
Figure 10 (A) SEM images of oil shale (Y), (B) SEM image of concentrated oil shale (YC), (C) SEM image of the activated oil shale (YCS).

Desorption and regeneration tests

In this study, 0.1 mol L^{-1} HCl and NaOH were used as desorption solutions for the regeneration of activated oil shale (YCS). The concentrations of cadmium (II) ions were determined using atomic absorption spectroscopy (AAS). Figure 11(a) show the desorption of Cd(II) ions using HCl was higher than 90% .



a



b

Figure 11 (a) Desorption test for cadmium (II) onto (YCS). (b) Adsorption desorption test for cadmium (II) onto (YCS), Conditions: [initial Cd(II) concentration: 20 mg L^{-1}, (YCS) dose: 0.06 g, pH: 5.0, contact time: 24 h, temperature: 25 °C, 50 mL of 0.1 mol L^{-1} HCl and NaOH].

However, the performance of desorption using NaOH solution does not exceed 13%. Based on these results, 0.1 mol L^{-1} HCl was used as desorption solution. The desorption performance of the activated oil shale (YCS) from the three cycles were 99.4, 96.6, 92.1, 88.1% and 82.3, 80.1, 77.0, 75.4% for adsorption respectively (Figure 11(b)). These results indicate that the activated oil shale (YCS) has great potential for adsorption of cadmium (II) ions.

CONCLUSION

The activation conditions for removal of Cd (II) ions by oil shale were optimized using response surface methodology under central composite design. The activated oil shale (YCS) was successfully prepared using a simple, low cost and highly efficient activation process. Under optimal activation conditions, the oil shale sample mixed with H_2SO_4 at 213.8°C during 30 min in a massic ratio of 1.76.The adsorption capacity of Cd (II) ions was 68.38 mg g^{-1}. The parameters for removal of Cd (II) ions were pH 5, contact time 60 min and 0.06 g (YCS) dose. The Langmuir isotherm showed a best fit with experimental data, the adsorption capacity was determined to be 68.02 mg g^{-1}. The non-linear kinetic indicate that the adsorption processes of Cd (II) ions can be described suitably by the pseudo-first order. After the study of thermodynamic parameters, it was found that the adsorption is endothermic process because of positive value of the enthalpy. The energy for the adsorption of Cd (II) ions onto the activated oil shale (YCS) is lower, showed the spontaneity of the adsorption process. All this results indicated that activated oil shale (YCS) has great potential for removal of Cd (II) ions, even after three cycles of adsorption-desorption of cadmium (II) ions.

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