Synthesis of hydroxyapatite from mussel shells for effective adsorption of aqueous Cd(II)

S. Meski, N. Tazibt, H. Khireddine, S. Ziani, W. Biba, S. Yala, D. Sidane, F. Boudjouan and N. Moussaoui

ABSTRACT

We report the synthesis of hydroxyapatite (HAP) powder from waste mussel shells (decomposed to CaO) and phosphoric acid at room temperature without pH control. The powder synthesized was utilized for cadmium removal from aqueous solutions using the batch technique. The effects of solution pH, adsorbent dose; initial $\text{Cd}^{2+}$ concentration, contact time, and temperatures were examined. Furthermore, the adsorption process revealed a pseudo-second-order reaction model and the Langmuir isotherm is the best-fit model to predict the experimental data and adsorption capacity was found to be 62.5 mg/g. Thermodynamic analysis revealed that because of the negative values of $\Delta G^\circ$ and the positive value of $\Delta H^\circ$, the adsorption process was spontaneous and endothermic. Cadmium immobilization occurs through a two step mechanism: rapid ion exchange followed by partial dissolution of hydroxapatite and precipitation of cadmium containing hydroxapatite.

Key words | cadmium, isotherm, mussel shell, pollution, sorption

INTRODUCTION

Environmental pollution is one of the most serious problems facing humanity and other life forms on our planet today. Environmental pollution is defined as ‘the contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected. Environmental pollution is the universal problem and most important pollutants are the heavy metals in aquatic network because of their toxicity, accumulation and bio-magnification by aquatic organisms (Guo et al. 2017; Jung et al. 2018).

Heavy metal toxicity has proven to be a major threat and there are several health risks associated with it. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Chronic level ingestion of toxic metals has undesirable impacts on humans and the associated harmful impacts become perceptible only after several years of exposure. Few metals, such as aluminium, can be removed through elimination activities, while some metals such as cadmium get accumulated in the body and food chain, exhibiting a chronic nature (Cui et al. 2018; Green & Planchart 2018; Tinkov et al. 2018).

Many methods have been proposed for the removal of toxic heavy metals from wastewaters. Chemical precipitation, filtration, complexing, solvent extraction, electrochemical technique and adsorption are some of the commonly used processes. Adsorption is considered an effective and economically viable technique especially if low cost adsorbent is used. Several authors (Saeed et al. 2005; Gong et al. 2012; Wang et al. 2015; Ali Siyal et al. 2018) have studied the viability of different materials for the removal of metals from aqueous solution. Thus, many studies have focused on use of mineral adsorbents to deal with water containing cadmium, including zeolites (Hernández-Montoya et al. 2013), dolomite (Cao et al. 2018), tourmaline (Jia et al. 2017), and modified clays (Murray 2000). As a large class of inorganic mineral materials (Ivanets et al. 2016; Markovića et al. 2019), apatites may be good potential candidates.

Hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility, high stability under reducing and oxidizing conditions (Fihri et al. 2017; Wei et al. 2017). Calcium hydroxyapatite is a principal component of hard tissues and has been of interest in industry and medical fields (Szczesń et al. 2017). Its synthetic particles find many applications in bioceramic, chromatographic adsorbents to separate protein
and enzyme, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation, and powders for artificial teeth and bones paste germicides (Tschoppe et al. 2011).

Despite its prolific use in the biomedical domain, hydroxyapatite remains a rather expensive material due to the use of high purity reagents (Dupoirieux et al. 1999). This leads to a search for low-cost materials as alternative adsorbents. It is well-known that hydroxyapatite can be prepared from a variety of raw materials. The most frequently used precursors are animal bones, coral, etc.

Important issues in the industrial process are minimization of wastes, recovery of precious materials, and regeneration of wastes and energy. Among these, mussel shell has traditionally been partially recycled as an amendment to increase the pH of acid soils by farmers in coastal areas, mainly due to its pH correction potential in acid environments, and it has shown to be of agronomic value (Álvarez et al. 2011). Besides, new potential applications are being developed, including use as a low-value material for concrete production (Ballester et al. 2007) or for the treatment of polluted soil and waters (Paradeloa et al. 2016).

In the present study, mussel shells were used as a carbonate calcium source to synthesize the hydroxyapatite. Physical and chemical properties of the hydroxyapatite prepared from mussel shell were determined, and the potential use of this hydroxyapatite in the removal of cadmium was studied.

**MATERIALS AND METHODS**

**Materials**

Mussel shells were collected from Bejaia beach, Algeria. To remove impurities and pollutants, the samples were cleaned in boiling water for 30 min and then rinsed several times with deionized water and subsequently dried at 80°C for 24 h in a hot air oven. The dried mussel shells were ground and the resulting powder was calcined at 900°C for 30 min to obtain calcium oxide (CaO). An amount of calcium oxide (CaO) was dissolved in 200 mL of mixture (100 mL of water + 100 mL of ethanol) and the mixture was stirred for 1 h and 30 min. Then a volume of 200 mL of 0.06 M NH4H2PO4 was added drop wise at a rate of 4 mL/min to the Ca solution and the liquid mixture was stirred for 48 h. The obtained white precipitate was washed with the mixture (distilled water + ethanol) and dried in the hot air oven at 80°C for 24 h in order to get the final product. The synthesis route of HAP powder is shown in Figure 1.

**Physico-chemical characterization**

The solid phase was subjected to X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric (TG) analyses, as well as the determination of the point zero charge PZC. The details are as follows.

The XRD analysis was performed using a PHILLIPS Xpert proof, analytical, system MPD diffractometer with Cu Ka radiation. The data were collected over the 2θ range 0–80° with a step size of 0.02° and a count time of 10 s. The obtained diffractograms were used for a qualitative phase analysis.

The FTIR spectrum was obtained using the KBr technique. 2 mg of the dried sample powder was compacted with 300 mg potassium bromide using pressure. The measurements were run in the wavenumber range from 400 to 4,000 cm⁻¹ at a 4 cm⁻¹ resolution averaging 64 scans. The FTIR analysis was performed using a Shimadzu-8300 interferometer.

The thermal transformation and the stability of the powders synthesized were studied by using a thermogravimetric analyzer (LINSEIS STA-PT 1600). The TG analysis of the sample was recorded from 25°C to 900°C at a heating rate of 10°C/min in a stream of nitrogen.

The point of zero charge (pH_{PZC}) was measured by a batch equilibration technique, with 0.1 N of NaCl as an inert electrolyte (Bell et al. 1973). The results were plotted using the ORIGIN-6 software.

**Determination of the sorption capacity**

The batch equilibrium technique was employed at room temperature. Cadmium ions solutions with different concentrations were prepared by dissolving (Cd(NO₃)₂,4H₂O) in deionized water. Typically, a certain amount of HAP is added to 250 mL of the Cd²⁺ solutions after adjusting the pH. Next, the mixture was shaken at a speed of 250 rpm for different times. After a specific time, the sorbents were filtered from the solution. The final Cd²⁺ concentration was measured by atomic absorption spectrophotometry (ICE 3000 SEIES AA Spectrometer).

The equilibrium sorption capacity, qₑ, of HAP, which is defined by the equilibrium amount (in mg) of Cd²⁺ ions adsorbed per gram of sorbent (simply the unit will be noted as mg/g), was calculated using the general equation:

\[ qₑ = \frac{(C₀ - Cₑ)V}{m} \]
where \( C_0 \) and \( C_t \) represent, respectively, the cadmium concentrations before and after adsorption (mg/L), \( V \) is the volume of the cadmium solution (L) and \( m \) is the amount (g) of the sorbent used in the reaction mixture.

The removal percentage (\( Y\% \)) is defined as the percentage ratio of difference in metal concentration before and after adsorption (\( C_0 - C_t \)) to the initial concentration of \( Cd^{2+} \) in the aqueous solution (\( C_0 \)). It was calculated using the equation follow:

\[
Y(\%) = \frac{(C_0 - C_t)}{C_0} \times 100
\]  
\[\text{(2)}\]

**Adsorption isotherm study**

Adsorption isotherms are very important for understanding the adsorption systems. Adsorption isotherms were obtained using 4 g/L of the apatite with different concentrations of cadmium between 10 and 500 mg/L at pH = 2. Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. The most widely used models are the Langmuir and Freundlich adsorption isotherm models.

The Langmuir equation used generally for high concentrated solution (Rengaraj et al. 2004).

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
\]

\[\text{(3)}\]

where \( q_e \), the amount of metal adsorbed par unit of HAP at equilibrium (mg/g), \( q_m \), the maximum amount of metal ion per unit of HAP (mg/g), \( K_L \), a constant related to the affinity of the binding sites (energy of adsorption) (L/mg); \( C_e \), the residual metal concentration in solution et equilibrium (mg/L).

The Freundlich equation also adapted for high concentrated solution (Allen et al. 2003).

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

\[\text{(4)}\]

where \( q_e \), the amount of metal adsorbed par unit of HAP at equilibrium (mg/g), \( K_f \), a Freundlich constant related to the
adsorption capacity (L/mg); \( C_e \), the residual metal concentration in solution at equilibrium (mg/L); \( n \), Freundlich constant related to adsorption intensity.

**Adsorption kinetics models**

In order to examine the controlling step of cadmium adsorption, pseudo-first-order model and pseudo-second-order model have been used to analyze experimental data.

The pseudo-first-order equation is one of the most commonly used for the adsorption of solute from solution (Ho & McKay 1999; Meski et al. 2010a). The model is represented as follows:

\[
\log\left( \frac{q_e}{q_t} \right) = \log \left( \frac{q_e}{K_1} \right) \times t \quad (5)
\]

where \( K_1 \) (l/min) is the rate constant of pseudo-first-order adsorption and \( q_e \) and \( q_t \) (mg/g) denote the amount of cadmium adsorbed at equilibrium and at time \( t \), respectively.

The pseudo-second-order equation based on the adsorption equilibrium capacity can be expressed as:

\[
\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} \times t \quad (6)
\]

where \( K_2 \) (mg/g · min) is the rate constant of pseudo-second-order adsorption.

**RESULTS AND DISCUSSION**

**Physico-chemical characterization**

**XRD analysis of the simples**

The X-ray diffractograms of the mussel shells powder before and after calcination at 900 °C is given in Figure 2(a) and 2(b). These diagram show the presence of a single carbonate phase on the powder before calcination, all of whose peaks identical to that of aragonite except for the two lines observed at values of 2\( \theta \) = 29.36° and 30.96° which correspond to calcite.

The diffraction patterns of mussel shells calcined at the temperature of 900 °C are characteristic of CaO phase as major phase, caused by the decomposition of CaCO₃ from the natural shell. Other peaks relating to carbonates (calcite) which are not converted into CaO are also observed. This indicates an incomplete transformation of the CaCO₃ in mussel shell to CaO. This may be due to the annealing time being not long enough.

According to Currie et al. (2007), in heating the shell above 500 °C, organic matter is burnt out; it also promotes that the crystal structure of calcium carbonate changes from the aragonite polymorph, with an orthorhombic crystal structure, to the calcite polymorph, with a trigonal-rhombohedral structure; and, finally, this heating allows transformation of carbonates to oxides.

![Figure 2](http://iwaponline.com/wst/article-pdf/80/7/1226/637124/wst080071226.pdf)

Figure 2 | X-ray diffractions of the mussel shell (a) before, (b) after calcination at 900 °C and (c) apatite synthesized.
The XRD patterns obtained for the synthesized powder (HAP) (Figure 2(c)), could be easily indexed by comparison of the JCPDS data sheet relative to the hydroxyapatite, with, however, broader peaks illustrating the low crystallinity of the prepared apatitic phase. The XRD pattern obtained was thus found to be characteristic of single-phase apatite, except for the three lines observed at values of 2\(\theta\) = 35.97\(^\circ\), 43.35\(^\circ\) and 48.32\(^\circ\) which correspond to calcite.

**FTIR spectra of the simples**

The FTIR spectrum of the mussel shells powder before and after calcinations at 900 °C is shown in Figure 3(a) and 3(b).

The spectra of the mussel shells before calcinations are composed of essential bands which are typically described for the vibrational modes of aragonite, a crystalline form of CaCO\(_3\) (Kwon et al. 2004). For example, the peak located at 1,082 cm\(^{-1}\) is characteristic of aragonite structure (Kamalanathan et al. 2014).

Figure 3(a) displays the FTIR spectra of the mussel shell powder. The results here reinforce the presence calcium carbonate by the characteristic vibrations of carbonate CO\(_3^{2-}\) (\(v_2\), 862, \(v_3\), 1,445, and \(v_4\), 708 cm\(^{-1}\)). Besides that, the small infrared absorption spectra were shown at 1,785, 2,521, and 2,894 cm\(^{-1}\) attributed to the combination modes of different CO\(_3^{2-}\) band (Loy et al. 2016). The large band observed at 3,200–3,600 cm\(^{-1}\) is related to the hydroxyl group of water.

The FTIR spectroscopy of calcined mussel shells at 900 °C is shown in Figure 3(b). Three frequency bands inherent to the structure of CaO are clearly observed. The broad bands at 1,441 cm\(^{-1}\) show the CO\(_3^{2-}\) band are shifted compared to the spectra of mussel shells before calcinations.

The peak at 3,457 and 3,651 cm\(^{-1}\) is related to –OH bond group present in CaO. The presence of moisture allows the CaO easily absorbed it and form Ca(OH). As the result, the CaO sample cannot be exposed to the environment for a long time to avoid the CaO with moisture to become Ca(OH)\(_2\) (Loy et al. 2016). Due to this reaction, the result may affects the characteristic of CaO. The same results were obtained by Khiri et al. (2017).

The characteristic peak band for CO\(_3^{2-}\) for mussel shells sample after calcination appear at 732 cm\(^{-1}\), 878 cm\(^{-1}\) and 2,511 cm\(^{-1}\) which attributed to the common characteristic feature of the carbonate ions in calcium carbonate. These results are in good agreement with those of the XRD which indicate the incomplete decomposition of CaCO\(_3\) of mussel shells.

The spectra of the apatite synthesized HAP (Figure 3(c)) reveals the presence of the characteristics groups of hydroxyapatite phase were identified in the spectra of HAP sample. The bands at about 1,100, 1,045 and 572 cm\(^{-1}\) can be attributed to different modes of PO\(_4^{3-}\). The carbonate CO\(_3^{2-}\) groups showed characteristic doublet at about 1,420–1,455 cm\(^{-1}\), and the band at 870 cm\(^{-1}\). Carbonate may occupy OH\(^-\) (type A apatite) or PO\(_4^{3-}\) (type B apatite). According to the substitution type, carbonate bands may...
appear at slightly different wave numbers. In general, the band appeared at 870 cm$^{-1}$ is characteristic of a type B apatite (Figueiredo et al. 2012). The band observed at about 713 characteristic of the CO$_3^{2-}$ confirms the presence of the calcite in the powder synthesized.

The broad peak, with the maximum at 3,000–3,500 cm$^{-1}$, was due to the vibrations of $\nu$-OH groups from different sources.

**Thermogravimetry analysis**

The TG curve recorded for hydroxyapatite powder obtained by the mollusk shell is shown in Figure 4. Three weight losses are observed. The first is obtained at temperature range 22–300 °C. The weight loss in this region is 1.25% and is due to the dehydration of the apatite. The second loss between 300–600 °C probably originated from loss of chemisorbed water.

A third loss range from 600 °C to 900 °C, which corresponds to the decomposition of carbonates, which are already detected by XRD diffraction and IR spectroscopy. Calcium carbonate reacts to form the oxide of calcium (CaO) according to the reaction:

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$ (7)

**Point of zero charge**

The result of pH$_{\text{pzc}}$ for the adsorbent synthesized are a slightly alkaline character (pH$_{\text{pzc}} = 10.2$). The pH$_{\text{pzc}}$ value is determined as the point where experimental curves intersect the line pH$_{\text{initial}} = $pH$_{\text{final}}$. The pH$_{\text{pzc}}$ value indicates that the surface of the sorbent is positively charged at pH values less than 10.2 and is negatively charged at pH value above 10.2.

**Effect of single variables**

**Effect of time and initial pH**

The effect of pH on the cadmium uptake of the powder synthesized is a very important parameter. The amount of the cadmium uptake on the apatite was examined at different pH values. The others parameters were fixed at these values: temperature ($T = 22 \pm 2 ^\circ$C), the amount of the apatite ($C_{\text{sus}} = 4 \text{ g/L}$), agitation ($W = 250 \text{ tr/min}$) and the initial concentration of the cadmium ($C_{\text{Cd}} = 100 \text{ mg/L}$).

Figure 5 shows that all values of the pH favor the sorption of cadmium on the apatite synthesized. Nevertheless, the measurement of the final pH for each initial pH value shows that for the pH$_{\text{initial}} \leq 3$, the final pH value is greater than 7. According to the cadmium phase diagram, for a pH = 7, the predominant phase is Cd(OH)$_2$ and, therefore, to avoid the contribution of the phenomenon of precipitation of Cd(OH)$_2$, we have chosen to work at pH = 2.

In addition, the results (figure not presented) indicated that for all initial pH, an important amount of the metal ions was removed on the first 30 min and no significant sorption was seen after 60 min of stirring. For a subsequent experiment, the contact time was thus maintained for 120 min to ensure that equilibrium could be achieved.

**Effect of initial concentration of cadmium on the sorption yield**

The evolution of cadmium sorption yield on the apatite synthesized (figure not presented) was given as a function of the initial concentration of the cadmium. The solution concentration of cadmium varied in the range 10–500 mg/L and the pH solution was adjusted to 2. It can be observed that for all initial concentrations of cadmium, the sorption yield increases rapidly at an initial stage of sorption and no appreciable increase was observed beyond this time which shows saturation of the active sites in the HAP. On the other hand, the results indicates that the removal yield decrease with increase of the initial concentration of cadmium. This can be explained by the competition between the metallic ions for the occupation of the active sites.
Effect of adsorbent dose on the sorption of cadmium

To study the effect of HAP sorbent dose on sorption of cadmium onto the apatite synthesized, the experiments were conducted with different amounts of HAP and with concentration of cadmium 100 mg/L at ambient temperature.

Figure 6 depicts the variation of the adsorption yield of cadmium versus the amount of apatite HAP. It was apparent that the removal efficiency increased rapidly with the increase of the adsorbent dose due to the greater availability of the adsorbent surface. The yield of cadmium obtained for 4 g/L of HAP is 97.5%. Then, a slight increase of the yield (from 1%) was observed for the amount of the adsorbent greater than 4 g/L. This possibly is caused by the saturation of the active sites. For this we chose 4 g/L as the optimum adsorbent dose.

Figure 5 | Evolution of the adsorption yield of cadmium and pHfinal versus pHinitial.

Figure 6 | Effect of amount of HAP on the sorption of cadmium (pH – 2, time – 120 min).
Adsorption isotherms studies

Equilibrium sorption isotherms are one of the most important types of data to help us to understand the sorption mechanism. All of the sorption parameters are presented in Table 1.

The suitability of the models also was assessed by the Marquardt’s percent standard deviation (MPSD) and average relative error (ARED) (Meski et al. 2010b).

Marquardt’s percent standard deviation (MPSD)

\[
\text{MPSD}(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^{N} (q_{\text{exp},i} - q_{\text{cal},i})^2}{N - 1}}
\]

The average relative error (ARED)

\[
\text{ARED}(\%) = \frac{\sum_{i=1}^{N} \left| \frac{q_{\text{exp},i} - q_{\text{cal},i}}{q_{\text{cal},i}} \right|}{N} \times 100
\]

where N is the number of experimental data points, qe,cal (mg/g) is the theoretically calculated adsorption capacity at equilibrium and qe, exp (mg/g) is the experimental adsorption capacity at equilibrium. The results obtained for the two errors are presented in the Table 1.

Comparing the values of R² and the two errors (MPSD and ARED) between the Langmuir and Freundlich models, the Langmuir isotherm equation was found to suitably fit the adsorption isotherm data. Due to the homogeneous distribution of active sites on the HAP surface, the removal of Cd(II) was a monolayer adsorption process.

Adsorption kinetics

Pseudo-first-order kinetic model

It could be seen that experimental data were fitted by the pseudo-first-order model with R² ranging from 0.2 to 0.96 (results not presented). The low values of R² implied the poor applicability of the pseudo-first-order.

Pseudo-second-order kinetic model

The pseudo-second-order parameters and the correlation coefficient R² are shown in Table 2.

It can be seen from these results that all value of R² are higher and the amounts of cadmium adsorbed (qe(cal)) calculated using the pseudo-second-order model kinetic are very close to the experimental values (Table 2). The high values of R² indicate that the pseudo-second-order model describes well the sorption of cadmium onto the apatite synthesized. This indicates that the sorption process occurs predominantly by chimisorption. Similar observations were made by Elkady et al. (2011).

Sorption thermodynamic characteristics

Thermodynamic parameters can help us to understand the inherent energetic changes involved in the sorption process. Furthermore, there are crucial data that provide information about the spontaneity, endothermic, or exothermic reaction of sorption and provides information about the potential increase or decrease of randomness at the solid-liquid interface during the sorption process (Bhatnagar & Anastopoulos 2017).

Changes in thermodynamic parameters, such as free energy of sorption (ΔG⁰), standard enthalpy (ΔH⁰), and standard entropy changes (ΔS⁰), were calculated using Equations (8)–(10).

\[
K_e = \frac{q_e}{C_e} \quad (8)
\]

\[
\ln K_e = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (10)
\]

where Ke is the thermodynamic equilibrium constant (L/g), T is the absolute temperature (°K); R is the gas constant (8.314 J/mol/K). The results of all these parameters are presented in Table 3.

The negative ΔG values indicate the spontaneity of adsorption of cadmium on the apatite synthesized. Positive

Table 1 | Parameters obtained from Langmuir and Freundlich model

<table>
<thead>
<tr>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>qm (mg/g)</td>
<td>K_L (L/mg)</td>
</tr>
<tr>
<td>62.5</td>
<td>0.082</td>
</tr>
</tbody>
</table>
the concentration of Cd\textsuperscript{2+} ions is the result of an ion-exchange process with Ca\textsuperscript{2+} cations. Ionic radius of cadmium (0.97 Å) will substitute for Ca\textsuperscript{2+} at accessible surface area (Elouaer et al. 2017). The mechanism ion exchange between Cd\textsuperscript{2+} and Ca\textsuperscript{2+} could be depicted by the following general reaction:

\[ \text{HA} - \text{Ca}^{2+} + \text{Cd}^{2+} = \text{HACd}^{2+} + \text{Ca}^{2+} \quad (11) \]

The evolution of the concentration of Cd\textsuperscript{2+} adsorbed and the concentration of Ca\textsuperscript{2+} released versus time was studied. The result obtained (result not presented) indicates that the concentration of cadmium ion sorbed by exchange is lower than the concentration of a calcium ion released from the ion exchange, then the mechanism exchange of cadmium and calcium is not equi-molar.

However, the higher amount of calcium released on the solution can be also attributed to the dissolution–precipitation process. At pH solution equal to 2, the surface of the HAP can be dissolved partly or totally according to the following reaction (Equation (12)). Then, Cd\textsuperscript{2+} could combine with released anions (H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} and OH\textsuperscript{−}) to form surface precipitate as shown in reaction (Equation (13)).

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 14\text{H}^+ \Leftrightarrow 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} \quad (12)
\]

\[
x\text{Cd}^{2+} + 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} \Leftrightarrow \text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2 + x\text{Ca}^{2+} + 14\text{H}^+ \quad (13)
\]

To confirm the contribution of the dissolution–precipitation process on the sorption of the cadmium, the precipitate obtained after sorption of different initial concentration of cadmium (100 and 500 mg/L) were characterized by XRD diffraction and IR spectroscopy. Elouaer et al. (2017) proposed non-apatite Ca-Mg phosphate used as adsorbent to remove Cd\textsuperscript{2+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+} and main mechanism including dissolution precipitation and ion exchange.

Table 2 | Parameters obtained from the pseudo-second-order model

<table>
<thead>
<tr>
<th>C (mg/L)</th>
<th>K\textsubscript{2} (g · mg\textsuperscript{−1} · min\textsuperscript{−1})</th>
<th>R\textsuperscript{2}</th>
<th>q\textsubscript{ecal} (mg/g)</th>
<th>q\textsubscript{exp} (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>−0.150</td>
<td>0.992</td>
<td>3.277</td>
<td>2.425</td>
</tr>
<tr>
<td>25</td>
<td>0.057</td>
<td>0.998</td>
<td>6.173</td>
<td>5.994</td>
</tr>
<tr>
<td>50</td>
<td>0.018</td>
<td>0.998</td>
<td>15.625</td>
<td>11.205</td>
</tr>
<tr>
<td>100</td>
<td>0.003</td>
<td>0.998</td>
<td>33.333</td>
<td>23.850</td>
</tr>
<tr>
<td>150</td>
<td>0.003</td>
<td>0.989</td>
<td>35.714</td>
<td>32.581</td>
</tr>
<tr>
<td>200</td>
<td>0.0011</td>
<td>0.963</td>
<td>47.619</td>
<td>41.908</td>
</tr>
<tr>
<td>500</td>
<td>0.0025</td>
<td>0.943</td>
<td>66.666</td>
<td>57.726</td>
</tr>
</tbody>
</table>

Table 3 | Thermodynamic parameters obtained from the adsorption of Cd(II) on the HAP

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Temperature (°C)</th>
<th>ΔG\textsuperscript{0} (kJ/mole)</th>
<th>ΔH\textsuperscript{0} (kJ/mole)</th>
<th>ΔS\textsuperscript{0} (J/mole · K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>295</td>
<td>−2.791</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>−4.297</td>
<td>30.213</td>
<td>112.26</td>
</tr>
<tr>
<td>HAP</td>
<td>312</td>
<td>−4.701</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>−6.147</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

values of ΔH\textsuperscript{0} indicate the endothermic nature of the adsorption process. The positive value of ΔS\textsuperscript{0} suggests increased randomness of the solid–solution interface during the adsorption of Cd(II) ions onto HAP. Similar results have been demonstrated in the sorption of cadmium onto different adsorbent including activated phosphate rock (Elouaer et al. 2008) and garbage ash (Qasemi et al. 2018).

Sorption mechanisms

In order to interpret the sorption mechanism of Cd(II) ions on a sorbent surface, a knowledge of Cd(II) speciation and the sorbent surface characteristics is essential.

Generally, HAP selectivity towards divalent metal cations is the result of an ion-exchange process with Ca\textsuperscript{2+} cations. Ionic radius of calcium (0.97 Å) slightly differs from that of Ca\textsuperscript{2+} (0.99 Å). It is, therefore, logical that Cd\textsuperscript{2+} will substitute for Ca\textsuperscript{2+} at accessible surface area (Shannon 1976). The mechanism ion exchange between Cd\textsuperscript{2+} and Ca\textsuperscript{2+} could be depicted by the following general reaction:

\[ \text{HACd}^{2+} + \text{Ca}^{2+} \rightarrow \text{HACa}^{2+} + \text{Cd}^{2+} \]

The FTIR spectra in Figure 8 reveal the changes in the absorption bands of the surface functional groups of HAP.
due to Cd(II) adsorption. The peak area for the phosphate at 948.5 cm$^{-1}$ decreases with increasing of cadmium concentration and disappears for higher concentration of cadmium (500 mg/L).

The peak area for the carbonate at 830 cm$^{-1}$ and 1,433 cm$^{-1}$ increase for the low concentration (100 mg/L) and decrease for the high concentration of cadmium (at 500 mg/L).
This result can be explained by the formation of the precipitate CdCO$_3$. Thus, the mechanism involved in the chemisorption of Cd on calcite surface is the exchange reaction between Ca$^{2+}$ and Cd$^{2+}$ owing to their similar ionic radii. The Cd$^{2+}$ can replace Ca$^{2+}$ from accessible surface sites and the dominant reaction mechanism at low initial Cd levels is chemisorption of Cd$^{2+}$ which can be written as Cd$^{2+}$ + CaCO$_3$ $\rightarrow$ CdCO$_3$ (ads) + Ca$^{2+}$. This mechanism gives no pH change during adsorption. Thakura et al. (2006) suggested that Cd is very effectively retained by CaCO$_3$ surface at very low solution Cd$^{2+}$ concentration by the mechanism of chemisorption.

CONCLUSION

In the present work, HAP was successfully synthesized via the wet chemical precipitation route using waste mussel shells as a calcium precursor to produce powder. The HAP prepared was investigated for the removal of cadmium from aqueous solution and the following conclusions can be drawn from the results of the present study:

- The kinetic study shows that the equilibrium time is reached at 60 min.
- The sorption experimental results of the cadmium sorption are in a good correspondence with the Langmuir isotherms.
- Thermodynamic studies indicate that sorption of cadmium on the HAP is an endothermic process.
- Our results support a two-step mechanism involved in the removal of Cd by HAP. Firstly, a rapid ion exchange with Ca$^{2+}$ followed by the dissolution of the hydroxyapatite and the precipitation of the CdHAP.

REFERENCES


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