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Adsorption of cadmium onto activated alumina: kinetics and thermodynamics studies

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ABSTRACT

In this study, Activated Alumina was assessed as adsorbent for the removal of cadmium ions from aqueous solutions. Langmuir, Freundlich and Dubinin-Redushkevich (D-R) models were used to study the adsorption equilibrium at different temperatures (283, 298 and 313 K). It was found that the maximum adsorption capacities increased with temperature indicating an endothermic phenomenon. Furthermore, the values of sorption energy estimated for the studied range of temperature by the D-R model were found to be higher than 8 kJ mol^{-1} suggesting a chemisorption reaction. In addition, the correlation of sorption data by kinetic equations showed that the adsorption of cadmium follows the Elovich and the pseudo-second order models which confirms the chemisorption process. The thermodynamic parameters showed that the adsorption of cadmium onto activated alumina was spontaneous, and the positive values of enthalpy change ($\Delta H°$) confirmed the endothermic character of adsorption. In order to further study the cadmium sorption, different techniques were used for the characterization of the activated alumina before and after adsorption. BET measurements shown an increase of the specific surface area. In addition, FTIR and XRD analysis were used to discuss the role of functional groups in cadmium adsorption. Besides, the technical viability of the process was investigated for a wastewater sample. It was found that the activated alumina is an efficient adsorbent for the removal of cadmium from contaminated water, as the reached percentage removal was above 99%.

Keywords: Cadmium; Adsorption; Activated alumina; Kinetic; Thermodynamics

1. Introduction

Heavy-metal pollution in the environment is a matter of global concern. This type of pollution is mainly due to various human activities and rapid industrialization. Since the heavy metals are non-biodegradable, they get bio-accumulated and bioconcentrated in living tissues. The occurrence of heavy metals beyond permissible limits in industrial effluents affects human health as well as natural ecosystems [1–3]. Toxic metals such as lead [4], mercury [5], cadmium [6] and chromium (VI) [7] are at the top of toxicity list. Cadmium is one of them and it is introduced into natural water resources by wastewater discharged from industries such as electroplating, smelting, alloy manufacturing, pigments, plastic, mining and refining industries. Cadmium exposure is responsible for breast cancer [8], injuries to the testes, liver and lungs. Chronic exposure leads to obstructive airway diseases, emphysema, renal complications, deregulated blood pressure, bone disorders and immune-suppression [9]. Therefore, it is necessary to eliminate the cadmium ions (Cd^{2+}) from water, in order to prevent the deleterious impact on ecosystem and public health. Because of the stricter environmental regulations, a cost effective alternate technology for the treatment of aqueous solutions is highly desired by the industries. Various methods [10], including precipitation, ion exchange, membrane process [11], and different electrolytic methods are used for removal and

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recovery of cadmium ions from aqueous solutions [12]. The adsorption of cadmium ions onto insoluble compounds used as adsorbents is more effective than the above-mentioned methods [13–18].

The adsorption process has many advantages such as: low cost of adsorbent, easy availability, utilization of industrial, biological and domestic waste as adsorbents, low operational cost, ease of operation compared to other processes, reuse of adsorbent after regeneration, capacity of removing cadmium ions over wide range of pH and ability to remove complex form of cadmium that is generally not possibly by other methods. In the last few years, several approaches have been studied in this area. The literature review suggested the use of different natural and synthetic adsorbents for the removal of cadmium ions from aqueous solutions. The advantage of activated alumina as adsorbent lies in the fact that it has high surface area, mechanical strength and amphoteric properties [19–21]. The present study deals with a series of batch adsorption experiments to investigate and explore the feasibility of activated alumina (Al_2O_3) as an adsorbent for removal of cadmium ions from aqueous solutions.

Within this work, we present a detailed study on the adsorption ability of the activated alumina toward cadmium. Besides the adsorption kinetics and the equilibrium, particular attention was paid to the characterization of activated alumina before and after adsorption, and to the adsorption mechanism. In addition, application for real samples was performed to estimate the feasibility of this process.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study are of analytical grade and purchased from Sigma Aldrich. The cadmium was used in the form of nitrate salts ($Cd\ (NO_3)_2 4H_2O$). The granular activated alumina (melting point 2313 K, molecular weight 101.96 g mol^{-1}, pore diameter 58 Å) was dried at 383 K for 24 h in order to eliminate the impurities.

2.2. Characterization

Morphology of activated alumina was characterized by Scanning Electron Microscopy. An image of the surface of activated alumina particles is illustrated in Fig. 1.

Fig. 1 shows that the activated alumina particles have a spherical shape and are of different sizes indicating that the surface was porous in nature.

ATR-FTIR measurements were performed using a Bruker Tensor 27 FTIR spectrometer equipped with a Platinum ATR. IR spectra were recorded from the range of 400–4000 cm^{-1}. XRD patterns were recorded from Bragg's angle (2θ) of 10° to 90° using XPert Pro MPD. Surface area was determined with a Micromeritics BET instrument by means of adsorption of ultra pure nitrogen.

2.3. Effect of pH on cadmium adsorption

Effect of pH on the adsorption of cadmium ions using activated alumina was compared over the pH range from 3 to 8. The pH value of cadmium ions solution was adjusted by adding 0.01 mol L^{-1} HCl or NaOH as required. After pH adjustment, 1 g of activated alumina was mixed with 100 mL of cadmium ions solution (10 mg L^{-1}) at different pH values. The suspensions were stirred at 140 rpm and 298 K for 150 min to reach the adsorption equilibrium. Afterwards, samples were withdrawn and filtered through Whatman N° 1 filter paper (0.45 µm). The filtrates were analyzed for residual cadmium ions concentration by potentiometric method using a specific electrode. The amounts of cadmium ions adsorbed on activated alumina (q_e) (mg g^{-1}) was calculated using Eq. (1).

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

where C_0 is the initial cadmium ions concentration (mg L^{-1}), C_e is the cadmium ions concentration at equilibrium (mg L^{-1}), V is the volume of the solution (L) and m is the amount of adsorbent used (g).

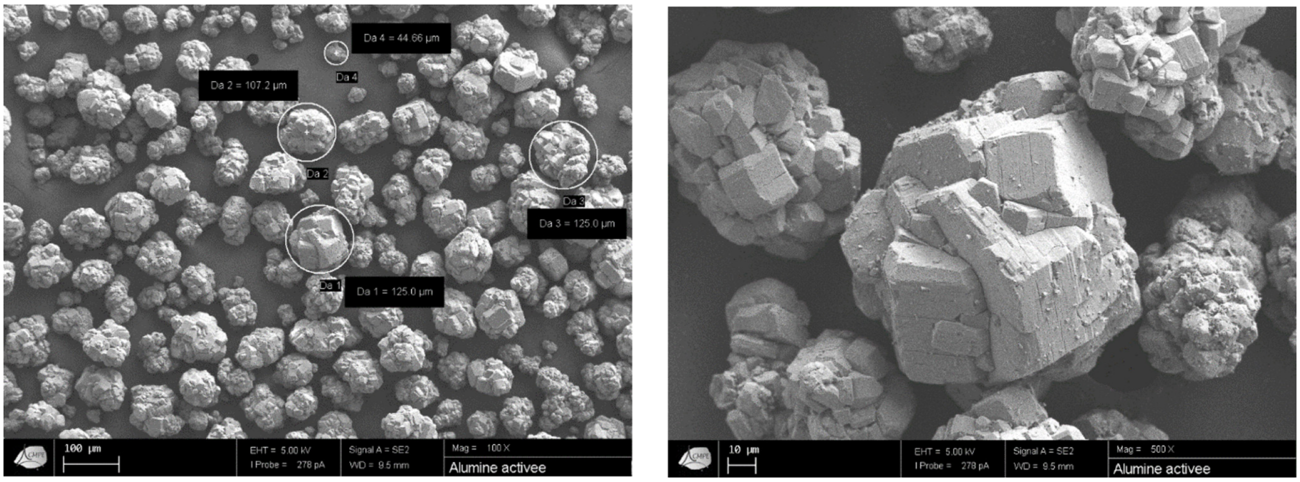

Fig. 1. Photomicrography of the surface of an activated alumina particles. (a) Magnification factor = 100 (b) Magnification factor = 500.

2.4. Adsorption isotherm experiments

Cadmium ions solution (100 mL, pH around 6) with a concentration of 10 mg L^{-1} and various amount of activated alumina (0.5–2 g) was added to each of 250 mL stopper conical flasks and stirred at 140 rpm and at various temperature (283, 298 and 313 K) for 150 min to reach the sorption equilibrium. Then the samples were filtered through a 0.45 µm membrane filter and the filtrates were analyzed for residual cadmium ions concentration by potentiometric method using a specific electrode.

2.5. Adsorption kinetic experiments

The kinetic study was done to find the rate of reaction for the adsorption of cadmium ions onto activated alumina. A volume of 100 mL of cadmium ions solution (10 mg L^{-1}, pH around 6) was mixed with 1 g of activated alumina at different temperature (283, 298 and 313 K) in several stopper conical flasks. The mixture was stirred with magnetic stirrer in a water bath at 140 rpm. Flasks were taken at appropriate time intervals, then the samples were filtered through a 0.45 µm membrane filter and the filtrates were analyzed for residual cadmium ions concentrations by potentiometric method using a specific electrode.

3. Results and discussion

3.1. Effect of pH on adsorption of cadmium

Solution pH is one of the main variables affecting the sorption process, influencing not only the speciation of metal, but also the surface charge of the sorbent and the degree of ionization of the adsorbate during the reaction [22]. Thus, the effect of initial pH on the adsorption of cadmium ions by activated alumina was determined within the pH range of 3–8 and the results are given in Fig. 1. Therefore, experiments were not conducted over pH 8 because the increased capacity of adsorption at pH > 8 may be a combination of both adsorption and precipitation of cadmium hydroxide on the surface of the adsorbent.

The effect of pH on adsorption efficiencies is shown in Fig. 2. A weak adsorption occurs in acid medium but it can be seen that higher pH lead to higher cadmium ions uptake. Acid conditions are not favorable for cadmium sorption. Competition between protons and metal species could thus explain the weak adsorption in acid medium. Generally, the cadmium ions in the aqueous solution may undergo solvation and hydrolysis [23].

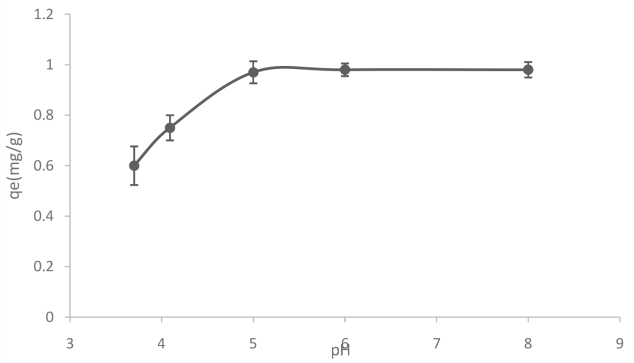

Fig. 2. Effect of pH on the amount of the cadmium ions adsorbed.

Maximum amount of cadmium adsorbed (q_e) was observed at pH between 5 and 8.

To achieve high efficiency and good selectivity, a pH of 6 was selected for subsequent work. The pH chosen should not be too high to avoid precipitation of cadmium as hydroxide. Several researchers investigated the effect of pH on adsorption of cadmium ions by using different kind of sorbents [16,17,22,24], in all cases, they observed a maximum metal ions adsorption between 5 and 6.

3.2. Adsorption isotherms

The study of adsorption isotherms indicates the adsorption capacities of adsorbent at experimental conditions.

In this study Langmuir [25], Freundlich [26] and Dubinin–Radushkevich (D–R) [27] isotherms models were used to investigate the adsorption equilibrium between the cadmium ions solution and the activated alumina phase.

The most widely used Langmuir equation, which is valid for monolayer sorption on a surface with a finite number of identical sites, is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \tag{2}$$

where C_e (mg L^{-1}) is equilibrium concentration of cadmium ions in solutions, q_e (mg g^{-1}) is the amount of cadmium ions adsorbed at equilibrium, q_{max} (mg g^{-1}) is the adsorption capacity and b (L mg^{-1}) is the Langmuir constant related to the affinity of binding sites. A linearized plot of C_e/q_e against C_e gives q_{max} and b.

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter R_L, which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the initial concentration of cadmium ions (mg L^{-1}). The R_L value indicates the shape of isotherm. R_L value between 0 and 1 indicate favorable adsorption, while $R_L > 1$, $R_L = 1$ and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption respectively.

The widely used empirical Freundlich equation is based on sorption on a heterogeneous surface. The heat of adsorption decreases in magnitude with increasing extent of adsorption. If the decline in heat of adsorption is logarithmic, it implies that adsorption sites are distributed exponentially with respect to an adsorption energy with differs between groups of adsorption sites. The Freundlich equation is given as:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

And the linear form of the Freundlich isotherms is:

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \tag{5}$$

where K_f and n are the Freundlich constants indicating sorption capacity and intensity, respectively. K_f and n can be determined from linear plot of log q_e against log C_e. The calculated results of the Langmuir and Freundlich isotherms constants at different temperatures are given in Table 1.

For the three different temperatures, the values of R_L were between 0 and 1, pointing out the favorable adsorption of cadmium ions onto the activated alumina. Freundlich coefficient K_f, which represents the adsorption capacity was found to increases with the increasing of temperature, which is nearly the same as that revealed by Langmuir coefficient 'q_{max}' (Table 1). The other Freundlich coefficient 'n' values fulfilled the condition of $0 < 1/n < 1$ for favorable adsorption. As can be seen from the isotherms table, the surface of activated alumina is favorable for adsorption phenomenon.

The values of q_{max} and b calculated from Langmuir plots were found to be 17.98 mg g^{-1} and 0.16 L mg^{-1} for the experiments carried out at 298 K. The values of both q_{max} and b increased with a rise in the solution temperature. The values of q_{max} increased from 17.82 to 19.72 mg g^{-1}, when the solution temperature increased from 283 to 313 K. The increase in the values of q_{max} with temperature indicates that the cadmium ions are favorably adsorbed by activated alumina at higher temperatures, which shows that the cadmium ions adsorption phenomenon is endothermic.

Table 2 shows the comparison of adsorption capacity of activated alumina with that of different adsorbents reported in previous literatures at standard conditions.

As shown in Table 2, the adsorption capacity of activated alumina for cadmium ions is quite high as compared to the other adsorbents mentioned. These adsorbents were chemically or physically modified to improve the amount of adsorption. In this study the activated alumina used did not undergoes specific modification before use. Therefore, it can be concluded that activated alumina has great potential for cadmium ions adsorption.

In order to determine the best isotherm that could describe adsorption process of cadmium ions, data analysis was performed using linear regression that fitness of the models is often evaluated based on the value of the correlation coefficients (R^2) (Table 1). However, both Langmuir and Freundlich isotherms give very high and close R^2 values that conclusion is not easy. Based on the values of R^2, Alemayehu et al. [34] and Kula et al. [28] whose studies used other adsorbents such as virgin volcanic rocks and activated carbon found that adsorption of cadmium ions (Cd^{2+}) follows both Freundlich and Langmuir type adsorption isotherms.

In this study, we used Chi-square test to determine the best isotherm model [22]. Chis-square analysis has the advantage that all isotherms were compared on the same abscissa, and ordinate could be used to determine the best-fitted models for isotherms. The Chi-square statistic test (Eq. (6)) is the sum of the squares of the differences between the experimental data and theoretically predicted data from models.

The Chi-square value is given as:

$$\chi^2 = \sum_{i=1}^{i=N} \frac{\left(q_e - q_{em}\right)^2}{q_{em}} \tag{6}$$

where q_{em} is equilibrium capacity obtained from the model (mg g^{-1}) and q_e is the equilibrium capacity (mg g^{-1}) from the experimental data. If data from the model were similar to the experimental data, χ^2 would be a small value and vice versa. The value χ^2 of each model were shown in table 1. The Freundlich isotherm has the lowest χ^2 values suggesting that the Freundlich isotherm provides the best fit to the experimental data. Therefore, adsorption of cadmium ions preferably follows the heterolayer adsorption process. Similar results have been reported for the cadmium ions adsorption on activated carbon[15], and on untreated Pinus halepensis sawdust [35].

The equilibrium data were examined using Dubinin–Radushkevich (D-R) isotherm in order to determine the nature of the sorption process as physical or chemical. The linear presentation of D–R isotherm equation is expressed by:

Table 2
Comparison of adsorption capacity of activated alumina for cadmium with that of different adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})	Refs.
Activated carbon prepared from olive stone	1.851	[28]
Apple Promace	4.45	[29]
Thiol-functionalized silica nano hollow sphere	15.45	[30]
Olive cake	10.56	[31]
Tea-industry waste	11.29	[32]
Formaldehyde modified bean husks	4.76	[33]
Pyridine modified bean husks	1.82	[33]
Activated alumina	17.98	Present work

Table 1
Adsorption isotherms parameters of cadmium ions onto activated alumina

Temperature (K)	Langmuir model					Freundlich model			
	q_{max} (mg g^{-1})	b	R_L	R^2	χ^2	K_f	$1/n$	R^2	χ^2
283	17.82	0.12	0.45	0.9904	0.480	1.97	0.91	0.9901	0.450
298	17.98	0.16	0.38	0.9933	0.120	2.64	0.94	0.9890	0.086
313	19.72	0.19	0.34	0.9982	0.054	3.34	0.94	0.9982	0.045

$$\ln q_e = \ln q_{\max} - B\varepsilon^2 \tag{7}$$

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{8}$$

where q_e is the amount of metal ions adsorbed (mg g^{-1}), q_{max} is the maximum biosorption capacity (mg g^{-1}), B is the activity coefficient related to sorption mean free energy (mol^2 kJ^{-2}) and ε the Polanyi potential (kJ mol^{-1} K^{-1}), R is the universal gas constant.

The ln q_e vs ε^2 plot should give a linear curve, allowing the determination of B. It was possible to evaluate the mean sorption energy, E from Eq. (9):

$$E = \frac{1}{\sqrt{2B}} \tag{9}$$

Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energy, it does not predict any saturation of the surface of the adsorbent by the adsorbate. Hence, infinite surface coverage could be predicted mathematically. In contrast, D-R isotherm relates the heterogeneity of energies close to the sorption surface. If a very small sub-region of the sorption surface is chosen and assumed to be approximately by the Langmuir isotherm, the quantity $\sqrt{2B}$ can be related to the mean sorption energy, E, which is the free energy for the transfer of 1 mol of metal ions from the infinity to the surface of the adsorbent. The estimated value of E was 8.45, 9.12 and 11.18 KJ mol^{-1} at the temperature of 283, 298 and 313 K respectively, which is the range expected for chemisorption (8–16 KJ mol^{-1}). Similar results have been reported by Naiya et al. [19].

3.3 Adsorption kinetics

The study of adsorption dynamics describes the solute uptake rate, and evidently, this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of cadmium ions adsorption on the activated alumina were analyzed using pseudo-first–order [36], pseudo-second–order [37] and Elovich [38] models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

3.3.1. Pseudo-first order kinetic model

The pseudo-first order equation of Lagrange is generally expressed as follows:

$$\frac{dq_t}{dt} = K_1\left(q_e - q_t\right) \tag{10}$$

where q_e and q_t are the amount of the cadmium ions adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively; K_1 (min^{-1}) is the rate constant of pseudo-first order equation.After integration and applying the boundary condition $q_t = q_t$ at $t = 0$ to $t = t$; the integration form of Eq. (10) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{11}$$

The plot of log (q_e – q) vs. t (Fig. 3) gives a straight line for the pseudo-first order adsorption kinetics, allowing the determination of the adsorption rate constants, k_1 (Table 3). It is noted that correlation coefficients for the three temperatures are less than the unity. It is also observed that k_1 increases and that q_e decreases with the temperature increase.

3.3.2. Pseudo-second order kinetics

The pseudo-second order rate expression is based on sorption capacity of the solid phases, which has been applied for analyzing chemisorption kinetics rate. It is given by:

$$\frac{dq_t}{dt} = K_2\left(q_e - q_t\right)^2 \tag{12}$$

where q_e and q_t are the amount of the cadmium ions adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively; K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order kinetic equations.

The boundary conditions $q_t = 0$ and $q_t = q_t$ at $t = 0$ to $t = t$, respectively. The integrated form of equation becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{13}$$

A plot t/q_t vs. t (Fig. 4) gives a straight line from which K_2 and q_e can be evaluated.

The fitting kinetic parameters estimated by linear regression analysis were summarized in Table 3. It is clear that the pseudo-second order model with all the determined coefficients (R^2) higher than 0.99 can better describe the adsorption of cadmium ions on activated alumina at 283–313 K than the pseudo-first order model. This result is in a good agreement with Kilic et al. [39], Boparai [40] and Wasewar [41] whose studies used other adsorbents such as bio-char, nano zerovalent iron particles, granular activated carbon and activated clay.

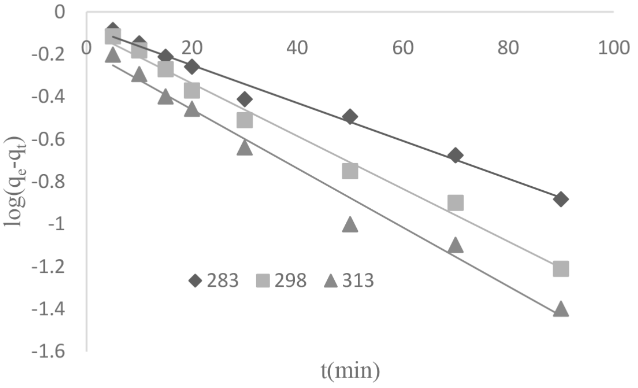

Fig. 3. Plots of the pseudo-first-order kinetics at different temperatures.

Table 3
Kinetic parameters for the removal of cadmium ions by activated alumina

Temperature (K)	Pseudo-first order		
	K_1 (min)	q_e (mg g^{-1})	R^2
283	0.020	0.84	0.986
298	0.027	0.81	0.989
313	0.032	0.65	0.981
Temperature (K)	Pseudo-second order		
	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
283	0.022	1.16	0.997
298	0.035	1.14	0.997
313	0.078	1.06	0.998
Temperature (K)	Elovich model		
	β (g mg^{-1})	α (mg g^{-1} min^{-1})	R^2
283	4.10	0.068	0.987
298	3.92	0.099	0.990
313	4.64	0.183	0.989

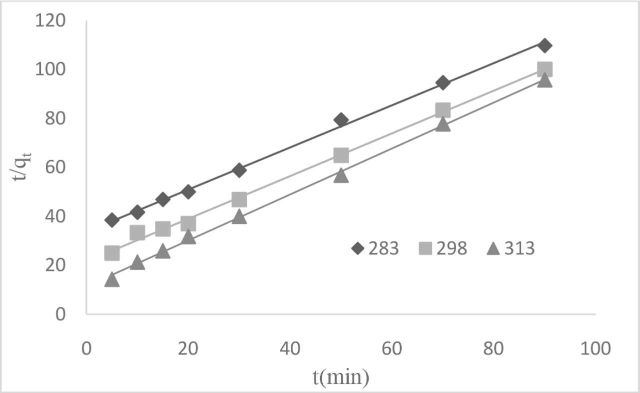

Fig. 4. Plots of the pseudo-second–order kinetics at different temperatures.

3.3.3. Elovich kinetic model

One of the most useful models describing chemical adsorption is the Elovich kinetic model, given in its linear form by Eq. (14):

$$q_t = \frac{1}{\beta}Ln(\alpha\beta) + \frac{1}{\beta}Ln(t) \tag{14}$$

where α (mg g^{-1} min^{-1}) is the initial adsorption rate and β (g mg^{-1}) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. The Elovich equation was used in this study to correlate the experimental data. As shown in Fig. 5, the data produced linear curves. This linear relationship between q_t and $Ln\ t$ indicate that Elovich's model is well verified and confirms the chemical adsorption reaction type. The determinates constants α, β and R^2 are listed in Table 3. The R^2 values support the idea of chemisorption.

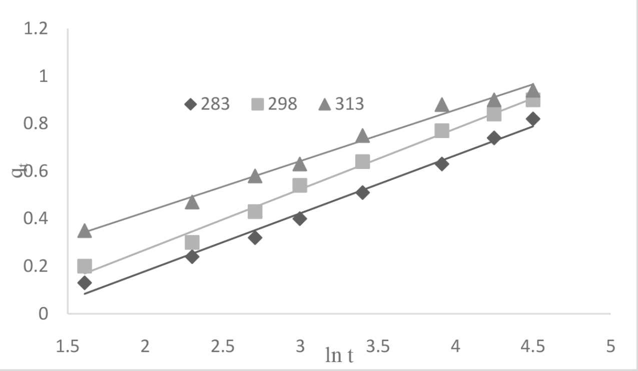

Fig. 5. Plots of Elovich model kinetics at different temperatures.

3.4. Thermodynamic modeling

Adsorption experiments to study the effect of temperature were carried out at 283–313 K at pH value of 6, adsorbent dosage level of 1 g and initial concentration of cadmium ions of 10 mg L^{-1}. The increase or decrease in adsorption with rise in temperature may be due to the strengthening or weakening of adsorptive forces between the actives sites of the adsorbents and adsorbate species and between the adjacent molecules of the adsorbed phase respectively.

Temperature dependence of the adsorption process is associated with several thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and the entropy change (ΔS°). Thermodynamic parameters for adsorption of cadmium ions onto activated alumina were estimated using the following equations:

$$K_L = \frac{C_a}{C_e} \tag{15}$$

$$\Delta G^0 = -RTLnK_L \tag{16}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{17}$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{18}$$

where K_L is the distribution coefficient, C_a and C_e are equilibrium concentration of cadmium ions on the adsorbent and in the solution, respectively (mg L^{-1}).

The values of $\Delta H°$ and $\Delta S°$ parameters can be calculated from the slope and intercept of the plot of ln K_L versus 1/T, respectively.

The thermodynamic parameters are listed in Table 4. The negative $\Delta G°$ values suggest that the adsorption of cadmium ions onto activated alumina is a spontaneous process. The $\Delta G°$ values decrease when the temperature increases, hence, the process is efficient at higher temperature. The enhancement of the adsorption capacity of adsorbent at higher temperature may be attributed to the increase in pore size and/or to the activation of the adsorbent surface [42,43]. At higher temperatures, solvated cadmium ions are readily desolvated, the pores increase quickly, and adsorption processes become highly favorable [44].

As given in Table 4, the enthalpy change of cadmium ions adsorption on activated alumina is 21.446 kJ mol^{-1}, indicating that the adsorption of cadmium ions on activated alumina is an endothermic process, the entropy change for cadmium adsorption on activated alumina is 100.23 J mol^{-1} K^{-1}. The positive values of $\Delta S°$ reflect the affinity of activated alumina for cadmium ions and shows the increasing randomness at the solid/liquid interface during the sorption of metal ions on activated alumina. Similar results have been reported by Qingzhu et al. [24], who applied esterified spent grain to adsorb cadmium ions and noted that $\Delta H°$ = 3.29 kJ mol^{-1} and $\Delta S°$ = 38.45 J mol^{-1} K^{-1}, claiming that their adsorption was endothermic and some structural changes occurred in the adsorbate and adsorbent. In applying chemically modified apple promace to adsorb cadmium ions, Chand et al. [29] determined that $\Delta H°$ = 3.17 J mol^{-1} and $\Delta S°$ = 16.93 J mol^{-1} K^{-1}, adsorption in this case was endothermic and the randomness at the solid/solute interface was increased. Krika et al. [45], who applied Algerian crok biomass to adsorb cadmium ions, determined that $\Delta H°$ = 110.47 kJ mol^{-1} and $\Delta S°$ = 0.3795 kJ mol^{-1} K^{-1} suggesting endothermic nature of adsorption and more efficiently adsorption of cadmium ions on cork powder at higher temperatures.

Table 4
Thermodynamic study

T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
283	−6.919	21.446	100.23
298	−8.422		
313	−9.926		

3.5. Characterization of activated alumina and possible mechanisms of cadmium adsorption

The BET surface area of activated alumina was determined in order to examine the changes dealing with the surface properties taking place during the adsorption process, its value after adsorption was higher (165.76 m^2 g^{-1}) than that of the sample before adsorption (156.74 m^2 g^{-1}). A possible explanation for this could be that cadmium ions can be possibly adsorbed on the surface of agglomerated particles and create a new porous structure [46].

Fig. 6 shows the XRD patterns of activated alumina before (a) and after (b) adsorption of cadmium ions. Sharp intensity XRD peaks have been observed in both XRD patterns. The Sharp peaks present in the figures indicated the crystalline nature of the material.

The characteristic peaks of gamma alumina at 2θ of 45.69° and 67.26° are observable in both XRD patterns. This can be associated with its crystalline region [47].

There is a slight dissimilarity in the XRD pattern of adsorbent plotted after the cadmium adsorption. The characteristic new peaks observed at 2θ = 20.36 and 2θ = 18.62 after adsorption process (Fig. 7b) predict the possibility of the specific adsorption of cadmium ions onto activated alumina.

The functional groups of activated alumina (Al_2O_3) before and after cadmium adsorption were determined using Fourier Transform Infrared (FTIR) spectroscopy. A comparison of the FT-IR spectrum of activated alumina before and after adsorption of cadmium was illustrated in Fig. 7. As seen in Fig. 7, the difference between the two spectra was in the wavenumber and intensities. It is evident that some functional groups (present in Al_2O_3) are involved in the adsorption process and there is an interaction between cadmium and Al_2O_3. The absorption band at 1428 cm^{-1} and 1355 cm^{-1} should correspond to CO_2 and carbonates.

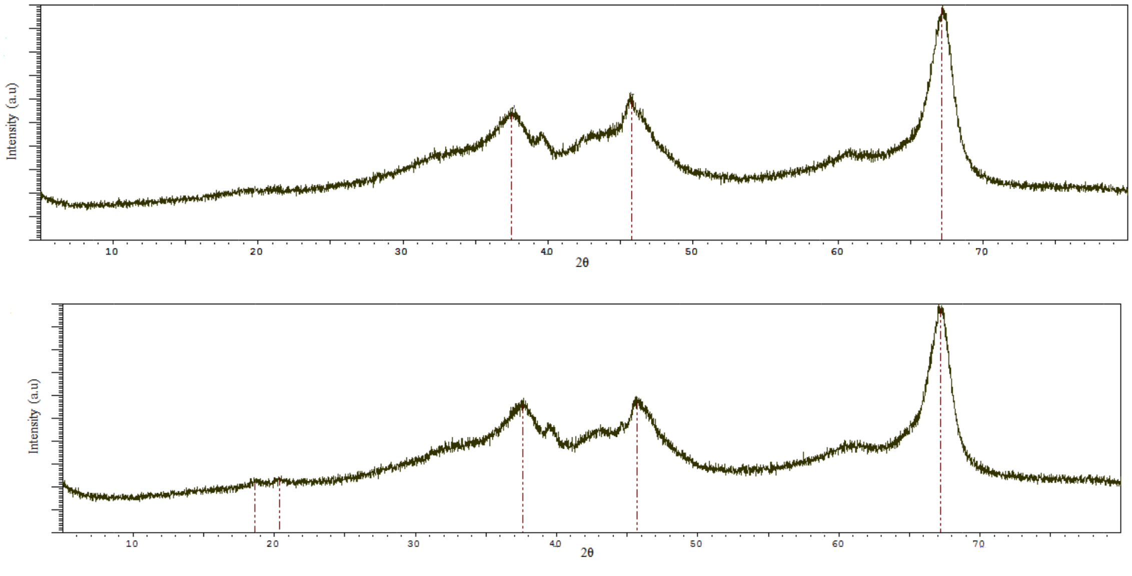

Fig. 6. XRD patterns of activated alumina before (a) and after (b) adsorption of cadmium.

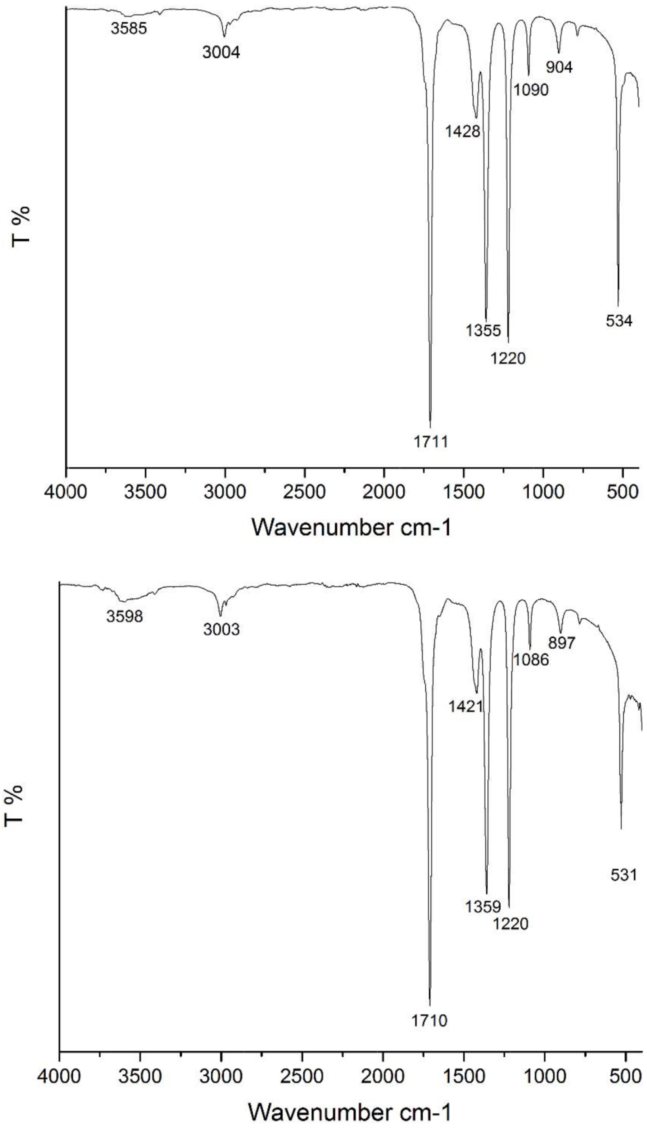

Fig. 7. FT-IR spectrum of activated alumina before (a) and after (b) adsorption of cadmium.

The vibrations of Al-O can be seen at 534 and 1090 cm^{-1} [48–50].

The decrease in the intensity of 534 cm^{-1} peak after cadmium adsorption confirmed the involvement of Al–O bonds in the cadmium adsorption process and indicating that metal-adsorbent interactions has been formed between cadmium ions and functional sites.

The O–H deformed band was observed at 904 cm^{-1} that corresponds to the binding Al–OH. This peak also decreased in intensity and in the wavenumber after adsorption, indicating that metal-adsorbent interactions has been formed and Cd–O complex probably formed [22,29].

The intensity of the –OH band at around (3200–3600) cm^{-1} became sharper after adsorption, indicating the presence of free hydroxyl groups which is due to increasing in number of water molecules after adsorption study.

Table 5
Characteristics of wastewater

	Wastewater sample
pH	5.1
[Cd^{2+}] (mg L^{-1})	5.2
[Ca^{2+}] (mg L^{-1})	250
[Mg^{2+}] (mg L^{-1})	110
Salinity (mg L^{-1})	4850

Acetone was used as solvent to deposit alumina on the crystal of the instrument. It does not contribute to the mechanism. Acetone has C–H bonds (stretching frequencies 3003 cm^{-1}) and C=O bond (stretching frequency 1710 cm^{-1}).

3.6. Application for real samples

Wastewater samples was obtained from ONAS Company in Tunisia, which neutralizes hazardous wastes. The samples obtained came from wastes produced during electrochemical processes. The sample was filtered before analysis through a 0.45 µm membrane filter. Some characteristics of the wastewater are shown in Table 5. To evaluate the effect of real matrices on the removal efficiency of cadmium, a batch adsorption studies using the wastewater sample was carried out. Cadmium in the sample was the subject of adsorption process and its percentage removal was found to be 99.1%. It seems that the simultaneous presence of high concentration of other cations such as calcium and magnesium does not affect the effectiveness of cadmium removal. Cadmium concentration in the treated sample was 0.04 mg L^{-1}, suggesting that activated alumina could be employed as an efficient adsorbent for the removal of cadmium from real samples.

4. Conclusions

The present study proves the capability and effectiveness of activated alumina for cadmium removal from aqueous solutions. The kinetic, thermodynamic and equilibrium isotherm tests were conducted at 283, 298 and 313 K. The adsorption process followed the pseudo-second order reaction and the Freundlich adsorption theory best describes cadmium ions adsorption on activated alumina.

It was observed that the isotherm constant increased with increasing temperature. The values of q_{max} increased from 17.82 to 19.72 mg g^{-1}, when the solution temperature increased from 283 to 313 K, which proves that the adsorption process is endothermic.

The Dubini–Redushkevich model indicates the presence of a chemical sorption model, which is confirmed by the Elovich kinetic model. The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ show a chemically favored, spontaneous and endothermic adsorption.

The adsorption process was accompanied by increase of the value of specific surface area. The obtained results could be of significant interest, since cadmium ions can be possibly adsorbed on the surface of agglomerated particles and create a new porous structure.

Mechanism study was performed using XRD and FTIR analysis and indicates that Cd–O complex was probably formed.

Studies on batch adsorption using real sample indicates that activated alumina is an efficient adsorbent for the removal of cadmium.

Symbols

C_0 – Initial cadmium ions concentration (mg L^{-1})
C_e – Cadmium ions concentration at equilibrium (mg L^{-1})
V – Volume of the solution (L)
m – The amount of adsorbent used (g).
q_e – The amount of Cd^{2+} adsorbed at equilibrium (mg g^{-1})
q_{max} – The adsorption capacity (mg g^{-1})
b – Langmuir constant (L mg^{-1})
R_L – Dimensionless constant of separation factor
K_f – Adsorption capacity
n – Freundlich constant
B – Constant gives the mean free energy (mol^2 kJ^{-2})
ε – Polanyi potential (kJ mol^{-1} K^{-1})
R – The gas constant (8.314 J mol^{-1} K^{-1})
E – The mean sorption energy (KJ mol^{-1})
q_t – The amount of the cadmium ions adsorbed at time t (mg g^{-1})
K_1 – Rate constant of the pseudo-first order adsorption (min^{-1})
K_2 – Rate constant of the pseudo-second order adsorption (g mg^{-1} min^{-1})
β – The desorption constant (g mg^{-1})
α – The initial adsorption rate (mg g^{-1} min^{-1})
$\Delta G°$ – Gibbs free energy (kJ mol^{-1})
$\Delta H°$ – Enthalpy (kJ mol^{-1})
$\Delta S°$ – Entropy (kJ mol^{-1} K^{-1})

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