

Factorial experimental design applied to adsorption of cadmium on activated alumina

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ABSTRACT

The effective removal of heavy metals from industrial wastewater is a very important issue for many countries. This paper examines the removal of cadmium ions from aqueous solutions and industrial effluents by adsorption on activated alumina. The Brunauer–Emmett–Teller (BET) specific surface area, pore diameter and pore volume of the activated alumina were 156.7 m²/g, 58.4 Å and 0.23 cm³/g, respectively. Factorial experimental design was applied to evaluate the main effects and interactions among dose of activated alumina, initial cadmium concentration, pH of the solution and temperature. Analysis of variance, the F-test and the Student's *t*-test shows that dose of activated alumina, initial cadmium ion concentration and temperature are the most significant parameters affecting cadmium ion removal and pH is the least significant parameter. Under optimal conditions, cadmium removal from industrial effluent samples was >98%. Furthermore, desorption and regeneration studies were carried out in order to evaluate the cost-effectiveness of activated alumina.

Key words | adsorption, cadmium, factorial design, removal, wastewater

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INTRODUCTION

Heavy metals released into the environment pose a significant threat to the environment and human health because of their toxicity and persistence.

Cadmium is one of the most toxic heavy metals affecting humans, animals and plants; it has no known metabolic role and does not seem biologically essential or beneficial to the metabolism of living beings (Bhattacharyya 2009). Cadmium is mostly introduced into natural water resources by wastewater discharged from industrial effluents. The most common industries releasing cadmium in their effluents are metal plating; manufacture of cadmium–nickel batteries, plastic stabilizers, paints and pigments, and petrochemicals; and mining (Krika *et al.* 2011). When it enters the human body, most cadmium goes directly to the kidney and liver

and persists for many years causing serious damage to these organs. Itai-itai, renal damage, emphysema, hypertension and testicular atrophy are all harmful diseases occurring in people exposed to cadmium (Lalor 2008; Suwazono *et al.* 2010; Swaddiwudhipong *et al.* 2012). At the cellular level, cadmium affects cell cycle progression, differentiation and DNA replication (Bertin & Averbek 2006; Swaddiwudhipong *et al.* 2015).

Recovered water is now a part of Tunisia's overall water resources balance. It is considered as an additional water resource and as a potential source of fertilizing elements; as a result, the legislation on industrial wastewater discharges has become increasingly strict. According to the Tunisian NT106.002 standard, the limit on concentration of cadmium to release into sewerage systems is 0.1 mg/L.

Therefore, it is a great challenge to remove cadmium ions from wastewater. Removal of cadmium ions from aqueous solutions has been traditionally carried out by chemical

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doi: 10.2166/wrd.2017.112

precipitation. However, chemical precipitation is usually used to treat wastewater containing high concentrations of heavy metal ions and it is ineffective when the metal ion concentration is low. In addition, chemical precipitation can produce large amount of sludge which can be treated only with great difficulty. Membrane processes such as ultra-filtration, reverse osmosis and nanofiltration can remove cadmium ions with high efficiency, but problems such as process complexity, membrane fouling and low permeate flux have limited their use in cadmium removal. Flocculation-coagulation involves chemical consumption and generation of increased sludge volume. Electrocoagulation has also been used for the removal of cadmium from wastewater; however, the disadvantages of this method are the high cost and generation of toxic sludge (Fu & Wang 2011).

Adsorption, on the other hand, is considered as an ideal process because of its convenience, ease of operation, low operational cost and simplicity of design. The literature suggests the use of various natural and synthetic adsorbents for the removal of cadmium from wastewater (Da Fonseca *et al.* 2006; Tajar *et al.* 2009; Hydari *et al.* 2012; Chand *et al.* 2014). Among the different adsorbents appropriate for heavy metal removal, activated alumina (AA; Al_2O_3) appeared to be a promising medium combining high efficiency with a low-cost process (Kasprzyk-Hordern 2004). It is highly efficient in eliminating several heavy metals (Hua *et al.* 2012; Marzouk *et al.* 2013).

Previous researchers used the traditional 'one variable at a time' experiments to determine the individual effect of various factors on the adsorption process. However, factorial experimental design can be used to provide a large amount of information and reduce the number of experiments, time and total research costs. The most important advantages of this technique are that the effects of individual parameters as well as their relative importance are obtained and that the interaction of two or more factors can be ascertained (Saadat & Karimi-Jashni 2011; Geyikçi & Büyükgüngör 2013). Nevertheless, there are limited studies concerning the application of this method to the adsorption of cadmium on AA.

One of the goals of this study is to apply a factorial design at two levels in order to determine the influence of various parameters and their interactions on the removal efficiency of cadmium and then assess the importance of

the AA as adsorbent to remove cadmium from industrial effluent in Tunisia. In addition, regeneration studies were performed to estimate the potential of this process in industrial applications.

MATERIALS AND METHODS

Materials

The granular AA used was provided by Sigma-Aldrich. It was dried at 110°C for 24 hours in order to eliminate impurities and to prepare it. An aqueous stock solution of cadmium ions (1 g/L) was prepared using reagent grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Different initial concentrations of cadmium ions (Cd(II)) (10 mg/L to 100 mg/L) were prepared by dilution from the stock solution in distilled water.

Batch adsorption experiments

Adsorption experiments were carried out in a stirred thermostatic bath (Grant[®]) to study the effects of pH, initial Cd(II) concentration, temperature (10°C – 40°C) and the adsorbent dose (0.5–1.5 g). The pH value of the cadmium solution was adjusted by adding HCl or NaOH (0.01 mol/L) as required. For the batch adsorption experiments, 100 ml of the test solution was added to a 250 mL stoppered conical flask and stirred at constant rate of 140 rpm. Samples were withdrawn after a measured time interval and filtered through Whatman No. 1 filter paper ($0.45\ \mu\text{m}$). The filtrates were analysed to determine residual Cd(II) concentration.

Chemicals and analytical methods

The residual concentration of cadmium was determined by the potentiometric method using a specific electrode (Thermo Scientific, Orien 9448SC).

The solution pH was measured by a pH-meter (Metrohm, 708 pH meter). Chloride and nitrate ions were analysed by anion chromatography using a Metrohm 761 compact ion chromatograph. The analyses of Ca and Mg were conducted by the titrimetric method.

The percentage removal of cadmium (%Cd) was calculated using Equation (1):

$$\%Cd = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cd(II) respectively (mg/L).

RESULTS AND DISCUSSION

Characterization of adsorbent

The total pore volume was determined from the adsorption of N_2 at 77.37 K on an ASAP 2020 apparatus. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distribution was obtained from the desorption branch of isotherms using the Barrett–Joyner–Halenda (BJH) method. Detailed textural characteristics of AA are summarized in Table 1.

The textural properties were determined from the N_2 adsorption–desorption isotherms, which are given in Figure 1 together with the pore size distribution. According to the IUPAC classification, the corresponding isotherm can be classified as type IV which is characteristic of a mesoporous material. This is a good model for AA because of its tight pore size distribution and its massive surface areas, providing a vast number of sites where adsorption processes can occur.

The BJH pore size distribution also shows that AA has the pore size distribution in the mesoporous range (2–50 nm).

From the steepness of the adsorption isotherm, it can be seen that the mesopore structure is not well ordered and has a broad pore size distribution. Moreover, evidence of the appearance of open pores in the AA is shown by the presence of the hysteresis loop (Diallo et al. 2014).

Table 1 | BET analysis of the AA

Property	Value
Specific surface area (m^2/g)	156.7
Total pore volume (cm^3/g)	0.23
Average pore diameter (\AA)	58.4

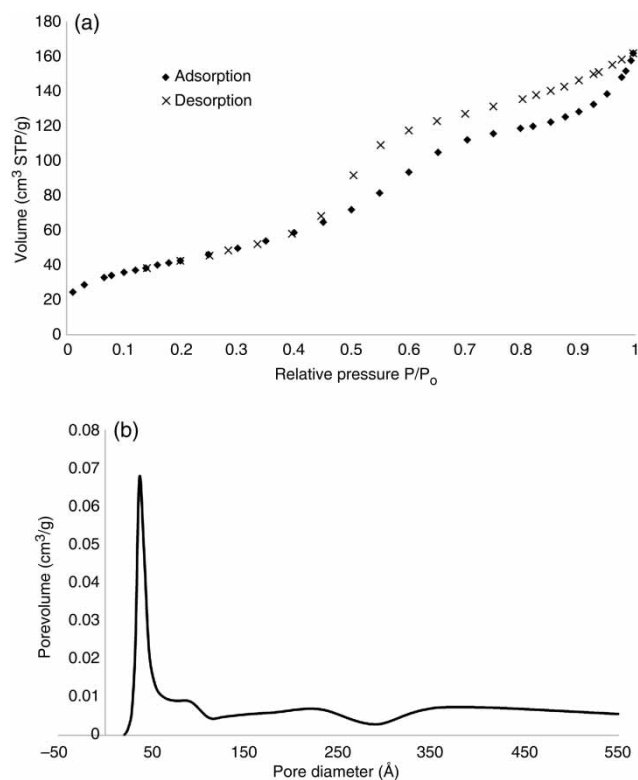


Figure 1 | (a) N_2 adsorption–desorption isotherms and (b) pore size distribution of AA.

Validation of the analytical method

Several parameters have been taken into account in order to validate the method for determining residual Cd(II) concentration by the potentiometric method using a specific electrode. We have evaluated linearity, specificity and fidelity (repeatability and reproducibility). In the whole validation, the calibration curve for the measurements was always prepared with at least six points, as recommended by the French standard XPT 90-210. Table 2 gives experimental validation of the analytical method.

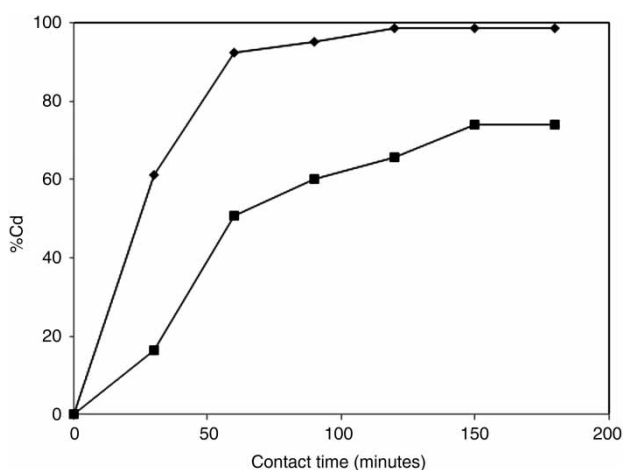
According to the values of Table 2, the analytical method by specific electrode is valid and appears as an efficient method.

Effect of contact time

The effect of contact time was determined by studying adsorption of Cd(II) at initial concentrations of 10 mg/L and 100 mg/L with 1 g/100 mL of AA. As clearly seen in Figure 2, at up to 50 minutes of initial contact time, the

Table 2 | Validation parameters

Test	Experimental value	Critical value	Conclusion	
Linearity	$F_1 = 2093.88$ $F_{nl} = 1.4553$	$V_{Cl} = 8.10$ $V_{Cnl} = 4.94$	Linear	Linearity approved
Specificity	$t_{obs} = 2.46$ $t'_{obs} = 0.082$	$t_{(8,0.995)} = 3.355$	No curvature	Specific
Cochran	$C_{xobs} = 0.222$	$C_{cochran, \alpha=5\%} = 0.544$ $C_{cochran, \alpha=1\%} = 0.633$	Slope equal to 1	Point group is considered non aberrant Point group is considered non suspect
Fidelity	$CV_r = 0.422\%$; 0.604% ; 0.455% ; 0.464% $CV_R = 0.5\%$	$CV_r < 5\%$ $CV_R < 5\%$	Repeatable	Faithful
			Reproducible	

**Figure 2** | Effect of contact time on the percentage removal ($C_0 = 10$ mg/L (◆) and $C_0 = 100$ mg/L (■)).

Cd(II) adsorption rate was very fast, and slower kinetics followed until equilibrium. The rapid adsorption during the first time interval is related to the availability of a large number of active sites on the adsorbent surface, which improves Cd(II) diffusion to the adsorbent surface. A contact time of 150 min was sufficient to ensure saturation of the Cd(II) sorption capacity by AA, so this contact time was used for the rest of the adsorption experiments.

Effect of pH

The effect of pH was studied in the range 3–8 for both initial concentrations of 10 mg/L and 100 mg/L with 1 g/100 mL of AA. It was essentially found that the removal yield increases with pH. A decrease in the pH value (from 5 to 3) involves a decrease in the removal yield from 97%

to 41% and from 65% to 30% for an initial concentration of 10 mg/L and 100 mg/L, respectively. This may be due to the modification of adsorbent surface below pH 5 (Kasprzyk-Hordern 2004).

Similar results have been reported in the literature. Afkhami *et al.* (2010) evaluated the effect of pH in cadmium removal using nano-alumina in a pH range 1.5–5.5. It was found that removal of Cd(II) increases with increasing solution pH and a maximum value was reached at an equilibrium pH of around 5.0. El-Latif *et al.* (2013) investigated the removal of cadmium by alumina oxide nano composite over the pH range 2–9. They reported that removal efficiency increased with increasing pH and a maximum adsorption capacity was obtained at pH 6.

Therefore, for the statistical analysis, experiments were performed at above pH 5 to avoid the modification of adsorbent surface and below pH 8 to avoid precipitation of cadmium in the presence of hydroxide ions ($\text{Cd}(\text{OH})_2$).

Statistical analysis

For any process, it is important to know the influence of different physicochemical parameters (also termed control factors) upon the results of the process. Factorial design is used to reduce the total number of experiments in order to achieve the best percentage removal (%Cd) of cadmium ions (Mason *et al.* 2003). The factorial design determines which factors have important effects on a response (%Cd) as well as how the effect of one factor varies with the level of the other factors. The number of experimental runs at two levels is 2^k , where k is the number of factors. Today, the most widely used kind of experimental design, to

estimate main effects as well as interaction effects, is the 2^k factorial design in which each variable is investigated at two levels (Ricou-Hoeffler *et al.* 2001; Carmona *et al.* 2005; Geyikçi & Büyükgüngör 2013). The four factors considered were the dose of AA, initial Cd(II) concentration, pH and temperature. The high and low levels represented by +1 and -1, respectively defined for the 2^4 factorial designs were listed in Table 3. The low and high levels for the factors were selected according to preliminary experiments.

A matrix was created according to their high and low levels and 16 experiments were carried out. A centre point was duplicated and added to the matrix in order to verify the linearity of the studied model. The response is the percentage removal of cadmium (%Cd). The experiments, presented in Table 4, were executed in a random order to avoid systematic errors.

The effect of a factor is defined as the change in response produced by a change in the factor level.

The codified mathematical model employed for the factorial design was:

$$\%Cd = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4. \quad (2)$$

where b_0 represents the global mean, b_i represents the estimation of the principal effect of the factor i for the response %Cd and b_{ij} represents the estimation of interaction effect between factor i and j . X_1 , X_2 , X_3 and X_4 are the dimensionless coded factors of the following parameters: dose of AA, initial Cd(II) concentration, pH and temperature, respectively. The results were analysed with MINITAB 16 software.

The mathematical model representing Cd(II) removal efficiency in the experimental region studied can be

expressed by Equation (3):

$$\begin{aligned} \%Cd = & 63, 25 + 14, 67X_1 - 20, 23X_2 - 5, 17X_3 + 13, 54X_4 \\ & + 2, 3X_1X_2 + 3, 45X_1X_3 + 0, 89X_1X_4 + 0, 83X_2X_3 \\ & + 0, 64X_3X_4 + 3, 29X_2X_4 \end{aligned} \quad (3)$$

There are several methods to estimate the significance of the effects of coefficient of a full factorial design 2^k . Applications of experimental design and analysis of variance (ANOVA) to sensitivity analysis were described by Kleijnen & Sargent (2000).

The ANOVA for adsorption study of cadmium was used in order to ensure a good model. The results of the full factorial design model fitting in the form of ANOVA are given in Table 5.

From the p -values defined as the smallest level of significance leading to rejection of the null hypothesis, it appears that the main effect of each factor and the interaction effects are statistically significant when p -values are less than 0.05. Since for a 95% confidence level and 16 factorial tests, $F_{0,05,1,16}$ is equal to 4.49, all the effect with F -values higher than 4.49 are significant.

Student's t -test was carried out to determine whether the calculated main and interaction effects were significantly different from zero. With a 95% confidence level and five degrees of freedom, the t -value was equal to 2.571.

Absolute values of the main factors and the interaction of factors are illustrated in Pareto chart (Figure 3) in the horizontal columns. The vertical line indicates minimum statistically significant effect magnitude for an α risk of 5%.

According to the obtained F -value, p -value (Table 5) and Pareto chart (Figure 3), it seems that the effect of initial cadmium concentration, dose of AA and temperature are statistically significant. The bar representing pH (C) is inside the reference line in the Pareto chart, showing that this term contributed the least to the prediction of Cd(II) removal efficiency. Moreover, it can be seen that the first-order interactions are insignificant implying that the main factors are independent of each other.

To graphically verify the normality assumption for data, a normal probability plot was performed to examine the distribution of the residual values, defined as the differences between the predicted (model) and the observed (experimental) values.

Table 3 | Experimental ranges and levels of the factors studied in the factorial design

Variables	Factors	Low level	High level
X_1	Dose AA (g) (A)	0.5	1.5
X_2	Initial Cd(II) concentration ([Cd]), mg L ⁻¹ (B)	10	100
X_3	pH (pH) (C)	5	8
X_4	Temperature (T, °C) (D)	10	40

Table 4 | Studied parameters in their reduced and normal forms

Experiment	A	X ₁	B	X ₂	C	X ₃	D	X ₄	%Cd
1	0.5	-1	10	-1	5	-1	10	-1	68.38
2	1.5	1	10	-1	5	-1	10	-1	94.62
3	0.5	-1	100	1	5	-1	10	-1	23.34
4	1.5	1	100	1	5	-1	10	-1	35.78
5	0.5	-1	10	-1	8	1	10	-1	35.78
6	1.5	1	10	-1	8	1	10	-1	94.13
7	0.5	-1	100	1	8	1	10	-1	16.24
8	1.5	1	100	1	8	1	10	-1	29.83
9	0.5	-1	10	-1	5	-1	40	1	95.88
10	1.5	1	10	-1	5	-1	40	1	99.09
11	0.5	-1	100	1	5	-1	40	1	41.22
12	1.5	1	100	1	5	-1	40	1	89.08
13	0.5	-1	10	-1	8	1	40	1	84.43
14	1.5	1	10	-1	8	1	40	1	95.50
15	0.5	-1	100	1	8	1	40	1	23.34
16	1.5	1	100	1	8	1	40	1	85.75
17	1	0	55	0	6.5	0	25	0	73.54
18	1	0	55	0	6.5	0	25	0	73.21

Table 5 | ANOVA of the 2⁴ design

Term	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
A	3443.34	1	3443.342	10.25589	0.023929
B	6548.05	1	6548.046	19.50316	0.006916
C	428.90	1	428.904	1.27748	0.309653
D	2933.31	1	2933.306	8.73676	0.031672
A × B	85.47	1	85.470	0.25457	0.635319
A × C	190.58	1	190.578	0.56763	0.485145
A × D	12.92	1	12.924	0.03849	0.852180
B × C	11.26	1	11.256	0.03353	0.861912
B × D	173.32	1	173.317	0.51622	0.504623
C × D	6.68	1	6.682	0.01990	0.893317
Error	1678.71	5	335.743		
Total sum of squares	15512.54	15			

The normal plot displayed in Figure 4 indicated that the predicted values of Cd(II) removal and the actual experimental data were in good agreement, providing evidence for the validity of the regression model.

Effect of process variables

The main effects of each parameter on the Cd(II) removal efficiency are shown in Figure 5. From the analysis of the

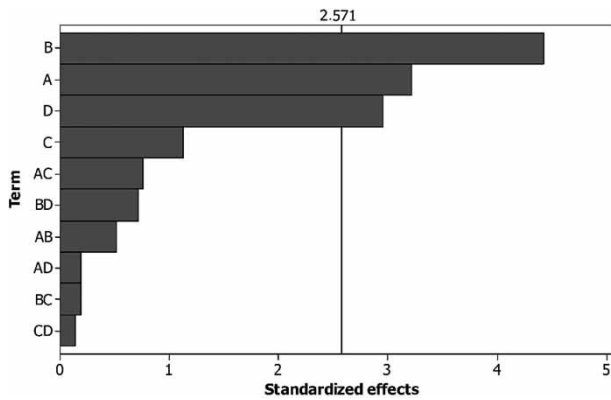


Figure 3 | Pareto chart for standardized effects.

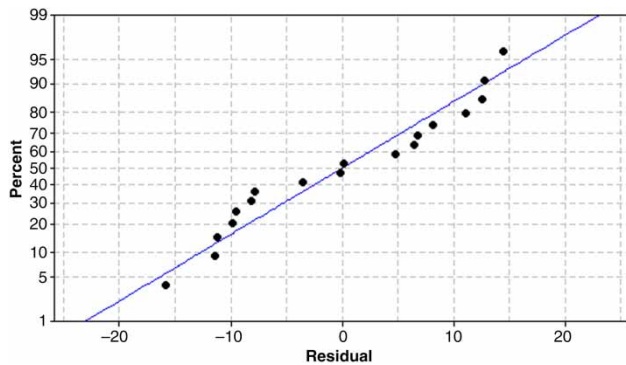


Figure 4 | Normal probability plot.

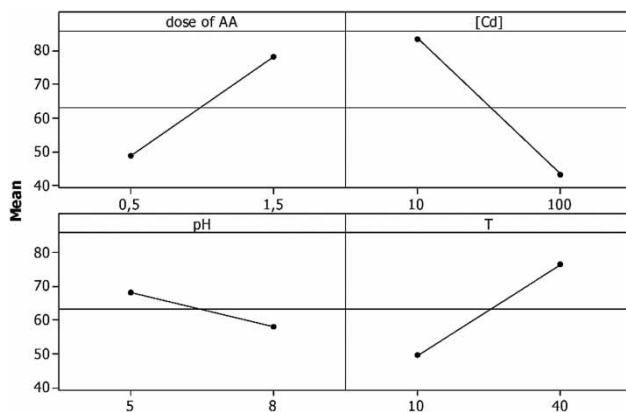


Figure 5 | Main effect plot for cadmium removal.

graphs and the coefficients of Equation (3), we can conclude that the initial cadmium concentration is the most important variable on the cadmium removal efficiency since its coefficient is the largest in absolute value (20.23). The negative

sign of this coefficient means that the intensification of this parameter decreases the amount of Cd(II) removal. However, the effects of adsorbent dose (AA) and temperature are positive since an increase in percentage removal of cadmium is observed when these factors change from low to high. With an increase in adsorbent dose, the number of sites available for cadmium adsorption increases, which facilitates an increase in the percentage removal of Cd(II).

The pH of the solution is the least significant variable since its coefficient is the lowest in absolute value (5.17).

The interaction effects were also studied and are shown in Figure 6. The parallel lines in this figure indicate that there are no significant interactions between the studied factors. However, the most important interaction is observed between pH and adsorbent dose. This indicates that decreasing pH from 8 to 5 enhances the cadmium removal efficiency at low adsorbent dose (0.5 g). This interaction remains non-significant since the pH of the solution has no significant effect in the range of values studied.

For a better understanding of the relationship between factors and a response, a cube plot was produced (Figure 7). The cube plot shows that increasing adsorbent dose from 0.5 to 1.5 g enhances significantly the Cd(II) removal (from 52.08% to 94.37%) at low temperature (10 °C), while at higher temperature (40 °C), changes in adsorbent dose do not have a greater effect (an increase of only 7.14%). In addition, increasing initial Cd(II) from 10 to 100 mg/L, at higher adsorbent dose (1.5 g), diminishes the percentage removal from 94.37% to 32.80% at lower temperature. A change of only 9.88% is observed at higher temperature. This means that both the effect of variation of initial Cd(II) concentration and adsorbent dose are higher when the temperature is low.

The highest percentage removal in this study was 97.29%, obtained at higher temperature (40 °C), adsorbent dose of 1.5 g and initial cadmium concentration of 10 mg/L.

Application studies on industrial effluents

The real application of Cd(II) removal by adsorption on AA was performed on wastewater, containing cadmium ions, which was collected from a battery manufacturing plant in Tunisia. The sample was stored in a polyethylene container

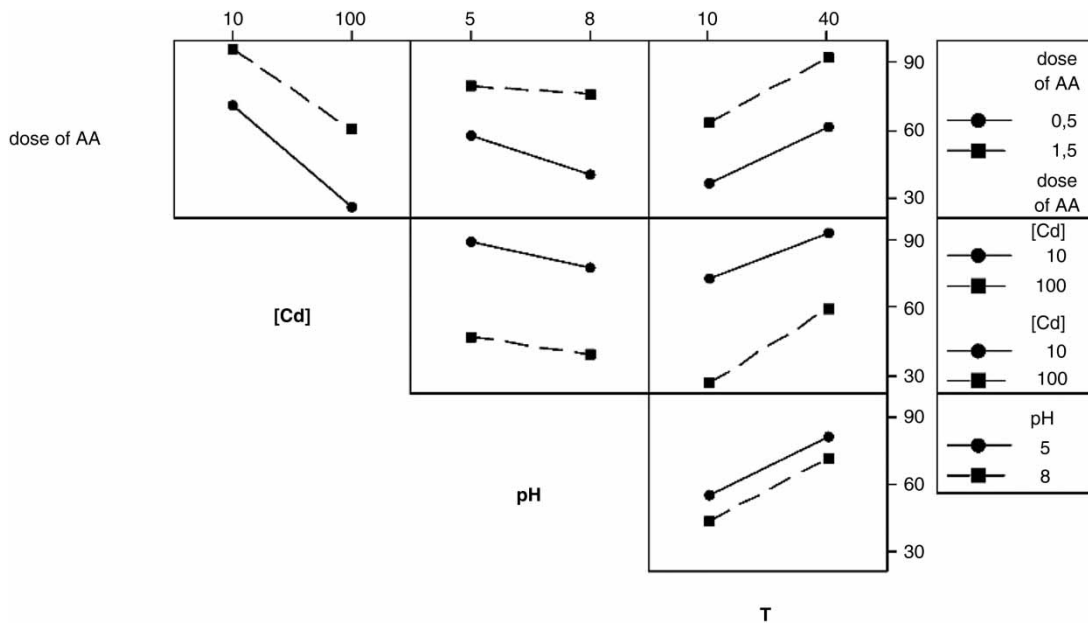


Figure 6 | Interaction effects plot for cadmium removal.

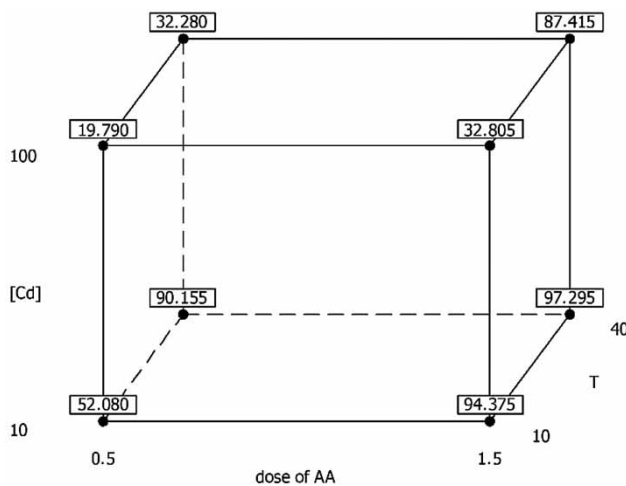


Figure 7 | Cube plot for cadmium removal (%).

in a refrigerator at a temperature below 4 °C until analysed. To reduce the cadmium concentration and to possibly reuse the wastewater, batch adsorption studies using the sample were carried out under the optimum conditions found previously (adsorbent dose of 1.5 g and stirred in a thermostatic bath for 150 minutes at 40 °C). The physico-chemical characteristics of the effluent before and after the adsorption process were measured. The results are summarized in Table 6.

Table 6 | Characteristics of wastewater collected from a battery manufacturing plant in Tunisia before and after treatment

	Battery effluent before treatment	Battery effluent after treatment
pH	5.4	5.6
Cd ²⁺ (mg/L)	6.35	0.07
Pb ²⁺ (mg/L)	1.04	0.12
NO ₃ ⁻ (mg/L)	110.87	108.46
Cl ⁻ (mg/L)	280.29	273.39
Ca ²⁺ (mg/L)	120.65	197.34
Mg ²⁺ (mg/L)	78.26	71.53
Salinity (mg/L)	2,690	2,240

After batch adsorption, the amount of Cd(II) in the treated effluents was 0.07 mg/L thereby meeting the Tunisian NT106.002 standard. Moreover, the results show that the efficiency of Cd(II) removal was not affected by the presence of excess amounts of Ca(II) and Mg(II) in real waters and it should be mentioned that the adsorption process on AA can be used for removal of other pollutants like lead Pb(II) from real wastewaters.

These results suggested that AA has an excellent potential application for the removal of cadmium from wastewater.

Desorption and re-adsorption studies

Desorption and reusability of AA is an important step for practical application in wastewater treatment technology. After Cd(II) adsorption with initial concentrations of 10 mg/L and 1.5 g of AA, the adsorbent was filtered and oven-dried at 80 °C, and the adsorbed Cd(II) was desorbed with 0.1 mol/L HCl. The desorbed Cd(II) was separated by filtration and analysed. The spent adsorbent after filtration was washed several times with deionized water to remove residual acid, and dried for repeated Cd(II) adsorption from aqueous solutions. Four successive cycles of adsorption and desorption of Cd(II) were carried out in the batch system to assess the reusability of AA for Cd(II) adsorption. As shown in Figure 8, more than 94% Cd(II) removal is possible after four cycles of adsorption–desorption.

CONCLUSION

The full factorial design based on two levels and four factors was used to determine the effect of dose of AA, initial Cd(II) concentration, pH and temperature on the percentage removal of Cd(II). Based on the statistical analysis, the normal plot indicates that the predicted values of the percentage removal of cadmium and the experimental data were in good agreement. The initial Cd(II) concentration, the adsorbent dose and the temperature are the most significant parameter affecting the Cd(II) removal, with *t*-values greater than 2.57 and *F*-values greater than 4.49. Adsorbent dose and temperature have a positive effect, whereas initial

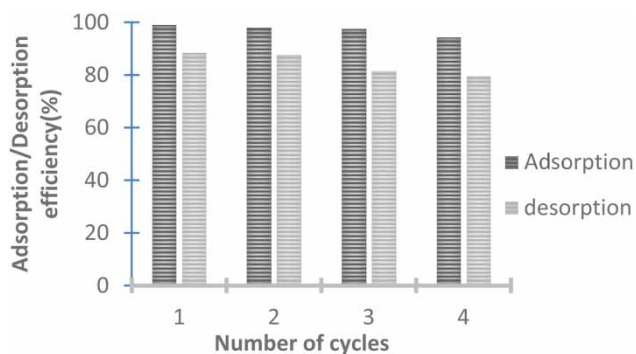


Figure 8 | Four adsorption–desorption cycles for AA.

Cd(II) concentration exhibits a negative influence on removal efficiency.

The highest percentage removal of cadmium in this study was obtained at higher temperature (40 °C), adsorbent dose of 1.5 g and initial cadmium concentration of 10 mg/L.

The adsorption studies on industrial effluent under optimal conditions indicate that AA has good potential to remove cadmium from wastewater samples since Cd(II) concentration in the treated effluents were 0.07 mg/L thereby meeting the Tunisian NT106.002 standard. Moreover, the high surface area of AA (156.7 m²/g) and the advantage of recycling and reuse make it an attractive wastewater treatment option.

REFERENCES

- Afkhami, A., Saber-Tehrani, M. & Bagheri, H. 2010 Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2,4-dinitrophenylhydrazine. *J. Hazard. Mater.* **181**, 836–844. DOI:10.1016/j.jhazmat.2010.05.089.
- Bertin, G. & Averbek, D. 2006 Cadmium: cellular effects, modifications of biomolecules, modulation of DNA repair and genotoxic consequences (a review). *Biochimie* **88**, 1549–1559. DOI:10.1016/j.biochi.2006.10.001.
- Bhattacharyya, M. H. 2009 Cadmium osteotoxicity in experimental animals: mechanisms and relationship to human exposures. *Toxicol. Appl. Pharmacol.* **238**, 258–265. DOI:10.1016/J.TAAP.2009.05.015.
- Carmona, M. E. R., Da Silva, M. P. & Leite, S. G. F. 2005 Biosorption of chromium using factorial experimental design. *Process Biochem.* **40**, 779–788. DOI:10.1016/j.procbio.2004.02.024.
- Chand, P., Shil, A. K., Sharma, M. & Pakade, Y. 2014 Improved adsorption of cadmium ions from aqueous solution using chemically modified apple pomace: mechanism, kinetics, and thermodynamics. *Int. Biodeterior. Biodegrad.* **90**, 8–16. DOI:10.1016/j.ibiod.2013.10.028.
- Da Fonseca, M. G., De Oliveira, M. M. & Arakaki, L. N. H. 2006 Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral. *J. Hazard. Mater.* **137**, 288–292.
- Diallo, M. S., Fromer, N. A. & Jhon, M. S. 2014 *Nanotechnology for Sustainable Development*. Springer International Publishing, Switzerland.
- El-Latif, A. M. M., Ibrahim, A. M., Showman, M. S. & Abdel Hamide, R. R. 2013 Alumina/iron oxide nano composite for cadmium ions removal from aqueous solutions. *Int. J. Nonferrous. Metall.* **2**, 47–62.
- Fu, F. & Wang, Q. 2011 Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.* **92**, 407–418. DOI:10.1016/j.jenvman.2010.11.011.

- Geyikçi, F. & Büyükgüngör, H. 2013 Factorial experimental design for adsorption silver ions from water onto montmorillonite. *Acta Geodyn. Geometer.* **10**, 363–370. DOI:10.13168/AGG.2013.0035.
- Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L. & Zhang, Q. 2012 Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *J. Hazard. Mater.* **211**, 317–331. DOI:10.1016/j.jhazmat.2011.10.016.
- Hydari, S., Shariffard, H., Nabavinia, M. & Parvizi, M. R. 2012 A comparative investigation on removal performances of commercial activated carbon, chitosan biosorbent and chitosan/activated carbon composite for cadmium. *Chem. Eng. J.* **193**, 276–282. DOI:10.1016/j.cej.2012.04.057.
- Kasprzyk-Hordern, B. 2004 Chemistry of alumina, reactions in aqueous solution and its application in water treatment. *Adv. Colloid. Interface Sci.* **110**, 19–48. DOI:10.1016/j.cis.2004.02.002.
- Kleijnen, J. P. C. & Sargent, R. G. 2000 A methodology for fitting and validating metamodells in simulation. *Eur. J. Oper. Res.* **120**, 14–29. DOI:10.1016/S0377-2217(98)00392-0.
- Krika, F., Azzouz, N. & Ncibi, M. C. 2011 Adsorptive removal of cadmium from aqueous solution by cork biomass: equilibrium, dynamic and thermodynamic studies. *Arabian J. Chem.* **137**, S2. DOI:10.1016/j.arabjc.2011.12.013.
- Lalor, G. C. 2008 Review of cadmium transfers from soil to humans and its health effects in the Jamaican environment. *Sci. Total Environ.* **400**, 162–172. DOI:10.1016/j.scitotenv.2008.07.011.
- Marzouk, I., Dammak, L. & Hamrouni, B. 2013 Adsorption of chromium onto activated alumina: kinetics and thermodynamics studies. *Water Environ. Res.* **85**, 99–104. DOI:10.2175/106143012X13560205144137.
- Mason, R. L., Gunst, R. F. & Hess, J. L. 2003 *Statistical Design and Analysis of Experiments*. Wiley-Blackwell, Hoboken, NJ, USA.
- Ricou-Hoeffler, P., Lecuyer, I. & Le Cloirec, P. 2001 Experimental design methodology applied to adsorption of metallic ions onto fly ash. *Water Res.* **35**, 965–976. DOI:10.1016/S0043-1354(00)00341-9.
- Saadat, S. & Karimi-Jashni, A. 2011 Optimization of Pb(II) adsorption onto modified walnut shells using factorial design and simplex methodologies. *Chem. Eng. J.* **173**, 743–749.
- Suwazono, Y., Uetania, A., Akesson, A. & Vahter, M. 2010 Recent applications of benchmark dose method for estimation of reference cadmium exposure for renal effects in man. *Toxicol. Lett.* **198**, 40–43. DOI:10.1016/j.toxlet.2010.04.015.
- Swaddiwudhipong, W., Limpatanachote, P., Mahasakpan, P., Krintratun, S., Punta, B. & Funkhiew, T. 2012 Progress in cadmium-related health effects in persons with high environmental exposure in northwestern Thailand: a five-year follow-up. *Environ. Res.* **112**, 194–198. DOI:10.1016/j.envres.2011.10.004.
- Swaddiwudhipong, W., Mahasakpana, P., Jeekeeree, W., Funkhiewa, T., Sanjum, R. & Apiwatpaiboon, T. 2015 Renal and blood pressure effects from environmental cadmium exposure in Thai children. *Environ. Res.* **136**, 82–87.
- Tajar, A. F., Kaghazchi, T. & Soleimani, T. 2009 Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells. *J. Hazard. Mater.* **165**, 1159–1164. DOI:10.1016/j.jhazmat.2008.10.131.

First received 17 June 2016; accepted in revised form 3 November 2016. Available online 8 February 2017