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Optimization of cadmium ions biosorption by fish scale from aqueous solutions using factorial design analysis and Monte Carlo simulation studies

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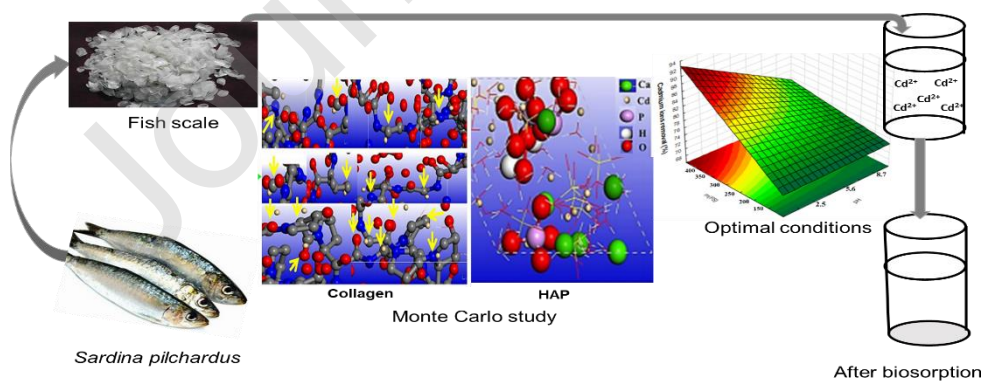
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Graphical abstract



Highlights

- Fish scales of *Sardina pilchardus* was used as biosorbent in the removal of Cd(II)
- The biosorption capacity of the biosorbent for Cadmium ions was 52.08 mg g⁻¹
- The parameters were analyzed and optimized using full factorial design methodology
- Pseudo-second order kinetics and Langmuir isotherm model gave the best fit
- The sorption of Cd(II) onto Fish scale was studied by a Monte Carlo simulation

Journal Pre-proof

ABSTRACT

This work investigated cadmium ions biosorption on Fish scales (FS) of *Sardina pilchardus*. Different relevant parameters such as initial pH in the range 2.14 – 7.76, initial cadmium concentration from 35 to 150 mg L⁻¹, and biosorbent dose in the range 50 – 300 mg L⁻¹, were examined. The effect of these parameters on the cadmium removal was analyzed and optimized using full factorial design methodology and the analysis of variance. The kinetics were modeled for pseudo-second order and pseudo-first order models. Results showed that the pseudo-second order kinetic gave the best fit for equilibrium data. The biosorption isotherms were investigated for Freundlich and Langmuir models. Langmuir isotherm model gave the best fit and led to a maximum biosorption capacity of Cd(II) on FS of 52.08 mg g⁻¹. The results indicated that FS was effective in the removal of cadmium ions. Optimum Cd(II) removal of 88.2% was calculated for pH 3, 75 mg L⁻¹ of Cd(II) and 250 mg L⁻¹ of FS. Monte Carlo simulation was used as relatively greener pathway to study the biosorption behavior of Cd(II) ions onto FS. It showed that the interaction Cd(II) – hydroxyapatite was more favored than Cd(II) – collagen.

Key words: Biosorption; Cadmium ions; Fish scale; Full factorial design; Analysis of variance; Monte Carlo method

1. Introduction

Heavy metals constitute a large class of persistent pollutants in the environment. Various techniques have been employed to remove heavy metals from waters or soils, such as phytoremediation [1], adsorption onto low-cost materials [2,3] or solvent extraction [4]. The choice of the treatment depends upon the nature of the matrix and the concentration of the targeted metals. Among these treatments, adsorption onto various materials is the main process which allows efficient and easy removal of heavy metals [5-7]. Among these metals, cadmium is known as one of the most harmful toxicants [8-10] and a lot of techniques have been investigated for its removal from water, such as precipitation, membrane filtration and adsorption [11], electrocoagulation [12-15] or membrane separation [16,17]. Physical processes require complex equipment and this fact explains the success of adsorptive removal of cadmium by low-cost adsorbents [18,19] and nano-adsorbents [20,21]. These adsorbents are particularly interesting in the context of the present work because, like fish scales, they contain nano-hydroxyapatite. Indeed, several studies have shown that nano crystallites of hydroxyapatite (HAP) and collagen fibers are the main constituents of fish scales [22,23].

Many waste materials, including by-products arising from fish processing industries [24], have been used as biosorbent. Particularly, fish scales (FS) have been investigated as biosorbents of pollutants [23,25,26] and heavy metals [22,27-30]. The adsorption of cadmium ions has been rarely investigated [31]. For the first time, in the present work, the use of FS of *Sardina pilchardus* was studied as biosorbent of Cd(II) ions in synthetic waste waters. The process parameters such as effect of initial pH, biosorbent dose and initial cadmium ions concentration were studied. Langmuir and Freundlich isotherm models were applied. The kinetics was also analyzed for pseudo-first order and pseudo-second order models. Thermodynamic parameters were calculated to complete the investigation of Cd(II) removal. Design Of Experiments (DOE) has been used as a method to establish the relationship between different factors influencing a process and its output [32]. The DOE method can be divided in full factorial design (FFD), where all combinations of the parameter levels are evaluated in order to analyze the results. Full factorial design was used to optimize and analyze the effect of these parameters. Several researchers used full factorial DOE methods in their works [32]. In addition, Monte Carlo simulation was applied to evaluate the biosorption behavior of cadmium ions onto the two main constituents of FS, the nanoparticles of hydroxyapatite and the fibers of collagen.

2. Materials and methods

2.1. Reagents

Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was purchased from Sigma Aldrich. The other chemicals, sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from Scharlau Chemie.

2.2. Preparation of FS

FS of *Sardina pilchardus* were collected from a local restaurant in June 2019, in the city of Safi, Morocco. They were rinsed with distilled water two times and then dried at 353 K for 24 h. Finally, the dried FS was cut into small pieces using domestic mixer. The biosorbent FS was stored in a glass bottle for further use without further treatment.

2.3. Adsorption studies

Biosorption experiments were conducted by adding 250 mg of FS to a set of 100 mL conical flasks containing 50 mL of cadmium solutions with initial concentrations of 75 mg L⁻¹ at pH 3. The flasks were shaken at a constant agitation speed, and at room temperature for 1 h. The effect of the biosorbent mass was carried out by varying the FS mass from 50 mg to 300 mg.

For all other experiments, 250 mg of biosorbent were used. These experiments were carried out by changing the initial cadmium concentration from 35 mg L⁻¹ to 150 mg L⁻¹, the pH from 2.14 to 7.76. The initial pH was adjusted by adding 0.1 M NaOH or 0.1 M HCl. Each experiment was replicated three times.

After each biosorption experiment the samples were centrifuged at 4000 rpm for 4 min to separate the liquid phase from the solid phase. The concentration of the Cd(II) ions in the solution was determined using an atomic absorption spectrometer (SavantAA-GBC) at maximum wavelength, $\lambda_{\text{max}} = 326.2$ nm. The percentage removal of cadmium ions was given by Eq. (1) where $[\text{Cd}^{2+}]_i$ is the initial concentration of cadmium ions, and $[\text{Cd}^{2+}]_t$ is the concentration of cadmium ions at reaction time t .

$$\text{Percentage removal (\%)} = \left(\frac{[\text{Cd}^{2+}]_i - [\text{Cd}^{2+}]_t}{[\text{Cd}^{2+}]_i} \right) \times 100 \quad (1)$$

The biosorbed amount at time t , q_t (mg g⁻¹), was computed from the concentration of the Cd(II) solution according to Eq. (2) where C_i (mg L⁻¹), and C_t (mg L⁻¹) are initial

concentration and concentration at time t of Cd(II) ions, respectively, V is the volume of the cadmium solution (L), and m is the mass of FS (g).

$$q_t = (C_i - C_t) \frac{V}{m} \quad (2)$$

2.4. Kinetic study

Kinetic study represents an important experiment to understand the adsorption process. The pseudo-first order and the pseudo-second order models have been used in this study. The pseudo-first order equation is expressed by Eq. (3) [33] where k_1 (min^{-1}) is the rate constant of pseudo-first order sorption, t is time, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the sorption capacities at equilibrium and at time t , respectively.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)$$

The pseudo-second order kinetic equation is expressed by Eq. (4) [34] where k_2 is the rate constant of the pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$), t is time, and q_e (mg g^{-1}) and q_t (mg g^{-1}) are the sorption capacity at equilibrium and at time t , respectively.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

2.5. Biosorption isotherm models

The sorption isotherms obtained were tested with the Langmuir and Freundlich isotherm equations. The Langmuir isotherm model assume that the adsorption of molecules occurs at specific homogeneous sites of the adsorbent and, once a molecule occupies a site, no additional adsorption can occur there (monolayer coverage) [35]. The Freundlich isotherm model assumes the molecules undergoes adsorption onto the heterogeneous surface of adsorbent. This model describes a multilayer adsorption with interaction between adsorbed molecules [35].

Langmuir isotherm can be represented by Eq. (5) [36] where q_e and C_e are adsorbed amount (mg g^{-1}), and adsorbate concentration in solution (mg L^{-1}) at equilibrium, respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (5)$$

The plot of $1/q_e$ versus $1/C_e$ should give a straight line. The slope has the value of $1/K_L q_m$, where K_L (L mg^{-1}) is the Langmuir constant and q_m (mg g^{-1}) is the maximum biosorption capacity. From the highest initial dye concentration C_o (mg L^{-1}) and the Langmuir constant K_L (L mg^{-1}), the dimensionless equilibrium parameter R_L can be expressed by Eq. (6) [37]:

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

The nature of the biosorption process is characterized by the R_L value, e.g. unfavorable ($R_L > 1$); linear ($R_L = 1$); favorable ($0 < R_L < 1$); irreversible ($R_L = 0$) [38]. Freundlich model [39] considers mono-layer biosorption of solute by the biosorbent and assumes that the biosorbent has an energetically heterogeneous surface or surface supporting sites of varied affinities and the existence of an interaction between the molecules that are adsorbed onto that heterogeneous surface [39]. The Freundlich equation suggests that the biosorption energy exponentially decreases on completion of the active centers of a biosorbent. The Freundlich biosorption isotherm is given by Eq. (7) [40] where q_e (mg g^{-1}) is the adsorbed amount and C_e (mg L^{-1}) is the adsorbate concentration at equilibrium.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Biosorption capacity (K_F) and intensity of biosorption (n) are Freundlich constants, which affect the biosorption process. The constants K_F and n are calculated from the previous equation by plotting $\ln(C_e)$ versus $\ln(q_e)$ (intercept = $\ln(K_F)$ and slope = $1/n$). In addition, the n value is a measure of the nature and strength of the biosorption process and of the distribution of active sites. The intensity of biosorption less than one ($n < 1$) demonstrates that the biosorption process is of chemical nature. Whereas, the intensity of biosorption more than one ($n > 1$) indicates favorable biosorption conditions [41].

2.6. Full factorial design

Statistical analysis was performed using JMP software [42-44]. Data was analyzed by the analysis of variance (ANOVA). A full factorial design of 24 experiments (three factors at two levels) with duplicates was carried out to investigate the influence of the three factors including their interactions on the biosorption of cadmium ions onto FS biosorbent. The three factors were the pH (2.5 and 5.6), the dose of Cd^{2+} (60 and 100 mg L^{-1}) and mass of the biosorbent (200 and 300 mg), as shown in Table 1. The response to be analyzed is the Cadmium ions removal (%).

Table 1

Parameters, experimental range and level of independent variables.

		Coded variables X_1, X_2, X_3	
Natural variables (x_j)	Units	-1	1
$x_1 = \text{pH}$	-	2.5	5.6
$x_2 = [\text{Cd}^{2+}]$	mg /L	60	100

$x_3 = m(\text{FS})$

mg

200

300

2.7. MC simulation

The MC simulation [44] was performed using a different Miller plans of HAP ((211), (112), (300) (002), (310), (213) and (411) with cell dimensions of $a=b=9.342 \text{ \AA}$, containing a vacuum layer of 20 \AA along the *C*-axis; and then their optimizations were completed utilizing Materials studio software version 8.0 [45] using DMol3 module at the DNP+ basis set and B3LYP functional. Concerning the original structure of type I collagen was extracted from the Protein Data Bank under its PDB form [46], and then the entire structure of Collagen was subjected to achieve its corresponding biosorption simulation (Cd(II)–Collagen). Moreover, the biosorption behavior of the systems is studied by MC simulation in two environments, in vacuum (60Cd(II)/HAP or collagen) and in acidic solution (60Cd(II), 200H₂O, 20H₃O⁺, 5SO₄²⁻/HAP or Collagen) using COMPASS II force field [47] by means the biosorption locator module [44] integrating in Biovia Materials studio version 8.0.

3. Results and discussion

3.1. Effect of initial pH for the removal efficiency of cadmium ions

The pH effect on biosorption behavior of cadmium ions onto FS was investigated in the pH range 2.14–7.76, because in alkaline solutions the precipitation of Cd(OH)₂ occurs [11,48]. The results are presented in Fig. 1. The maximum uptake can be observed at initial pH 3.00. In a strong acidic medium, Cd(II) ions slowly adsorbed on the surface which is already saturated by H⁺ ions. Because these protons compete with the Cd(II) ions. This effect is absorbed by increasing the pH, because there is a decrease in the competition between the H⁺ ions in solution and the metal cations at the surface biosorption sites. However, in the strong basic medium Cd(II) ions react with HO⁻ ions and lead to cadmium hydroxide Cd(OH)₂. Consequently, the initial pH is fixed at 3 for the other studies.

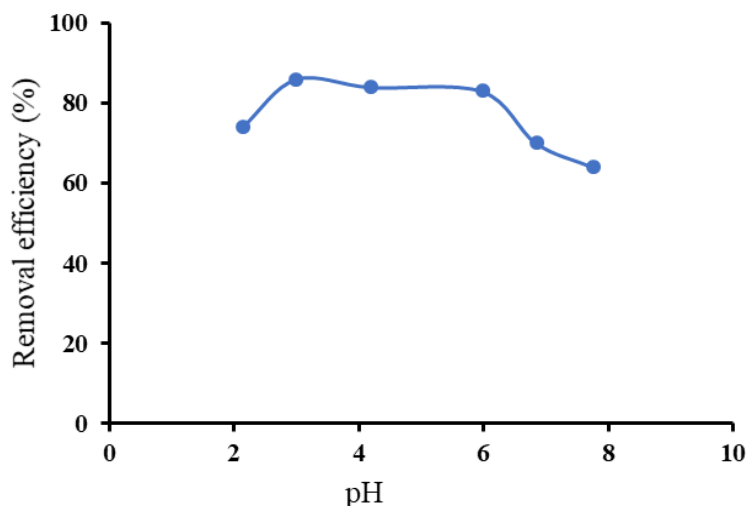


Fig. 1. Effect of pH on the cadmium biosorption onto FS ($[Cd^{2+}]_i = 75 \text{ mg L}^{-1}$, $m_{(FS)} = 250 \text{ mg}$, $t = 1 \text{ h}$, $V = 50 \text{ mL}$, $pH = 3$, $T = 298 \text{ K}$).

3.2. Effect of adsorbate concentration

The influence of initial cadmium concentration on its biosorption was also investigated at room temperature using constant biosorbent dose. Fig. 2 shows the influence of the cadmium concentration on its biosorption. Five concentrations of cadmium ions were considered (35, 50, 75, 100 and 150 mg L^{-1}). Fig. 2 reveals that biosorption efficiency is higher at lower initial cadmium concentration (35 mg L^{-1}) and a slow decrease in Cd(II) biosorption by FS was observed with increasing initial Cd(II) concentration. The reason for the decrease in cadmium removal efficiency at higher initial concentration may be due to saturation of the active sites of the adsorbent by the cadmium ions and hence.

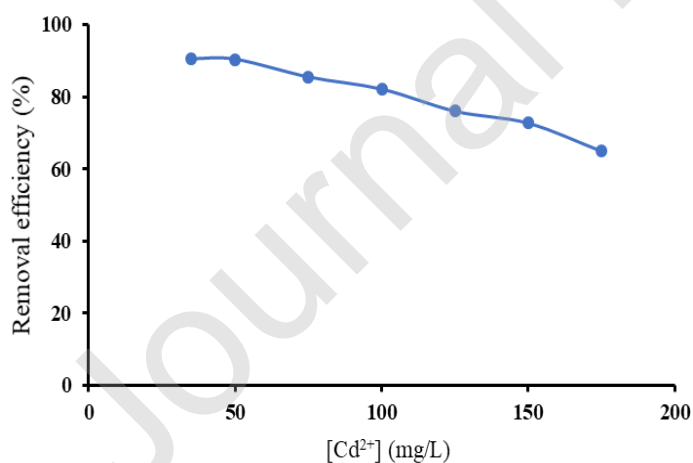


Fig. 2. Effect of cadmium dose on its biosorption ($m_{(FS)} = 250 \text{ mg}$, $t = 1 \text{ h}$, $V = 50 \text{ mL}$, $pH = 3$, $T = 298 \text{ K}$).

3.3. Effect of FS dose

The effect of biosorbent dose on cadmium removal is shown in Fig. 3. Results show that the biosorption efficiency of FS increases with the increase in biosorbent dose. After 60 min of stirring the cadmium ions solution and FS, the cadmium removal percentage varied from 20.90% for 50 mg of FS to 89.44% for 300 mg of FS. The increase in the removal efficiency of Cd(II) may be attributed to the fact that with the increase in biosorbent dose, the available surface for biosorption increases for the cadmium ions to be adsorbed [49,50]. The best dose of biosorbent was found to be 250 mg of FS per 50 mL of cadmium ions solution for the following studies, because this amount gives 88.20% of cadmium removal, almost same removal percentage of 300 mg (89.44%).

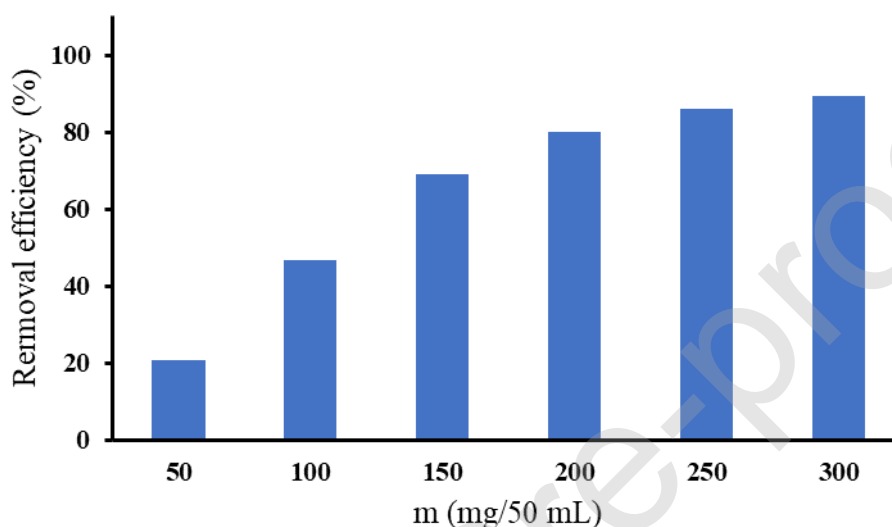


Fig. 3. Effect of FS dose on the biosorption of cadmium ($[Cd^{2+}]_i = 75 \text{ mg L}^{-1}$, pH 3, $t=1\text{h}$, $V=50\text{mL}$, $T=298 \text{ K}$).

3.4. Kinetic of biosorption

The results of Lagergren pseudo-first order kinetic are given in Table 2. A large gap is observed between the experimental $q_e(\text{exp})$ and calculated $q_e(\text{cal})$ values. Hence, the biosorption of Cd(II) onto FS does not obey the pseudo-first order kinetic model. The results of pseudo-second order are gathered in Table 2. The experimental $q_e(\text{exp})$ and calculated $q_e(\text{cal})$ values are very close (12.94 for 12.72 mg g^{-1}). The results indicate that the pseudo-second order model fitted very well to the experimental data, showing high correlation coefficient R^2 value. Similar results have been reported for the adsorption of Cd(II) by Mg–Al–CO₃-layered double hydroxide [51].

Table 2

Kinetic parameters of the biosorption of the cadmium onto FS.

Kinetic models	Parameters	Value
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	k_1 (min ⁻¹)	0.067
Pseudo-first order	q_{exp} (mg g ⁻¹)	12.94
	q_{cal} (mg g ⁻¹)	10.63
	R^2	0.9874
	k_2 (g mg ⁻¹ min ⁻¹)	0.008
Pseudo-second order	q_{cal} (mg g ⁻¹)	12.72
	R^2	0.9999

3.5. Biosorption isotherms

The results of the experimental data by both isotherm models (Langmuir and Freundlich) are gathered in Table 3. The value of the correlation coefficient (R^2) of the biosorbent estimated from the Freundlich model was lower than that the one of the Langmuir model (0.93 instead of 0.96), indicating that the Langmuir equation provides a better fit for the experimental data than the Freundlich model.

Therefore, the Langmuir model represents a better biosorption process which saturated monolayer biosorption of adsorbate molecules on the biosorbent surface, and the energy of biosorption is constant, there is no transmigration of adsorbate molecules, in agreement with the assumption of the Langmuir model. Besides, the Langmuir constant R_L value ($R_L = 0.22$) for the biosorption of cadmium indicated the favorability of the biosorption.

Table 3

Isotherm parameters for biosorption of cadmium ions onto FS.

Isotherm models	Parameters	Values
Langmuir	K_L (L mg ⁻¹)	0.023
	q_m (mg g ⁻¹)	52.08
	R^2	0.96
	R_L	0.22
Freundlich	K_F (mg g ⁻¹)	2.04
	n	1.48
	R^2	0.93

3.6. Comparison of biosorbents

A comparative evaluation of the adsorption capacities of other adsorbents for the adsorption of cadmium ions is given in Table 4. It is obvious that FS shows a good biosorption efficiency when it is compared to activated carbon or sodium montmorillonite

with 3.65 mg g⁻¹ or 16.66 mg g⁻¹, respectively. Regarding the removal of Cd(II), FS is a better adsorbent after *Carp (Cyprinus carpio)* scales, *S. filipendula* and NaOH treated *Aloe vera* wastes.

Table 4

Maximum biosorption capacity of cadmium ions by other adsorbents.

Biosorbent	q_m (mg g ⁻¹)	Experimental conditions	Reference
<i>S. filipendula</i>	103.5	[Cd ²⁺]=50.8 mg L ⁻¹ , t=1 h, pH=5.7, m=0.99 g, T=308K, V=1 L	[52]
<i>Carp (Cyprinus carpio)</i> scales	68.6	[Cd ²⁺]=5 mg L ⁻¹ , 2 h, pH=6, m=10 mg, T=298K, V=100 mL	[31]
Sodium Montmorillonite	16.66	[Cd ²⁺]=20 mg L ⁻¹ , 1 h, pH=4, m=0.5 g, T=295K, V=100 mL	[53]
Activated carbon	3.65	[Cd ²⁺]=20 mg L ⁻¹ , 1 h, pH=4, m=1 g, T=295K, V=100 mL	[53]
NaOH treated <i>Aloe vera</i> wastes	104.20	[Cd ²⁺]= 50 mg L ⁻¹ , 6 h, pH=5, m=15 mg, T=298K, V=10 mL	[54]
Fish scales of <i>Sardina</i> <i>pilchardus</i>	52.08	[Cd ²⁺]=75 mg L ⁻¹ , t=1 h, pH=3, m=250 mg, T=298K, V=50 mL	This work

3.7. Full factorial design

The 24 experiments proposed by JMP were performed. The *i*th line of this matrix defines the experimental conditions of the *i*th experiment. To minimize the error due to the experiments, the design is carried out with randomized order; the results obtained are subsequently grouped in Table 5. The exploitation of results is based on the analysis of variance of the model. The computation of the factor coefficients, their interactions and determining their significance are based on specific statistical tests [32].

Table 5

The experimental data for response according to central composite design

N° Experience	pH	[Cd ²⁺] (mg L ⁻¹)	m(FS) (mg)	
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Actual order	Random order	X ₁	x ₁	X ₂	x ₂	X ₃	x ₃	Cadmium ions removal (%)
1	3	-1	2.5	-1	60	-1	200	75.39
2	15	-1	2.5	-1	60	-1	200	75.67
3	21	-1	2.5	-1	60	-1	200	76.70
4	10	1	5.6	-1	60	-1	200	85.50
5	18	1	5.6	-1	60	-1	200	85.35
6	24	1	5.6	-1	60	-1	200	85.70
7	14	-1	2.5	1	100	-1	200	73.40
8	17	-1	2.5	1	100	-1	200	73.60
9	20	-1	2.5	1	100	-1	200	73.29
10	1	1	5.6	1	100	-1	200	60.56
11	11	1	5.6	1	100	-1	200	63.60
12	12	1	5.6	1	100	-1	200	59.84
13	13	-1	2.5	-1	60	1	300	95.67
14	16	-1	2.5	-1	60	1	300	97.20
15	23	-1	2.5	-1	60	1	300	96.40
16	4	1	5.6	-1	60	1	300	89.60
17	19	1	5.6	-1	60	1	300	88.09
18	8	1	5.6	-1	60	1	300	88.65
19	2	-1	2.5	1	100	1	300	78.40
20	5	-1	2.5	1	100	1	300	79.20
21	6	-1	2.5	1	100	1	300	80.06
22	7	1	5.6	1	100	1	300	69.41
23	9	1	5.6	1	100	1	300	68.38
24	22	1	5.6	1	100	1	300	66.80

3.8. Variance analysis

Variance analysis evaluates if the selected variables of the model have a significant effect on the response [55]. According to analysis of variance (Table 6), the $F_{statistics}$ value of regression for Cadmium ions removal (%) is higher than $F_{th}(F_{0.01}(6.17) = 6.56)$. The large value of F indicates that the variation in the response can be explained by the regression equation.

The associated p -value confirms the interpretation determined by Fisher test. The p -value of the model is lower than 0.05. Consequently, these results mean that there is no statistical difference between the experimental values and the estimated values of the models [56].

Table 6

Variance analysis (ANOVA)

Source	Degree of freedom	Sum of squares	Mean square	$F_{statistics}$	Prob. > F
Model	6	2529.7332	421.622	46.6344	<.0001*
Residual	17	153.6971	9.041		
Total	23	2683.4303			

$F_{statistics}$: Experimental Fisher factor

* significant to 1 % ($F_{0.01}(6.17) = 6.56$)

3.8. Graphical study of the effect of the factors

The graphs illustrated in Fig. 4 describe the effect of the three factors on the response. First factor, it should be noted that the pH reflects a small negative effect on the Cd(II) ions removal. The second factor, which is the dose of Cd²⁺, has a negative effect on the response. Because increasing the concentration of Cd²⁺ significantly decreases the Cd(II) ions removal. The mass of the biosorbent has a positive effect on the rate. In fact, to increase the Cd²⁺ removal, the mass of the biosorbent must be increased.

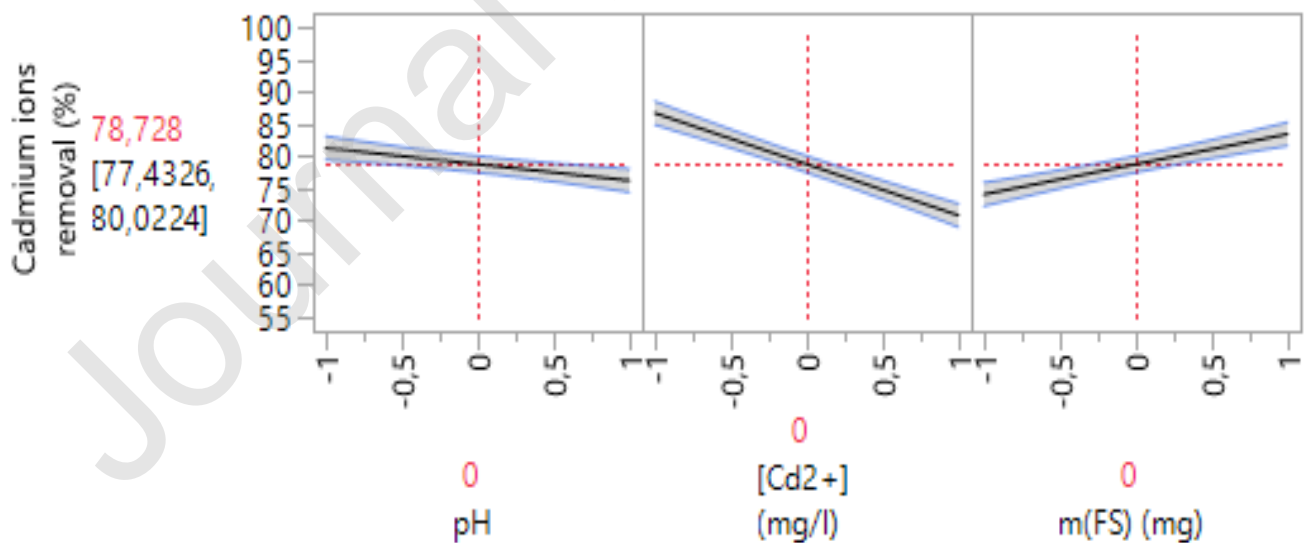


Fig. 4. Main effects plot of parameters on the response.

3.10. The statistical study of factors effects

The main effects of the three variables studied and their interactions are presented in Table 7. Each coefficient is associated with the statistical values of $F_{experimental}$ and a p -value.

The Fisher test is used to determine the importance and significance of the effects of the factors and interactions between the variables on the responses studied. Generally, the largest amplitude of F corresponds to the smallest value of p [55].

We note in Table 7 that for a confidence level of 99.9% the linear effects of the three factors have a significant effect on the removal of Cadmium ions (%), with a values of $F_{experimental}$ (16.8687, 167.0378, 58.0794 for the pH , the Cd^{2+} dose and the mass of the biosorbent respectively) largely higher than the critical value of Fisher ($F_{th} = 5.99$). Similarly, we note that the two interactions $pH*[Cd^{2+}]$ and $pH*m(FS)$ have a significant effect on the response with very high values of the $F_{experimental}$. On the other hand, we note that the interaction $[Cd^{2+}]*m(FS)$ has no significant effect on the removal of Cd(II) ions (%).

Table 7

Result of multiple linear regression of the Cd(II) ions removal (%)

Model term	Estimation	Sum of squares	$F_{experimental}$	Prob. > F	Significance
Constante	78.7275	-	-	<.0001	***
pH	-2.520833	152.5104	16.8687	0.0007	***
$[Cd^{2+}]$	-7.9325	1510.1894	167.0378	<.0001	***
m(FS)	4.6775	525.0962	58.0794	<.0001	***
$pH*[Cd^{2+}]$	-3.009167	217.3220	24.0374	0.0001	***
$pH*m(FS)$	-1.895833	86.2604	9.5410	0.0067	**
$[Cd^{2+}]*m(FS)$	-1.264167	38.3548	4.2423	0.0551	NS

*** : significant to 0.1% ($F_{0.001}(1.17) = 15.72$) ;

** : significant to 1% ($F_{0.01}(1.17) = 8.40$) ;

* : significant to 5% ($F_{0.05}(1.17) = 4.45$) ;

NS : not significant

3.11. Modelization

To describe the variation of the responses according to influencing factors, we choose to use a polynomial model that will be descriptive and representative of the model (Eq. (9)):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (9)$$

Where:

- Y: the value of the calculated response,
- X_i : the value of the coded variable "i"
- b_i : The coefficient of the variable X_i model,
- b_{ij} : The coefficient of the interaction model between X_i and X_j .

This model has 7 terms:

- Constant term = 1
- Linear term = 3
- Rectangle term = 3

The mathematical model only considers the factors having p -value < 0.05 . This model is written as follows (Eq. (10)):

$$\text{Cadmium ions removal (\%)} = 78.7275 - 2.520833 \text{ pH} - 7.9325 [\text{Cd}^{2+}] + 4.6775 \text{ m(FS)} - 3.009167 \text{ pH} * [\text{Cd}^{2+}] - 1.895833 \text{ pH} * \text{m(FS)} \quad (10)$$

3.12. Validation of the model

The correlation between the predicted and experimental values is shown in Fig. 5, characterized by point clouds whose alignment is close to a straight line [57]. The condition of normality of the residuals is thus well respected for the model. Indeed, in this model, the value of R^2 was evaluated at 0.94 indicating that 94% of the established model could explain the variability of the response Cd(II) ions removal (%).

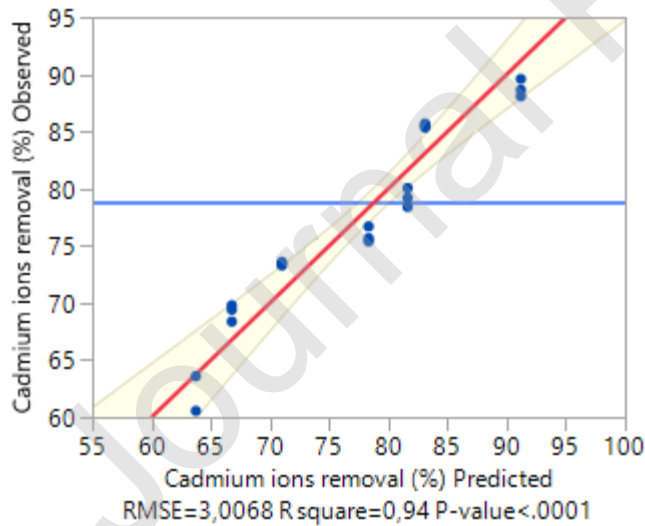


Fig. 5. Correlation between experimental and predicted values for the response (Cadmium ions removal (%)).

In addition, the model is characterized by very high values of the correlation coefficient and the adjusted coefficient of determination ($R_c = 0.9709$ of $R^2_A = 0.9225$)

indicates a very good correlation between the estimated values and the experimental results. Likewise, we found that the Durbin-Watson statistic ($D-W = 2.68$) is close to 2 indicating a good quality of the fit of the model. Therefore, a low value of the root-mean-square error ($RMSE = 3.0068$) confirms that the model explains perfectly the studied process.

The experimental values, the predicted values and their deviations are grouped in Table 7. After the analysis we see that there is no statistically significant difference between these values.

3.12. Optimization

The response surfaces as well as the iso-response curves (Fig. 6) were used to determine the best conditions for removing cadmium ions. The factors studied (pH (x_1) and the mass of FS (x_3) at a fixed value initial concentration of Cd^{2+} ions (x_2)) were evaluated to obtain the highest percentage removal of Cd^{2+} ions at the end of the process, with the convergence of the target (desirable) towards the maximum value.

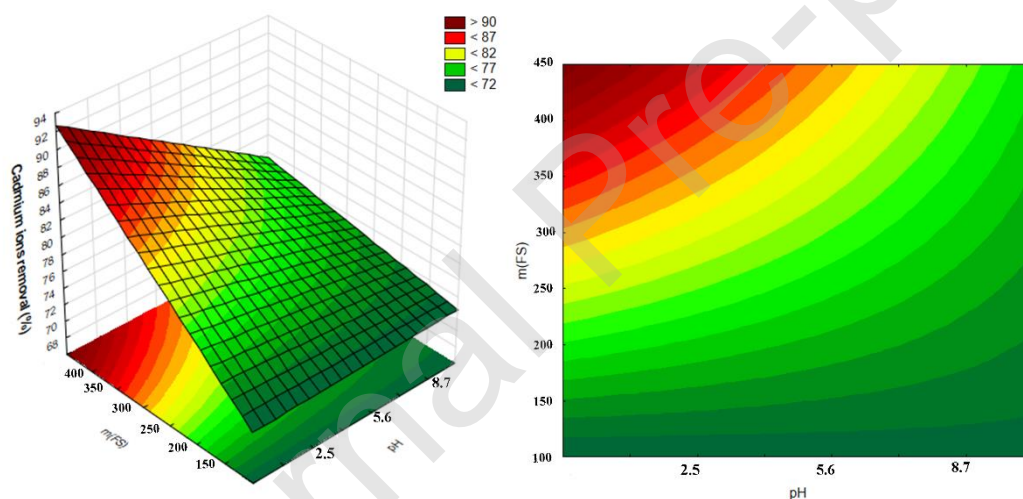


Fig. 6. Response surfaces (in left) and iso-response curves (in right) of percentage removal of Cadmium ions as a function of pH (x_1) and the mass of FS at a fixed value of the concentration of Cd^{2+} ions

Fig. 6 shows clearly that the most effective factor to the response (percentage of removal of Cd^{2+} ions) was the mass of FS. It is possible to verify that the linear term of the mass of FS as well as the interaction with the pH contributes positively to the response, since when this factor increases the response increases consequently. The optimum conditions of biosorption were determined to be pH (x_1) at 3, concentration of Cadmium

ions (x_2) at 75 mg L⁻¹ and mass of FS (x_3) at 250 mg. Thus, it was not necessary to carry out other experiments different from those proposed by the experimental design because the best working condition was that of the experimental points.

The best average experimental result was 88.20 % for the percentage removal of cadmium ions, and the value predicted by the model was 85 %. The difference between the experimental value and the predicted value was 3.20 %.

3.13. Biosorption behavior using MC simulations

The MC simulation can predict the biosorption behavior of Cd(II) ions onto major constituents of FS (HAP and collagen) separately, because this biosorption obeys a Langmuir isotherm model (monolayer biosorption and the energy of biosorption is constant). Fig. 7 exposes the top views of the equilibrium biosorption of the studied Miller plans of HAP in vacuum and in solution. Then, Fig. 8 shows the top views of the equilibrium biosorption of collagen in both vacuum and solution. Some parameters related to the biosorption of Cd(II) ions onto FS are calculated, such as the total energy (E_T) reports the global energy for the system, this parameter is calculated by optimizing the whole system; the biosorption energy (E_{ads}) which displays the energy required when the relaxed Cd(II) ions are biosorbed with the substrate, this parameter is commonly recognized to evaluate the strength and mechanism of biosorption; other term of energy namely the desorption energy dE_{ads}/dNi reflects the necessary energy which one entity of Cd(II) is removed to the system of 60 Cd(II)/vacuum or solution/substrate [58].

Therefore, biosorption behavior (*i.e.*, chemisorption, physisorption) related to the studied systems was evaluated from pair correlation function $g(r)$ analysis using Forcite calculation code [59] which attained after performing the MC simulation for these systems. This method was suggested as a powerful tool to estimate the lengths bonds into biosorption process. The appearance of peaks with lengths lower than 3.5 Å is considered an indication of small bonds, and is correlated with chemisorption, while physical biosorption behavior is associated with peaks greater than 3.5 Å [60].

From Table 8, we observed that all studied Miller plans have characterized with high negative values of E_T and E_{ads} energies in solution comparing to those in the vacuum; indicating clearly the prominent role of acidic medium to reaching high interaction and stability for biosorption interfaces. In other words, we noticed that E_T and E_{ads} energies related to the Cd(II) ions biosorption on HAP Miller plans in acidic solution increased in the order, HAP (002) < HAP (411) < HAP (300) < HAP (213) < HAP (310) < HAP (211)

< HAP (112). This result shows that the most stable and stronger biosorption related to the HAP (002) Miller plan of HAP.

Additionally, biosorption energy of Cd(II) ions with HAP (002) in acidic solution was estimated as $-901.449 \text{ kcal.mol}^{-1}$; while for Cd(II) ions with Collagen is $-233.996 \text{ kcal.mol}^{-1}$, suggesting that Cd(II)···HAP (002) interaction is more favored (high negative value of E_{ads}) than Cd(II)···Collagen, this is due probably to the enormous number of reactive centers and pores that characterize the hydroxyapatite compared to the collagen. This observation is confirmed by the comparison of the desorption energy values, which show the Cd(II)···HAP (002) system has the higher value of dE_{ads}/dNi ($-7.58.10^{-3} \text{ kcal.mol}^{-1}$) comparing to Cd(II)···Collagen ($-0.913 \text{ kcal.mol}^{-1}$). Furthermore, the calculated biosorption energies are negatives, revealing clearly that the studied biosorption is spontaneous. Consequently, the Cd(II) ions have qualitatively a biosorption capability to interact with the substrate [58].

As demonstrated in Fig. 7, we observed that the Cd(II) ion has more accessibility to incorporate pores surface of HAP, this is due probably to the Cd(II) ion has a low value of ionic volume ($3.823.10^{-3} \text{ nm}^3$) with respect to those of the interior pores of HAP [61]. This gives to Cd(II) ions more possibilities to be incorporated inside HAP structure. Fig. 8 reveals that the interactions of Cd(II) ions with collagen were more probable generated from reactive functional groups which contain nitrogen, oxygen and carbon atoms. As discussed above, the Cd(II) ions are more biosorbed on the HAP than Collagen; this difference, probably caused by the steric hindrance effects which generated from heteroatoms functional groups over collagen. This provides certainly a weak interaction between the Cd(II) ions and collagen. Fig. 9 shows that the biosorption type of Cd(II) ions towards HAP (002) and Collagen substrates is chemisorption behavior (peaks with lengths less than 3.5 \AA); indicates clearly high ability of Cd(II) ions to coordinate with HAP and Collagen substrates.

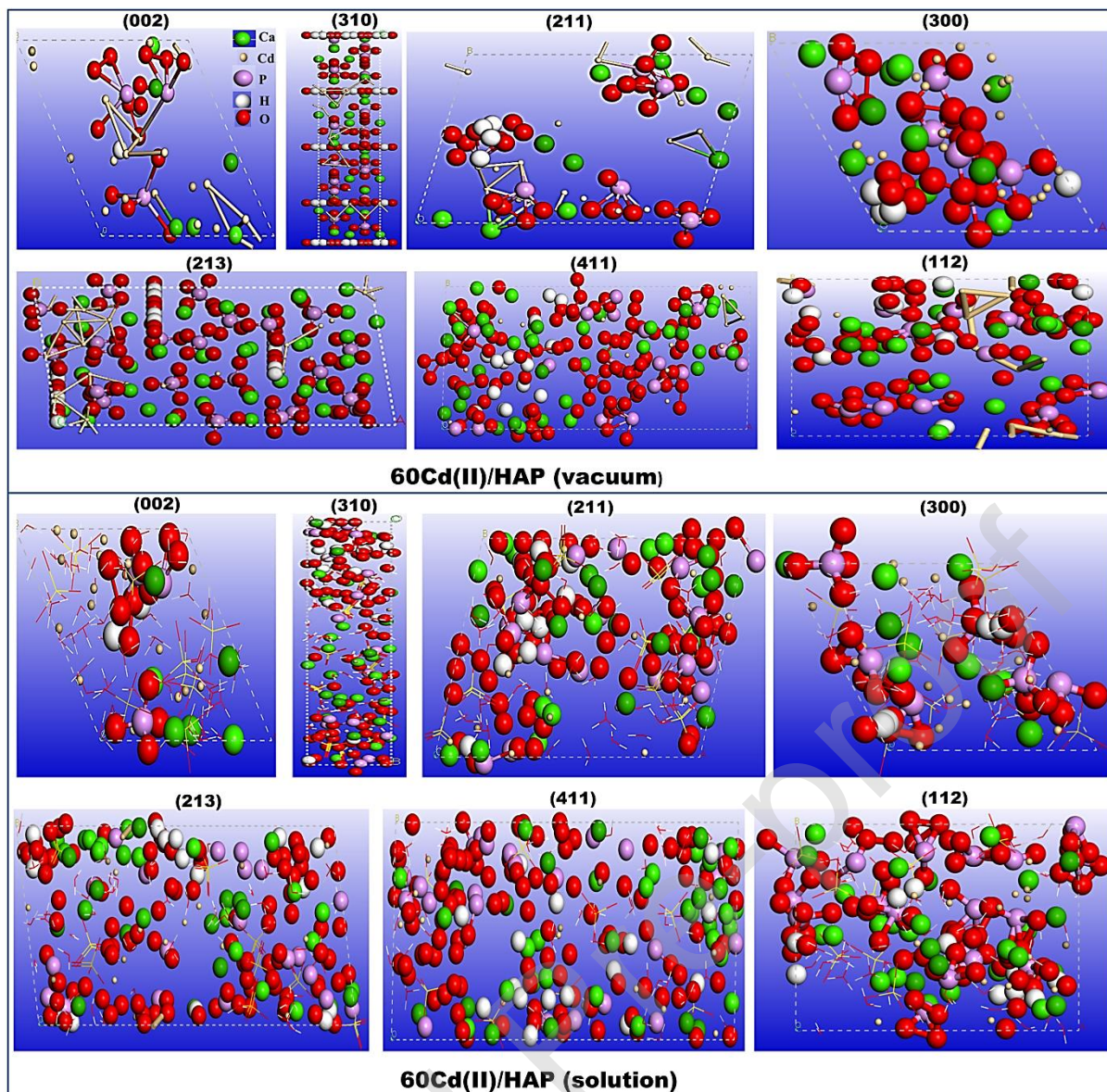


Fig. 7. Top views of stable adsorption configurations of Cd(II) ions on the HAP surfaces in vacuum (60Cd(II)/HAP surface) and in acidic solution (60Cd(II), 200H₂O, 20H₃O⁺, 5SO₄²⁻/HAP surface) at 298.15 K.

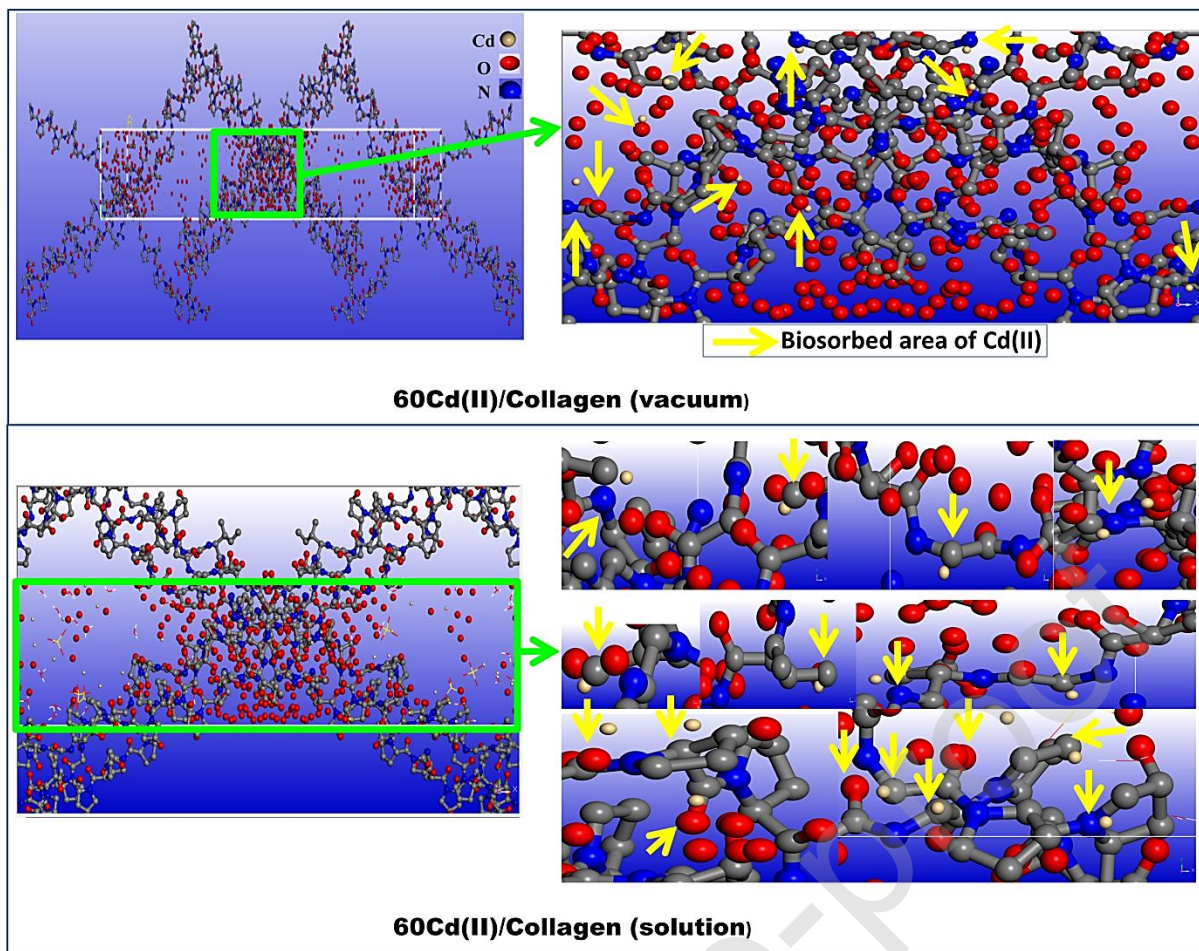


Fig. 8. Top views of stable adsorption configurations of Cd(II) ions on the collagen in vacuum (60Cd(II)/collagen) and in acidic solution (60Cd(II), 200H₂O, 20H₃O⁺, 5SO₄²⁻/collagen) at 298.15 K.

Table 8

Total energy E_T , biosorption energy E_{ads} , and necessary energy to exclude one Cd²⁺ ions from the surface dE_{ads}/dNi are given in vacuum (60Cd(II)/HAP or Collagen) and in acidic solution (60Cd(II), 200H₂O, 20H₃O⁺, 5SO₄²⁻/HAP or Collagen) at 298.15 K.

Substrate		E_T (kcal.mol ⁻¹)	E_{ads} (kcal.mol ⁻¹)	dE_{ads}/dNi (kcal.mol ⁻¹)
HAP (002)	Vacuum	-7.945	-7.945	-0.001
	Solution	-878.847	-901.449	-7.58.10 ⁻³
HAP (211)	Vacuum	-8.946	-8.946	-1.116
	Solution	-872.448	-895.050	-6.04310 ⁻²
HAP (310)	Vacuum	-41.980	-41.980	-1.689
	Solution	-875.410	-895.949	-0.002
HAP (213)	Vacuum	-43.509	-43.509	-1.498

	Solution	-875.434	-898.487	$-6.043 \cdot 10^{-2}$
HAP (411)	Vacuum	-7.453	-7.453	$-6.043 \cdot 10^{-2}$
	Solution	-877.948	-899.456	$-6.043 \cdot 10^{-2}$
HAP (300)	Vacuum	-17.834	-17.834	-0.001
	Solution	-875.444	-898.621	-0.001
HAP (112)	Vacuum	-19.669	-19.669	-0.005
	Solution	-870.181	-895.483	$-6.039 \cdot 10^{-2}$
Collagen	Vacuum	-109.818	-109.818	-1.309
	Solution	-609.236	-233.996	-0.913

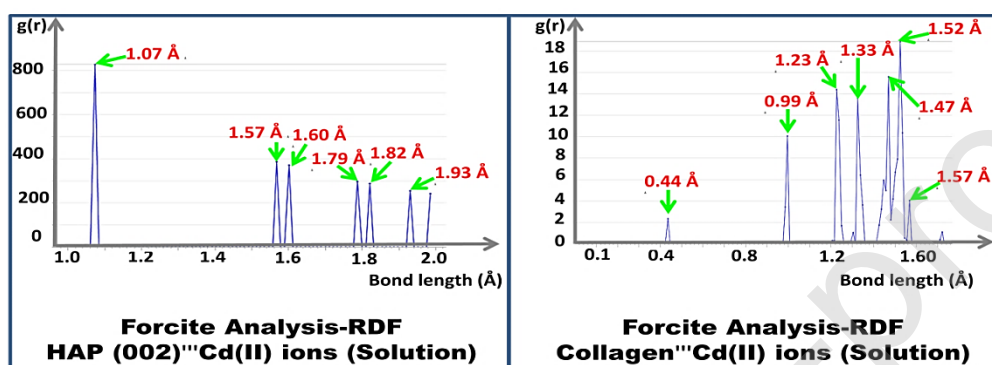


Fig 9. Paired correlation function $g(r)$ of the Cd(II) ions/solution/substrate interfaces

4. Conclusions

Fish scales of the *Sardina pilchardus* were found to be a low-cost biosorbent for the removal of cadmium ions from aqueous solutions. This biosorbent showed a good biosorption capacity for Cd(+II) and gave excellent removal efficiency. At the optimum condition (e.g. contact time, 1h; FS mass, 250 mg; cadmium concentration, 75 mg L⁻¹; V, 50 mL; pH, 3 and temperature, 298K), 88.20 % of cadmium ions was removed. The kinetic study showed that the biosorption phenomenon obeys the pseudo-second order. In addition, the feasibility of biosorption was confirmed by a good fitting with Langmuir isotherm model.

A full factorial design was used to describe the process by a model of first order, by controlling the principal factors affecting the treatment, namely initial pH, the dose of Cd²⁺ and the weight of adsorbent. The analysis of variance tests indicates a high significance of the model chosen with high values of the Fisher report. Elsewhere, the results of model

validation show that the model proposed agrees with experimental results with high values of the coefficient of determination R^2 .

MC calculations were achieved under two environments: in vacuum (60Cd(II)/HAP or Collagen) and in acidic solution (60Cd(II), 200H₂O, 20H₃O⁺, 5SO₄²⁻/HAP or Collagen). The computational results reveal the prominent role of acidic medium to reaching high interaction between Cd(II) ions and substrate. We mentioned that Cd(II) ions have a stronger interaction with HAP surfaces than with collagen. Furthermore, it is observed that the Cd(II) ions are more biosorbed onto (002) Miller plan of HAP compared to other Miller plans. In addition, the biosorption process was spontaneous. Pair correlation function ($g(r)$) analysis shows that the adsorption behavior is a chemisorption type.

Credit author statement

Adil Jaafar: Conceptualization, Investigation, Methodology, Software, Writing - Original Draft, Writing - Review & Editing, Visualization. **André Darchen** : Conceptualization, Methodology, Writing - Original Draft, Writing - Review & Editing. **Said El Hamzi** : Conceptualization, Methodology, Software, Visualization. **Zouhair Lakbaibi** : Conceptualization, Methodology, Software, Writing - Original Draft, Validation. **Anas Driouich** : Methodology, Software, Writing - Original Draft, Visualization., **Abdelghani Boussaoud** : Supervision. **Abdelrani Yaacoubi** : Supervision. **El Makhfouk Mohammed** : Supervision. **Mohsine Hachkar** : Supervision.

Conflict of interest

The authors declare that they have no conflict of interest.

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