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Removal of chromium by adsorption on activated alumina

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ABSTRACT

The removal of chromium (VI) from aqueous solutions by activated alumina has been investigated as a function of solution pH, initial chromium concentration, adsorbent dose of activated alumina and temperature. The pH and the adsorbent dose of activated alumina are the most significant parameters affecting chromium (VI) adsorption. The chromium concentrations were analyzed by reaction with 1,5-diphenylcarbazide. This method has been validated according to the French standard XPT-90-210. In order to optimize the effect of the main parameters and their mutual interaction for the adsorption process, a full factor design of the type n^k has been used. Thus, the total number of trial experiments needed for an investigation is 2^4. The Freundlich and Langmuir models have been applied and the equilibrium adsorption data were found to best fit the Freundlich and Langmuir adsorption isotherm. A comparison of kinetic models applied to the adsorption of chromium (VI) on activated alumina was evaluated for the first-order and the second-order models respectively. Results show that the second-order kinetic model was found to correlate the experimental data well.

Keywords: Cr(VI); Adsorption; Activated alumina; Freundlich; Langmuir

1. Introduction

The increasing contamination of urban and industrial wastewaters by toxic metal ions causes significant environmental pollution [1–3]. All over the world, chromium is abundantly available in nature. The most common forms of chromium are trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. It is used in various many industries such as electroplating, glass, ceramics, fungicides, rubber, fertilizers, tanning, mining, metallurgical, etc. [4–11]. Cr(VI) is highly mobile and considered toxic, carcinogenic and mutagenic to the living organisms. This results in a variety of diseases such as dermatitis, bronchitis, perforation of nasal septum, bronchogenic carcinoma, liver damage, ulcer formation [12–17]. Therefore, it is necessary to eliminate Cr(VI) from the environment, 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 Cr(VI) contaminated wastewater is highly desired by the industries [18]. There are various treatment technologies available to remove Cr(VI) from wastewater such as chemical precipitation [19,20], ion-exchange [21,22], membrane separation [23], electrocoagulation [24], solvent extraction [25], reduction [26], reverse osmosis [25], biosorption [27–29] and adsorption [16,30]. Adsorption is a very effective process for a variety of applications, and now it is considered an economical and efficient method for metal ions removal from wastewaters [31].

The present investigation deals with the application of activated alumina in the removal of chromium (VI) from aqueous solutions. The amount of chromium removed was determined on the basis of the following

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parameters: dose adsorbent of alumina, initial chromium concentration, pH and temperature. The experiments have been carried out using a 2^4 full factorial design to study the effect of the main and interaction parameters [31]. The Langmuir and Freundlich equation models are used to fit the experimental equilibrium isotherm data obtained in this study. A comparison of kinetic models applied to the adsorption of chromium (VI) ions on the activated alumina was evaluated for the first-order and the second-order kinetic models, respectively.

2. Experimental

2.1. Material and methods

2.1.1. Activated alumina

The granular activated alumina used was supplied by Sigma-Aldrich (particle size spherical 150 mesh, pH (in the water) 4.5, melting point 2040 °C, molecular weight 101.96 $g \cdot mol^{-1}$, pore diameter 58Å and surface area 155 $m^2 \cdot g^{-1}$). It was dried at 110 °C for 24 h in order to eliminate the impurities and to prepare the activated alumina.

2.1.2. Reagents

The stock solutions of chromium (VI) were prepared by dissolving 2.829 g of potassium chromate salt ($K_2Cr_2O_7$) in 1 l of distilled water to have an initial concentration of Cr(VI) 1 $g \cdot l^{-1}$. The activated alumina samples were placed directly in the solution. All other reagents used were analytical reagent grade.

2.1.3. Batch adsorption experiments

Adsorption experiments were carried out in mechanically agitated in a thermostatically bath, the beakers containing 100 ml of chromium with initial concentration 10 mg l^{-1} and with 1 g amount of activated alumina, for 90 min and at 25 °C. The solution pH values were measured by a pH-meter. The content was agitated with a constant stirring rate at 140 rpm. Samples were withdrawn after a definite time interval and filtered through What man N° 1 filter paper (0.45 µm). All the above experiments were carried out in duplicate to establish the accuracy of the procedure. The filtrates were analyzed for residual Cr(VI) concentration by reaction with 1,5-diphenylcarbazide followed by absorbance measurement at 540 nm using a UV-visible spectrophotometer (Tomos V 1100).

The amount of adsorption at equilibrium (q_e, mg g^{-1}) was calculated according to Eq. (1):

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

The removal percentage of chromium was calculated by using to Eq. (2):

$$\% \text{ Removal of } Cr = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg l^{-1}), V the volume of solution (l), m the weight of activated alumina (g).

2.2. Validation of the analytical method

Several parameters have been taken into account in order to validated the method for determining residual chromium (VI) concentration by 1,5-diphenylcarbazide. In fact, we have evaluated the linearity, specificity, fidelity (repeatability and reproducibility) and instrumental method detection limits and quantification. In the whole validation, the calibration curve for the measurements was always prepared with at least six points (blank not included), as recommended by the French standard XPT-90-210. Experimental validation of the analytical method is given by Table 1.

Table 1
Validation parameters

Test	Experimental value	Critic value	Conclusion	
Linearity	$F_l = 174850.4$	$V_{Cl} = 7.82$	Linear	Linearity approved
	$F_{nl} = 3.93$	$V_{Cnl} = 4.22$	No Curvature	
Specificity	$t_{obs} = 3.219$	$t_{(9,0,995)} = 3.250$	Slope equal to 1 Origin intercept is equal to 0	Specific
	$t'_{obs} = 1.270$			
Cochran	$C_{xobs} = 0.287$	$C_{cochran, \alpha=5\%} = 0.564$	Point group is considered no aberrant	
		$C_{cochran, \alpha=1\%} = 0.480$	Point group is considered no suspect	
Fidelity	$CV_r = 0.763\%$; 0.980%; 0.687%; 0.881%	$CV_r < 5\%$	Repeatable	Faithful
	$CV_R = 0.871\%$	$CV_R < 5\%$	Reproductible	

According to the values of Table 1, the method for chromium (VI) determination by 1,5-diphenylcarbazide is efficient and appears as a good method with DL = 0.0012 mg l^{-1} and QL = 0.0042 mg l^{-1} in the range of linearity 0.05 to 0.5 mg l^{-1} with a standard deviation (SD) of 1.7287%.

3. Results and discussion

3.1. Parameters affecting the adsorption

Adsorption processes are affected by several conditions, such as initial pH, initial concentration chromium (VI), adsorbent dose of alumina activated and temperature.

3.1.1. Influence of solution pH

The pH controls the adsorption at the water-adsorbent interfaces. Hence, optimization of pH for adsorption of chromium was done by studying the uptake of chromium over activated alumina as a function of pH. The effect of pH was determined by studying adsorption of Cr(VI) at an initial Cr(VI) concentration of 10 mg l^{-1} with adsorbent doses of 1 g per 100 ml for AA (activated alumina) over a pH range of 2–10 keeping the other parameters constants at 25 °C. The pH adjustments were made either with 0.1 M HCl or 0.1 M NaOH. The effect of pH on the adsorption of Cr(VI) by AA is shown in Fig. 1. We can remark that the percentage adsorption increased with increasing pH to a maximum value (pH 5–6) and then declines rather rapidly with further increase in pH.

Under acidic conditions, the surface of the adsorbent becomes highly protonated and favours the uptake of Cr (VI) in the anionic form (HCr_4O^-). Since the point of zero charge (pH_{pzc}) for different types of alumina is around 8.7–9.0 [33], the surface of activated alumina is positively charged till pH < pH_{pzc}. The anionic species would thus have stronger interaction with activated alumina and have higher uptake. Furthermore, as pH increases there is a competition between OH^- and chromate ions CrO_4^{2-}; the former being the dominant species at higher pH values.

3.1.2. Influence of adsorbent dose

To optimize the adsorbent dose for the removal of Cr(VI) from the solution, adsorption studies were carried out with different initial Cr(VI) concentration ranging from 0.5 mg l^{-1} to 200 mg l^{-1} with corresponding adsorbent doses 1 to 8 g, in the range of pH 5–6, during 90 min. For low concentration of chromium (0.5 mg l^{-1} and 10 mg l^{-1}), 1 g of activated alumina was enough to remove all the chromium present in the solution, but for high concentration (50 mg l^{-1} to 200 mg l^{-1}) the dose of activated alumina was more important (Fig. 2).

3.2. Empirical modeling

In order to obtain the optimum condition for the adsorption process, a full factor design of the type n^k has been used, where n = number of levels and k = number of factors under verification (here $n = 2$ and $k = 4$). Thus, the total number of trial experiments needed for an investigation is 2^4. If Y is the response variable, then the regression equation with four parameters and their interaction is given by Akhnazarova and Katarov [34] (see Tables 2 and 3):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \quad (3)$$

where b_0, b_1, b_2, b_3 and b_4 are the linear coefficients, b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} are the second-order interaction terms. X_1, X_2, X_3 and X_4 are the dimensionless coded factors of the following parameters studied pH, initial chromium (VI) concentration, dose of adsorbent

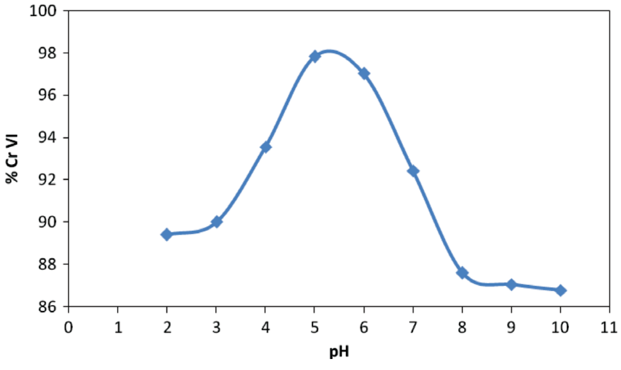

Fig. 1. Effect of pH on Cr(VI) removal.

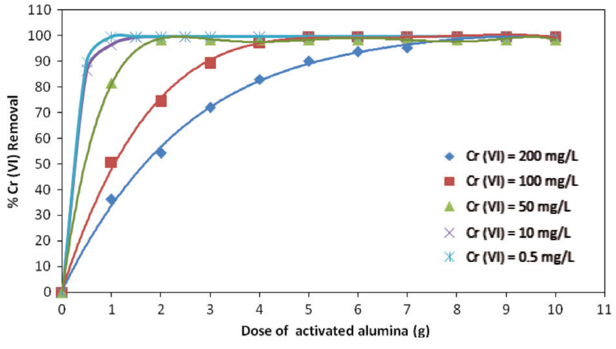

Fig. 2. Effect of adsorbent dose on chromium (VI) removal.

alumina and temperature, respectively. In the Table 2 the low and high levels are mentioned for the studied parameters.

According to the factorial design for chromium (VI) adsorption onto activated alumina, sixteen (2^4) experiments have been done following the matrix in Table 3.

The significant coefficients for chromium (VI) adsorption are shown in Fig. 3. The regression equation (3) becomes:

$$Y_{cr} = 66.83 + 13.67\ X_1 - 6.18\ X_2 - 21.23\ X_3 - 5.53\ X_4 + 3.44\ X_1X_2 + 5.06\ X_1X_3 - 1.12\ X_1X_4 + 0.78\ X_2X_3 + 0.68\ X_2X_4 - 3.29\ X_3X_4$$

It can be seen (Fig. 3) that the adsorbent dose of activated alumina and the pH have the most pronounced effect in increasing the chromium (VI) adsorption.

The Pareto effect (Fig. 4) shows that the adsorbent dose of activated alumina has the most positive pronounced effect in increasing the chromium (VI) adsorption, whereas the pH has the most negative effect on the process. However, the interaction pH—adsorbent dose of activated alumina has a positive effect.

Table 2
The 2^4 factorial design for chromium (VI) adsorption onto activated alumina

Variables	Low level	High level
Dose AA (*D*, *g*)(X_1)	0.5	2
Initial chromium concentration (*C*, mg l^{-1}) (X_2)	0.5	50
pH (*pH*) (X_3)	5	10
Temperature (*θ*, °C) (X_4)	10	40

3.3. Equilibrium adsorption isotherms

The distribution of Cr(VI) between the liquid phase and the solid adsorbent phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the isotherm models. The data was fitted

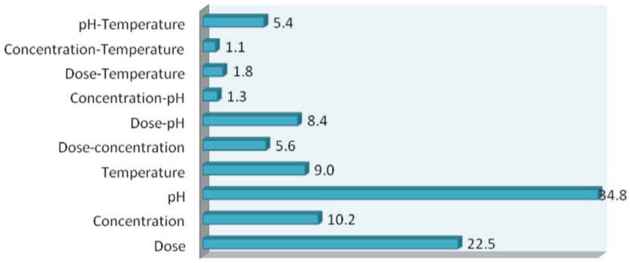

Fig. 3. Scatter diagram of the investigated adsorption model of chromium (VI).

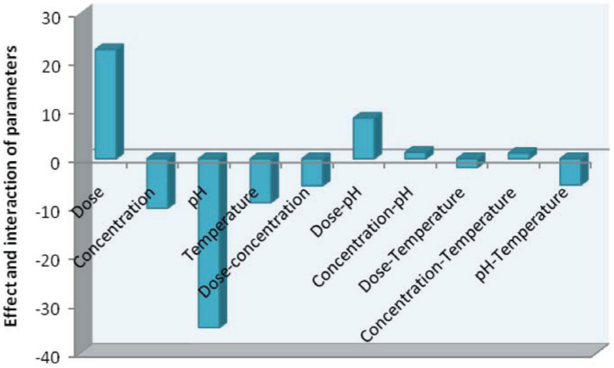

Fig. 4. Pareto effect in the adsorption of chromium (VI) onto activated alumina.

Table 3
Studied parameters in their reduced and normal forms

Experiment	D(g)	X_1	*C*(mg l^{-1})	X_2	pH	X_3	(°C)	X_4	Y_{cr}
1	0.5	–1	0.5	–1	5	–1	10	–1	96.0
2	2	1	0.5	–1	5	–1	10	–1	98.5
3	0.5	–1	50	1	5	–1	10	–1	68.4
4	2	1	50	1	5	–1	10	–1	98.3
5	0.5	–1	0.5	–1	10	1	10	–1	24.2
6	2	1	0.5	–1	10	1	10	–1	98.2
7	0.5	–1	50	1	10	1	10	–1	41.7
8	2	1	50	1	10	1	10	–1	53.6
9	0.5	–1	0.5	–1	5	–1	40	1	89.9
10	2	1	0.5	–1	5	–1	40	1	95.7
11	0.5	–1	50	1	5	–1	40	1	63.5
12	2	1	50	1	5	–1	40	1	94.2
13	0.5	–1	0.5	–1	10	1	40	1	13.5
14	2	1	0.5	–1	10	1	40	1	68.1
15	0.5	–1	50	1	10	1	40	1	28.1
16	2	1	50	1	10	1	40	1	37.4

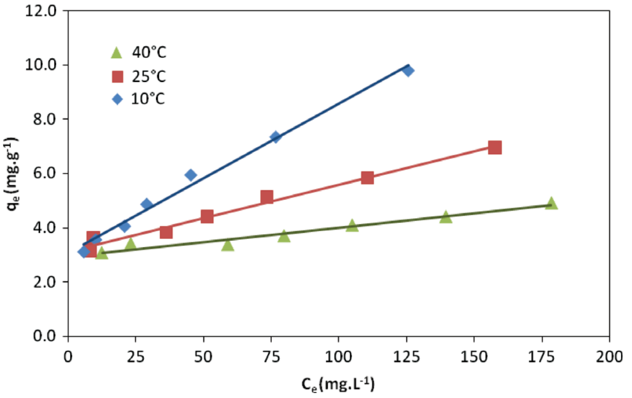

Fig. 5. Equilibrium adsorption isotherms of chromium (VI) onto activated alumina.

to Freundlich and Langmuir equations in linear form. Equilibrium adsorption study were carried out with different amount of the adsorbent ranging from 1 to 8 g while maintaining the initial chromium (VI) concentration 200 mg l^{-1} and the range of pH 5–6.

3.3.1. Freundlich isotherms

The Freundlich isotherm, which is an indicative of the surface heterogeneity of the adsorbent, is given Eq. (4):

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

where K indicates the adsorption capacity and $1/n$ is an arbitrary constant related to the adsorption intensity. K and n are empirical constants dependent on several environmental factors, and can be determined from the linear plot of log(q_e) versus log(C_e).

The linearized form of Freundlich equations is given Eq. (5):

$$\log(q_e) = \log(K) + \frac{1}{n}\log(C_e) \tag{5}$$

In order to evaluate the equilibrium chromium (VI) concentration C_e, adsorption studies were carried out for 180 min because it was found experimentally that 90 min was sufficient to achieve the equilibrium. If the adsorption data followed the Freundlich isotherm then log(q_e) versus log(C_e) would give a straight line from which K and n values could be calculated from intercept and slope, respectively (Fig. 5).

3.3.2. Langmuir isotherms

The Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by Eq. (6):

$$q_e = \frac{q_m \cdot b \cdot C_e}{(1 + b \cdot C_e)} \tag{6}$$

where C_e is the equilibrium aqueous chromium concentration (mg l^{-1}), q_e the amount of chromium adsorbed per gram of adsorbent at equilibrium (mg g^{-1}), q_m and b are constants related to the maximum adsorption capacity (mg g^{-1}) and the energy of adsorption (l mg^{-1}), respectively. The Langmuir constants q_m and b can be determined from the linearized form of Eq. (6); the plot of $1/q_e$ versus $1/C_e$ results in a straight line of slope $1/q_m$ and an intercept of $1/b\ q_m$ (Eq. 7):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e \cdot q_m \cdot b} \tag{7}$$

Alternatively, if adsorption followed Langmuir isotherm then a linear relationship would be obtained between $1/q_e$ and C_e from which the two constants q_m and b, could be calculated.

The values of Freundlich and Langmuir parameters are reported in Table 4. Both Freundlich and Langmuir isotherms fitted with a correlation coefficient greater than 0.98.

Decrease in q_m (which is a measure of the maximum adsorption capacity) has been observed with increasing the temperature. Freundlich constants K and n were also influenced by temperature. Increase temperature induces a decrease in (1/n) values which indicates the decreasing of

Table 4
Adsorption isotherm constants for chromium on activated alumina

Temperature	Freundlich constants			Langmuir constants		
	K	n	R^2	q_m(mg/g^{-1})	$b \cdot 10^3$ (l·mg^{-1})	R^2
10 °C	0.989	2.110	0.996	11.709	25.07	0.983
25 °C	0.956	2.489	0.996	8.525	21.65	0.982
40 °C	0.939	3.002	0.995	5.948	20.93	0.978

adsorption intensity. For studied temperatures, $1/n$ values are less than unity indicating favorable adsorption.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter r was determined by using the following Eq. (8):

$$r = \frac{1}{(1 + b \cdot C_0)} \tag{8}$$

The values of r indicated the type of Langmuir isotherm to be irreversible ($r = 0$), favorable ($0 < r < 1$), linear ($r = 1$) or unfavorable ($r > 1$).

The r value for the initial concentration 200 mg l^{-1} was found equal to 0.166, 0.187 and 0.192 at 10, 25 and 40°C respectively. The calculated values of r indicated that adsorption of chromium (VI) onto activated alumina was favorable.

3.4. Kinetic study of chromium (VI) adsorption

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 chromium (VI) adsorption on the activated alumina were analyzed using first-order [35] and second-order [36] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 value indicates that the model successfully describes the kinetics of chromium (VI) adsorption [37]. The kinetic study was carried out with 100 ml of chromium (VI) solution at 200 mg l^{-1} and 8 g of AA adsorbent in the range of pH 5–6, and at three temperatures 10, 25 and 40°C. The obtained results are given in Fig. 6.

3.4.1. First-order kinetics

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a first-order equation [38,39]. The non-linear form of the first-order equation is given by Eq. (9):

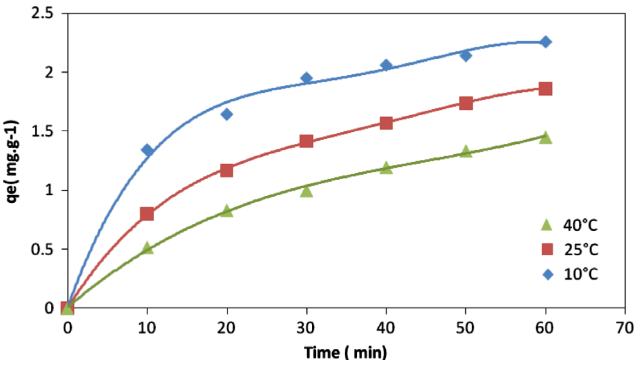

Fig. 6. Plot for adsorption of chromium (VI) on activated alumina at different temperatures.

$$\frac{dq}{dt} = K_1(q_e - q) \tag{9}$$

where, q_e and q are the amounts of Cr(VI) adsorbed (mg g^{-1}) at equilibrium time and at any instant of time, t, respectively, and K_1 (l min^{-1}) is the rate constant of the first-order adsorption operation. The integrated rate law after application of the initial condition of $q = 0$ at $t = 0$, becomes a linear equation as given by Eq. (10):

$$\log(q_e - q) = \log(q_e) - \frac{K_1 \cdot t}{2,303} \tag{10}$$

The plot of $\log(q_e - q)$ versus t gives a straight line for the first-order adsorption kinetics, from which the adsorption rate constant, K_1, is estimated.

The first-order kinetic equation differs from a true first-order equation in two ways: (i) the parameter $K_1(q_e - q)$ does not represent the number of available sites, and (ii) the parameter $\log(q_e)$ is an adjustable parameter and often it is found that it is not equal to the intercept of the plot of $\log(q_e - q)$ versus t, whereas in a true first-order model the value of $\log(q_e)$ should be equal to the intercept [39]. Hence, first-order kinetic model (Eq. [9]) is used for estimating K_1 alone, which is considered as mass transfer coefficient in the design calculations.

3.4.2. Second-order kinetics

As first-order kinetic model gives only K_1 and as q_e cannot be estimated using this model, applicability of the second order kinetics has to be tested for the estimation of q_e with Eq. (11):

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{11}$$

where K_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is the second-order rate constant. From the boundary conditions, $t = 0$ to t and $q = 0$ to q, the integrated form of the equation becomes Eq. (12):

$$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t \tag{12}$$

Eq. (11) can be written in a linear form, as given by Eq. (13):

$$\frac{t}{q} = \frac{1}{K_2\, q_e^2} + \frac{t}{q_e} \tag{13}$$

where $1/(q_e^2 K_2)$ that can be regarded as the initial adsorption rate as $t \to 0$.

Table 5
Comparison of correlation coefficients for the first- and second-order adsorption

Temperature	First-order			Second-order		
	K_1(min^{-1})	q_e (mg/g^{-1})	R^2	K_2 (g·mg^{-1}/min^{-1})	q_e (mg/g^{-1})	R^2
10 °C	1.612	2.807	0.9288	0.591	2.622	0.9975
25 °C	2.993	2.377	0.9683	1.413	2.532	0.9960
40 °C	4.145	2.027	0.9815	3.000	2.277	0.9924

Under such circumstances, the plot of t/q versus t should give a linear relationship, which allows the determination of q_e and K_2.

The correlation coefficients for the second-order kinetic plots obtained for initial chromium concentration of 200 mg l^{-1} at the studied temperatures were greater than 0.99 (Table 5). These results show that the adsorption processes were in the second-order reaction at 10, 25 and 40 °C. A similar phenomenon has been observed for silica [40], boron [41] adsorption on activated alumina. For instance, Hamadi et al. showed that a second-order kinetic equation is well suited for modeling the adsorption kinetic of Cr(VI) onto various adsorbents [42]. Similar results have been observed for Cr(VI) adsorption [43, 44].

4. Conclusion

Activated alumina was found to be a suitable adsorbent for the removal of chromium (VI) from water. The study effect of the main parameters shows that adsorption was strongly dependent on adsorbent dose and pH. The adsorbent dose of activated alumina has the most positive pronounced effect in increasing the chromium (VI) adsorption whereas the pH has the most negative effect on the process. However, the interaction pH – adsorbent dose of activated alumina has a positive effect. A maximum of 97% chromium removal could be achieved at pH 5–6. The method for determination Cr(VI) by 1, 5-diphenylcarbazide is efficient and can be considered as a good method with DL = 0.0012 mg l^{-1} and QL = 0.0042 mg l^{-1}. Kinetic and equilibrium experiments were conducted at 10, 25 and 40 °C. The adsorption process followed the second-order reaction. The regression analysis of the equilibrium data fitted the Langmuir and Freundlich adsorption isotherms.

Symbols

AA — Activated alumina
b — Energy of adsorption (l · mg^{-1})
b_0, b_1, b_2, b_3, b_4 — Linear coefficients
$b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, b_{34}$ — Second-order interaction terms
$C_{\text{cochran}, \alpha = 1\%}$ — Critical value of Cochran for α = 1%
$C_{\text{cochran}, \alpha = 5\%}$ — Critical value of Cochran for α = 5%
C_{xobs} — Experimental value of Cochran
C_0 — Initial concentration of chromium (VI) (mg l^{-1})
C_e — Equilibrium concentration of chromium (VI) (mg l^{-1})
CV_r — Coefficient of variation of repeatability (repeatability of standard deviation)
CV_R — Coefficient of variation of reproducibility (reproducibility of standard deviation)
D — Dose of activated alumina (g)
DL — Detection limit (mg l^{-1})
F_l — Experimental value of linearity
F_{nl} — Experimental value of non linearity
K — Adsorption capacity
K_1 — Rate constant of the first-order adsorption (l·min^{-1})
K_2 — Rate constant of the second-order adsorption (l·min^{-1})
m — Weight of activated alumina (g)
q — Amounts of Cr(VI) adsorbed at any instant of time (mg g^{-1})
q_e — Amounts of Cr(VI) adsorbed at equilibrium time (mg g^{-1})
QL — Quantification limit (mg l^{-1})
q_m — Constant related to the maximum adsorption capacity (mg g^{-1})
r — The dimensionless equilibrium parameter
$t_{(9,0,995)}$ — Student's constant
$t'_{\text{obs}}, t_{\text{obs}}$ — Student's constant calculated
V — Volume of solution (L)
V_{Cl} — Critical value of linearity
V_{Cnl} — Critical value of non-linearity
X_1, X_2, X_3, X_4 — Dimensionless coded factors of parameters
Y_{Cr} — Removal of Cr(VI) (%)

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