**ORIGINAL ARTICLE**

# Removal of heavy metals by chitin: equilibrium, kinetic and thermodynamic studies

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## Abstract

Adsorption is one of the most commonly used methods for the wastewaters treatment. In this work, we studied the impact of experimental conditions on the adsorption of heavy metals M(II) (M = Cd, Ni, Cu, Pb and Zn) in batch system using chitin obtained from crab shells. This biomaterial is selected because of its low cost, availability and efficiency. The M(II) adsorption was found to be dependent on the initial pH, contact time, initial concentration of M(II) and biomass dose. The kinetic models of Elovich, pseudo-first-order and pseudo-second-order kinetic models were successfully applied, providing the best fitting of the experimental data. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms and the thermodynamic parameters were also discussed. The adsorption capacity peaks at: 50, 47.61, 43.4, 40 and 38.46 (mg $L^{-1}$) for Pb(II), Cu(II),Ni(II), Cd(II) and Zn(II), respectively. The negative free energy ($\Delta G°$) and positive enthalpy ($\Delta H°$) indicated spontaneous and endothermic adsorption.

**Keywords** Adsorption · Heavy metals · Chitin · Kinetic · Isotherm

## Introduction

The natural environment is constantly contaminated by various pollutants coming from industrial sectors, which in turn showed a considerable change. Toxic metals are widespread and hazardous and affect the environment with a negative impact on the ecosystem, causing dangerous diseases to both animals and humans. Among toxic metals, one can cite Cd, Hg, Pb, As, Cr and Cu (Salem et al. 2012) which must be removed before discharge to the aquatic environment. Unlike organic pollutants, heavy metals are refractory and cannot be degraded and accumulate in living organisms (Ali and Ateeg 2015). The elimination of metals has been the subject of several works using different techniques like ion electrodialysis (Esalah et al. 2000), sedimentation (Gupta et al. 2001), ion exchange (Dąbrowski et al. 2004; Kang et al. 2008), biological operations (Rashid et al. 2014), coagulation/flocculation (Yue et al. 2009), nanofiltration (Hafiane et al. 2000), solid-phase extraction (Khezami and Capart 2005), adsorption (Abolhasani and Behbahani 2015; Behbahani et al. 2014) and electrokinetic remediation (Sawada et al. 2004). However, all these techniques suffer from high costs of capital and operations as well as the elimination of metallic sludge (Malairajan 2011). On the other hand, the adsorption has become advantageous for removing toxic metals because of its environmentally friendly characteristic, efficiency and low cost. In this regard, many marine wastes were used as adsorbents for both inorganic and organic pollutants (Copat et al. 2012; Izquierdo et al. 2014; Samiey and Ashoori 2012; Vilar et al. 2008).

In this respect, chitin and derived compounds were found to be effective because of their specific characteristics that motivate their utilization for the elimination of various pollutants, including metals. The ability of chitin to remove toxic metals by adsorption has already been reported elsewhere (Jaafarzadeh et al. 2014; Karthikeyan et al. 2005; Mohan and Syed-Shafi 2013; Sofiane and Sofia 2015; Xiong 2010), but the mechanism has not been fully explained (McKay et al. 1999; Volesky 1990). The use of the mass transfer models developed by Fulazzaky et al. (2011, 2013, 2015) for the determination of external,

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internal and global mass transfer factors can allow us to better understand the adsorption mechanism.

The present study is devoted to the adsorption of metals M(II) (M = Pb, Ni, Zn, Cu, and Cd) onto chitin obtained from the crabs shells. The optimization of the operating conditions (initial pH value, reaction time, M(II) concentration and biosorbent dose) in batch system allow an elimination percentage of 90%. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich adsorption isotherm were applied to the experimental data to get information on the interaction M(II)/chitin. Furthermore, the kinetic of M(II) adsorption has been studied by the pseudo-first-order, pseudo-second-order and Elovich models.

# Materials and method

## Adsorbent

The chitin was obtained from the crab shells. In order to study the mechanism of M(II) adsorption, it is crucial to determine the chemical composition of the biomass as well as its surface morphology. The BET specific area provides information on the morphological structure of the chitin, and it was determined by adsorption–desorption isotherms of $N_2$ at 77 K using a Micromeritics ASAP 2010 apparatus. The infrared spectroscopy was carried out by the Fourier transform infrared spectrometer type Nicolet 560 FTIR, in the range (4000–400 cm$^{-1}$). The scanning electronic microscopy (SEM), used to examine the morphological structure of chitin and to visualize its surface morphology, was carried out on a Jeol-JSM-6360LV microscope. The electrolyte addition method was used for determine the point of zero charge (PZC): 0.1 g of chitin was immersed in 50 mL of $KNO_3$ (0.05 M) at various pHs and shaken at a constant rate for 24 h. After decantation, the final pH of the suspension was measured and the difference between the initial and final pHs was plotted against initial pH (Pagnanelli et al. 2005).

## Adsorbate

Stock solutions of 1000 mg L$^{-1}$ of M(II) with which the experiments were conducted was prepared by dissolving amounts of nitrate salts of: $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$ and $Ni(NO_3)_2$, all of purity greater than 99% in distilled water, and other concentrations were prepared from the stock solution by dilution. The solutions of HCl and NaOH (1 N) were used for the adjustment of pH, monitored by a calibrated pH meter (HANNA instruments type).

## Analysis

The experimental tests were conducted in batch mode. The residual M(II) concentrations were measured by atomic adsorption spectroscopy (Perkin Elmer 3030). The concentration was deduced from a calibrated graph.

## Adsorption experiment and equilibrium study

Batch studies were realized with different M(II) concentrations. The M(II) removal was examined separately by changing the contact time, initial pH, M(II) concentration and chitin dose, in order to know the equilibrium time and effect of the contact time on the mechanism of M(II) adsorption onto chitin. 0.1 g of the biomass was added to 50-mL conical flasks containing M(II). The flasks were shacked in the water bath (30–180 min) using a shaking water bath (Memmert) to agitate the solutions.

The pH effect was investigated in the region (2–8), while the M(II) concentration was studied in the range (30–400 mg L$^{-1}$) under optimal values of pH and contact time. The dose effect of the biosorbent varied from 1 to 10 g L$^{-1}$ under fixed other parameters; the solutions were filtered with 41 filter paper. The amounts of M(II) adsorbed were calculated from the following equation:

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

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of M(II) (mg L$^{-1}$); m the amount of chitin (g) and V the volume of solution (L). The efficiency percentage (R) of M(II) removal was calculated as follows:

$$R = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

## Kinetic studies

The kinetic study was undertaken to delimit the step which governs the M(II) adsorption onto the chitin. For this purpose, three models have been tested: the pseudo-first-order, pseudo-second-order and Elovich models whose linear forms are given below:

The pseudo-first-order is given by the following relation (Chen 2015):

$$\ln\left(q_e - q_t\right) = \ln q_e - t k_1 \tag{3}$$

where $q_e$ and $q_t$ (mg g$^{-1}$) are the amount of M(II) adsorbed at equilibrium and time t (min), respectively, and $k_1$ the rate constant (min$^{-1}$). $q_e$ and $k_1$ are calculated from the slope and intercept of the linear plot $\ln\left(q_e - q_t\right)$ versus $t$, respectively.

The linear form of the pseudo-second-order equation can be written as:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \tag{4}$$

$k_2$ (g/mg min) is the equilibrium rate constant. The values of $q_e$ and $k_2$ are deduced from the plot of $\frac{t}{q_t}$ versus $t$.

The Elovich model has been applied satisfactorily to the chemisorption processes and can be expressed by the following relation:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \frac{1}{b} \ln t \tag{5}$$

$a$ (mg g$^{-1}$ min$^{-1}$) is the initial adsorption rate and $b$ (g mg$^{-1}$) the desorption constant related to the extent of the surface coverage and activation energy for the chemisorption (Madala et al. 2017). This equation is often validated for systems where the surface of the adsorbent is heterogeneous. The parameters (1/$b$) and (1/$b$) ln($ab$) are obtained from the slope and intercept of the linear plot of $q_t$ versus ln ($t$), respectively.

## Isotherm studies

The adsorption isotherm is important to describe how the solute interacts with the adsorbent, and four models have been used: Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R).

### Langmuir isotherm

The model assumes a monolayer adsorption on a uniform surface. When a site is filled, no additional adsorption occurs (Behbahani et al. 2015), and the linear form is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{6}$$

The constant ($K_L$), related to the adsorption energy, and the maximum adsorption capacity ($q_{max}$ mg/g) are calculated from the slope and intercept of the linear plot of $C_e/q_e$ versus $C_e$, respectively.

### Freundlich isotherm

This model describes systems where the adsorption is done on heterogeneous surfaces with interactions between the adsorbed molecules; the linear form is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

The constant ($K_F$), due to the bond energy, and the heterogeneity factor (1/$n$) which measures the deviation from the linear part are determined from the plot log $q_e$ versus log $C_e$.

### Temkin isotherm

The model is based on a uniform distribution of the binding energies which takes into account the indirect interaction adsorbate/molecules. Moreover, the model assumes that the adsorption heat of molecules in the layer decreases linearly with the coating due to adsorbent–adsorbate interactions (Erhayem et al. 2015). The linear form is given by:

$$q_e = RT \ln K_T + \frac{RT}{b_r} \ln C_e \tag{8}$$

where the constant $b_r$ is due to the adsorption heat (J mol$^{-1}$) and $K_T$ the isotherm constant (L/g), obtained from the plot $q_e$ versus ln $C_e$ (Table 1).

### Dubinin–Radushkevich (D–R) isotherm

The D–R model is applicable for physical processes, where the adsorption follows a mechanism of pores filling. The isotherm suggests that the adsorption has a multilayer character of Van der Waals interactions whose linear form (Hutson and Yang 1997) is expressed as:

$$\ln q_e = \ln q_{(D-R)} - \beta \varepsilon^2 \tag{9}$$

where $q_{D-R}$ is the D–R constant (mg/g), $\beta$ the constant related to free energy and $\varepsilon$ the Polanyi potential which is defined as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

The mean adsorption energy $E$ (kJ mol$^{-1}$) is calculated from the relation:

$$E = \frac{1}{\sqrt{2\beta}} \tag{11}$$

This parameter gives information about the physical or chemical adsorption, an ion-exchange mechanism. The magnitude of $E$ ($< 8$ kJ mol$^{-1}$) indicates that the adsorption is

**Table 1** Physicochemical characteristics of chitin

| Parameters | Values |
| --- | --- |
| pH$_{PZC}$ | 7.7 |
| Specific surface area (m$^2$ g$^{-1}$) | 4.35 |
| Average particle diameter (µm) | 160 |
| Ash (%) | 0.8 |

of physical nature, while values between 8 and 16 kJ mol$^{-1}$ indicate a chemical adsorption by ion-exchange mechanism (Deng et al. 2009; Özcan et al. 2005; Sarı and Tuzen 2008).

## Thermodynamic studies

The thermodynamic study was undertaken for the determination of the parameters ($\Delta G^{\circ}$, $\Delta H^{\circ}$ and $\Delta S^{\circ}$) (Bouberka et al. 2005):

$$\Delta G^{\circ} = -RT \ln K \tag{12}$$

$K$ is the equilibrium adsorption constant of the isotherms (Lima et al. 2015; Liu and Liu 2008), the Temkin constant $K$ ($= K_{T}$) determined from Eq. (8). The effect of temperature on the thermodynamic constant is determined by the relation:

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{13}$$

the thermodynamic functions $\Delta H^{\circ}$ and $\Delta S^{\circ}$ are calculated from the slope and intercept of the linear plot of ln $K$ versus $1/T$ while $\Delta G^{\circ}$ is given by:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{14}$$

## Results and discussion

### Characterization of biosorbent

According to Muzzarelli et al. (Kumirska et al. 2010), the crab shells consist mainly of chitin, protein/carotene and calcium carbonate with an average weight composition of 25, 35 and 40%, respectively. The characterization showed similarities with the yield and ash content of the chitin obtained from different sources (Artemia, shrimps). pH$_{PZC}$ of the chitin crab is equal to 7.7, a value close to that found by previously Jaafarzadeh et al. (2015).

**Table 2** FTIR analyses

| % transmittance cm$^{-1}$ | Interpretation |
| --- | --- |
| 3440 | Elongation of N–H and O–H |
| 2931 | Vibrations of elongation of C–H bonds in group CH$_2$ or CH$_3$ |
| 1665 | Valence vibration C=O (Amide I) |
| 1550 | Vibration of N–H (Amide II) |
| 1379 | Vibration of C–H-straining in group CH$_3$ |
| 1299 | Valence vibration of C–N |
| 1034 | Valance vibration of C–OH |

The FTIR spectroscopy allows the identification of the functional groups responsible of the M(II) adsorption; spectrum of chitin is shown in Fig. 1, and the characteristic bands and their meanings are given in Table 2.

The external morphology of chitin particles was characterized by SEM analysis. Extracted chitin particles are fiber-like and show distinctly microfibrillar crystalline structure with high diversity (Rasti et al. 2017). The micrograph illustrates the presence of "holes" on the surface that correspond to the pores present in the material. Such pores are responsible of the metals adsorption (Fig. 2).

### Effect of pH

It is now well established the pH has a strong influence on the M(II) adsorption, because it directly affects both the surface charge and the nature of ionic species of the adsorbate. The effect on M(II) removal onto the chitin was studied in the pH range (2–10). Figure 3 shows that the capacity of chitin to remove metals increases with raising pH. This can be explained as follows: at pH ~ 2, the adsorption capacity is minimal and increases slightly with augmenting the pH (4, 6, 8). At low pHs, the adsorbent surface is covered by H$^+$ ions, thus decreasing the

**Fig. 1** Infrared spectrum of the chitin crab. Fourier transform infrared (FTIR) spectra of the chitin and their meanings are shown in Table 2
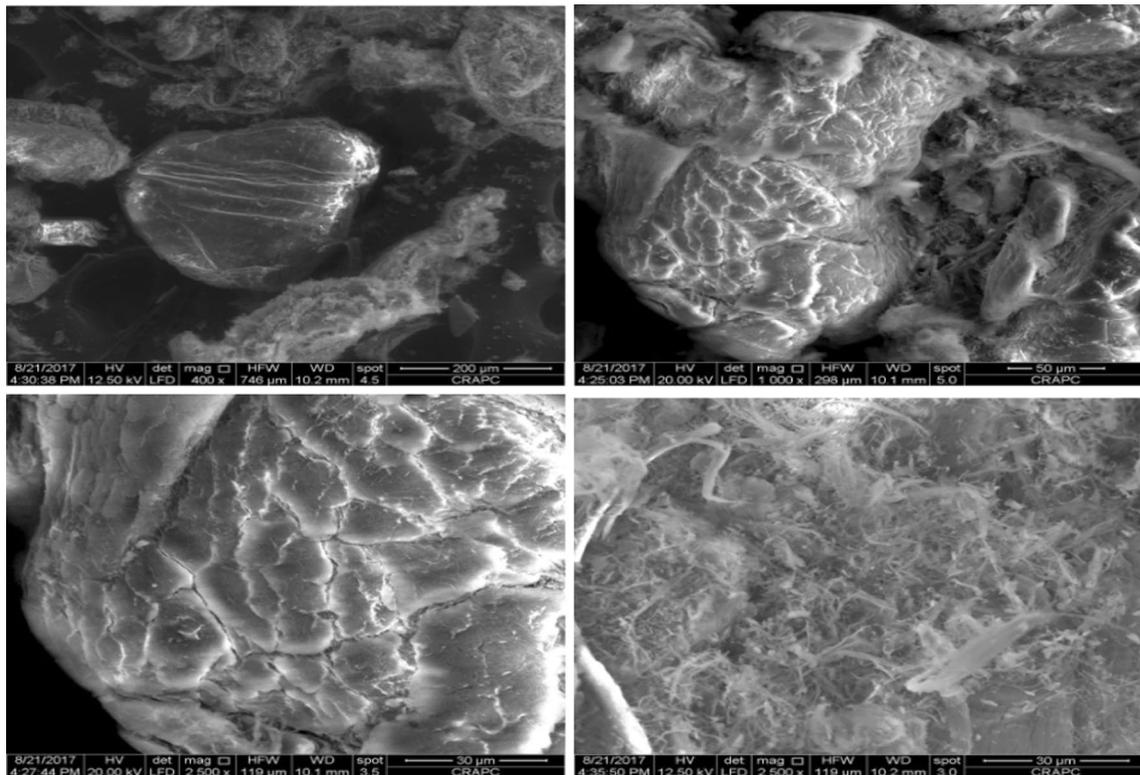
**Fig. 2** SEM image of the chitin



**Fig. 3** Effect of pH on the M(II) biosorption onto chitin
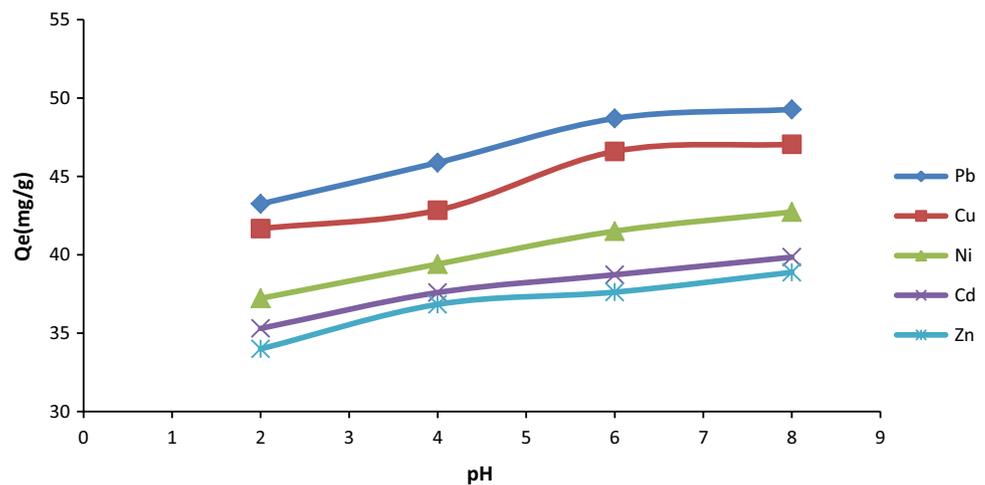
interaction M(II)/adsorbent sites by electrostatic forces. Hence, the decrease in the adsorption rate at low pHs is due to large concentrations and high mobility of $H^+$ ions which are adsorbed more than M(II) ions (Pérez-Marín et al. 2007). With increasing pH, the total surface area of the adsorbent becomes negative with increased liberated sites, leading to an enhanced adsorption. In the pH range (6–8), the metals hydroxide $M(OH)_{2(s)}$ begins to precipitate in the solution, a fact confirmed by Wang and Qin (2005), which makes the study of the adsorption phenomenon impossible. The solubility product (Ks) of the metals lies between $1.2 \times 10^{-14}$ for $CdOH)_2$ and $5.6 \times 10^{-20}$ for $Cu(OH)_2$ and should precipitate above pH ~ 8 for a M(II) concentration of $10^{-2}$ M. Therefore, above this pH, the adsorption and precipitation are responsible for the M(II) removal of in solutions.
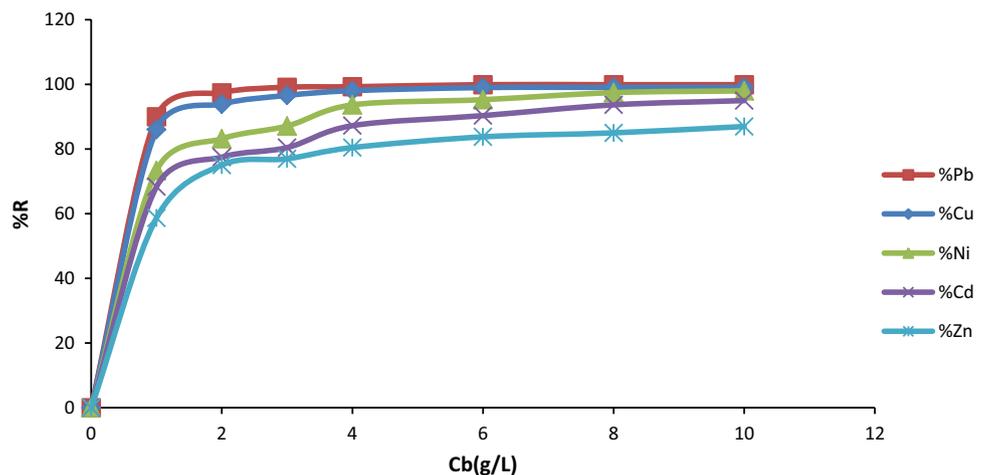
## Effect of biosorbent dose

In order to optimize the quantity of chitin used to achieve maximum M(II) adsorption, we selected the following quantities: 2, 4, 6, 8, 10 g L$^{-1}$ (Fig. 4) where the five curves exhibit the same shape. On the first stage, from 1 to 6 g L$^{-1}$, the quantity M(II) adsorbed increases rapidly with raising the quantity of chitin, and this can be explained by the fact that the greater the adsorbent mass the larger the contact surface area offered to M(II) ions. On the second stage (> 6 g L$^{-1}$), the amounts of Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) adsorbed remain nearly constant when the mass of chitin increases, and this results in the establishment of equilibrium between M(II)/chitin and non-adsorbed M(II) in solution (Igberase and Osifo 2015; Özer et al. 2004).

## Effect of initial concentration of heavy metals

The effect of initial concentration ($C_0$) of M(II) on the chitin adsorption indicates that the adsorption capacity increases with increase in the concentration $C_0$ (Fig. 5).

This is due to the increased driving force that comes from the concentrations gradient (Salameh et al. 2015).

## Effect of contact time

Figure 6 illustrates the change of adsorption capacity of different M(II) ions onto the chitin as the function of time. The curves show that the adsorption was very rapid at the first stage for all studied metals, due to well-aligned sites available for binding of M(II) ions under consideration, and then the adsorption slows down until equilibrium where all binding sites have been saturated; the adsorption equilibrium occurs within 30 min of all metals. It is instructive for a comparative purpose to report the values of the adsorption capacity of some adsorbents available in the literature, and Igberase (2017) have found similar results with Pb(II), Cu(II) and Ni(II).
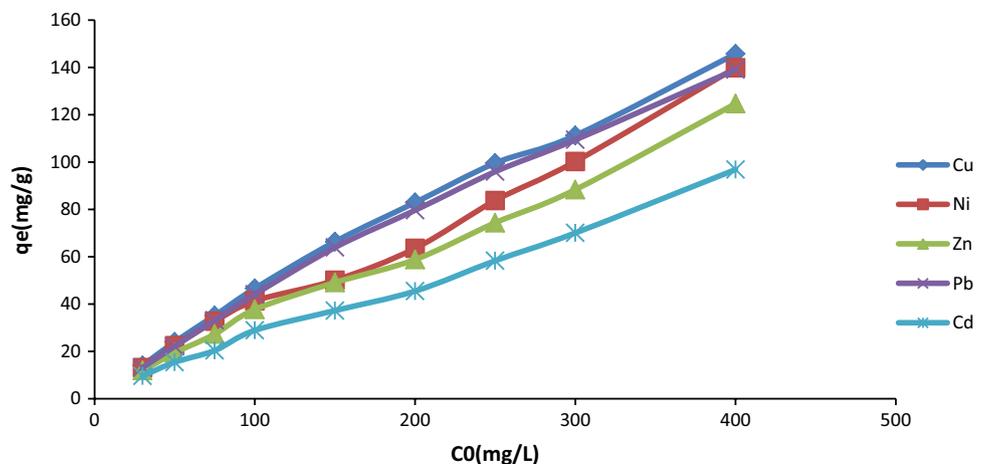
## Kinetic studies

The adsorption kinetic data were analyzed using the three most common models described above. The validity of each model could be checked by the fitness of the straight lines ($R^2$) values. The correlation coefficients ($R^2$) show that the experimental results that follow the retention kinetics of Pb(II), Zn(II), Ni(II), Cd(II) and Cu(II) are better described by the pseudo-second-order model (Table 3). The $q_{e,cal}$ values calculated from pseudo-first-order kinetic model differ appreciably from the experimental values and the coefficients $R^2$ of the pseudo-first-order model are small compared to unity. On the contrary, in the pseudo-second-order kinetic model the calculated $q_{e,cal}$ are very close to $q_{e,exp}$. Further, the correlation coefficients ($R^2$) are equal to 1. By contrast, the Elovich model does not apply to all metals.

The pseudo-second-order model is suitable to describe the adsorption of toxic metals on various biosorbents (Abdeen et al. 2015; Arshad et al. 2008; Safa and Bhatti 2011).

## Isotherm studies

The modeling of isotherms for M(II) adsorption onto the chitin by the above models was carried out with the linear form. The parameters of each model as well as the correlation coefficient $R^2$ established on the basis of the modeling curve are grouped in Table 4. For the Freundlich model, the adsorption is considered favorable when $0.1 < 1/n < 1$ (Karthikeyan et al. 2006; Mishra et al. 1998), whereas values less than $1/n$ indicate a stronger interaction adsorbent/metal, while $1/n = 1$ implies linear adsorption with identical energies for all sites (Febrianto et al. 2009).

**Fig. 6** Effect of contact time on the uptake of Zn(II), Ni(II), Cu(II), Pb(II) and Cd(II) by *chitin*
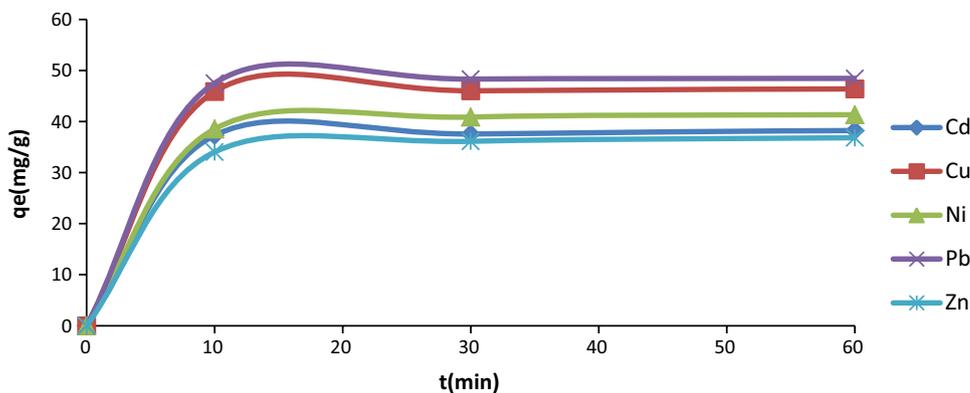


**Table 3** Constants of kinetic models during heavy metals biosorption

| Ions | First-order model | | | Second-order model | | | Elovich model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $k_1$ (min$^{-1}$) | $q_{exp}$ (mg/g) | $R^2$ | $k_2 \times 10^{-3}$ (mg g$^{-1}$ min$^{-1}$) | $q_{exp}$ (mg/g) | $R^2$ | $a$ (mg g$^{-1}$ min$^{-1}$) | $b$ (mg/g) |
| Cu(II) | 0.181 | 0.005 | 2.80 | 1 | 16 | 50 | 0.729 | 517.61 | 4 |
| Ni(II) | 0.350 | 0.014 | 2.37 | 1 | 29 | 47.61 | 0.943 | 340.37 | 2.77 |
| Pb(II) | 0.521 | 0.016 | 1.70 | 1 | 26 | 43.47 | 0.830 | 118.22 | 1.13 |
| Zn(II) | 0.389 | 0.018 | 2.79 | 1 | 28 | 40 | 0.960 | 201.3 | 2.04 |
| Cd(II) | 0.165 | 0.0052 | 2.51 | 1 | 19 | 38.46 | 0.911 | 79.91 | 0.92 |

**Table 4** Langmuir, Freundlich, Temkin and D–R models parameters for the biosorption of M(II) onto chitin

| Ions | Freundlich | | | Langmuir | | | Temkin | | | D–R | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $K_f$ (mg/g) | $n$ | $R^2$ | $q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $b_t$ (kJ/mol) | $K_T$ (L/mol) | $R^2$ | $q_d$ (mg/g) | $B$ | $R^2$ |
| Pb(II) | 21.32 | 2.38 | 0.92 | 142 | 0.108 | 0.952 | 61.93 | 247.52 | 0.990 | 1.01 | −100 | 0.88 |
| Cu(II) | 13.46 | 2.12 | 0.949 | 166.6 | 0.057 | 0.94 | 70.83 | 81.34 | 0.979 | 1.09 | −50.48 | 0.747 |
| Ni(II) | 6.68 | 1.75 | 0.977 | 138.8 | 0.028 | 0.793 | 58.53 | 100.35 | 0.994 | 1.09 | −58.03 | 0.715 |
| Cd(II) | 5.47 | 1.58 | 0.999 | 100 | 0.019 | 0.715 | 46.15 | 209.08 | 0.992 | 1.07 | −100.7 | 0.623 |
| Zn(II) | 3.0 | 1.53 | 0.979 | 142.85 | 0.015 | 0.724 | 46.15 | 113.77 | 0.991 | 1.1 | −47.64 | 0.633 |

**Table 5** Thermodynamic parameters for the adsorption of heavy metals onto *chitin* at various temperatures

| Ion | $\Delta H°$ (J/mol) | $\Delta S°$ (J/mol K) | $-\Delta G°$ (J/mol) | | |
|---|---|---|---|---|---|
| | | | 293 K | 303 K | 313 K |
| Pb(II) | 4822.22 | 25.29 | 2595.50 | 2784.27 | 2777.94 |
| Cu(II) | 7894.01 | 34.36 | 2103.51 | 2595.62 | 2808.35 |
| Ni(II) | 11,722.88 | 47.92 | 1350.23 | 2055.50 | 2268.98 |
| Cd(II) | 12,488.32 | 47.84 | 1350.2 | 2456.82 | 2268.98 |
| Zn(II) | 12,621.32 | 44.01 | 125.04 | 1216.17 | 838.75 |

The Freundlich model is efficient for analyzing the data of M(II) adsorption ($R^2 \geq 0.92$). Biological surfaces are expected to have heterogeneous energies for adsorbing metals, and therefore a good fit was expected (Sağ and Aktay 2000).

The Langmuir model was successfully used for analyzing the experimental data of Pb(II) and Cu(II) onto chitin ($R^2 \geq 0.92$), but becomes invalid for Cd(II), Ni(II) and Zn(II). By contrast, the adsorption data of all ions onto the chitin agree with the Temkin model ($R^2 \geq 0.92$) (Igberase 2017).

### Thermodynamic studies

The results of thermodynamic studies, gathered in Table 5, indicate a decrease in the free energy $\Delta G°$, thus confirming a spontaneous nature of the M(II) adsorption under the experimental conditions (Singh and Pant 2004). The positive enthalpy ΔH suggests endothermic adsorption (Atia et al. 2008; Chegrouche et al. 2009), while the positive value of $\Delta S$ confirms the increased randomness at the solid–liquid interface during M(II) adsorption (Kumar 2011). The necessity of large heats to remove the metals ions from the solution makes the adsorption endothermic (Al-Sou'od 2012).

This work is continuing, and as perspective, the models developed by Fulazzaky et al. (2017, 2018) in fixed bed column for the determination of external, internal and global mass transfer factors will be undertaken very soon.

### Conclusion

The main objective of the present contribution was focused on the development of marine biomass namely the crab shells which were used as natural supports for the retention of five heavy metals: copper, zinc, cadmium, nickel and lead in aqueous solution. It has been demonstrated that the mechanism of metal adsorption by chitin is dependent on the initial pH of the solution. Thus, at acidic pHs, the competition between protons and M(II) ion decreases the adsorption performance of chitin, whereas for pH greater than 7, a saturation of the adsorption capacity is observed.

The precipitation to hydroxides $M(OH)_2$ also accounts for this saturation because of the low-solubility products. An increase in the metal concentration and the mass of chitin favors the adsorption process. The adsorption isotherms of the five toxic metals by chitin is satisfactorily described by the Freundlich and Temkin models throughout the investigated concentrations for all metals, whereas the Langmuir model does not fit suitably the experimental data for Ni, Zn and Cd ions. The spontaneous and endothermic adsorptions of the metals were evidenced from the negative free energy ($\Delta G°$) and positive enthalpy ($\Delta H°$).

### Compliance with ethical standards

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