Optimizing the removal of fluoride from water using new carbons obtained by modification of nut shell with a calcium solution from egg shell

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Carbons loaded with specific chemical moieties were prepared from pecan nut shells employing a natural modifier agent obtained from egg shell, which is rich in calcium, for the selective adsorption of fluoride from water. A L9 orthogonal array of the Taguchi method was used to optimize the synthesis conditions for obtaining these selective carbons. The samples obtained were characterized and the elemental composition, textural parameters and morphology were determined. Fluoride adsorption experiments were performed in synthetic and real groundwater samples. Results showed that carbons obtained from pecan nut shells modified with a calcium solution extracted from egg shells (CMPNS) were more effective for fluoride removal than those using the nut shell precursor as such. The calcium chemical species on the carbon surfaces were more important in the fluoride adsorption process than the carbon textural parameters. In addition, hydrogen carbonate was found to be the main competitor for the active sites of CMPNS during the fluoride removal process.

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1. Introduction

The consumption of drinking water with fluoride concentrations higher than 1.5 mg l⁻¹, which is the limit established by the WHO, may give rise to the prevalence of dental fluorosis in some children, and higher concentrations eventually resulting in skeletal damage in both children and adults [1]. The excess of fluoride in drinking water is caused by natural or anthropogenic sources. Naturally in the United States of America, Africa and Asia, fluoride concentration in groundwater can be as high as 30 mg l⁻¹ and, according to the WHO, more than 260 million people world-wide consume drinking water with fluoride contents higher than 1.5 mg l⁻¹ [2]. In Mexico, the states of San Luis Potosí, Durango, Aguascalientes, Zacatecas and Jalisco are especially affected by this problem [3–5]. Particularly in Aguascalientes State, 43.7% of the wells used as resource of drinking water shows high fluoride contents. Consequently, the exposed population may develop different levels of dental fluorosis according to the classification suggested by Dean [6,7].

Nowadays, several techniques have been developed for treating fluoride-polluted waters. These techniques include: coagulation/precipitation, ion exchange, electrodeionization, reverse osmosis, Donnan dialysis and adsorption, among others [8,9]. The choice of a treatment technique usually depends on the concentration of the F⁻ ions, chemical species in the water source, operation costs, waste management and technical versatility. Limitations in terms of cost, production of significant amounts of waste and difficulties in end-use applications of some of the current treatment techniques have prompted the search for environmentally benign, reliable and low-cost alternatives.

Adsorption is an economical and efficient technology which produces high-quality water [10]. Activated carbon (AC) is considered the universal adsorbent for removing pollutants from water due to its highly developed porosity, large surface area, and versatile surface chemistry [11]. Since the operational costs of adsorption are mainly determined by the price of the adsorbent, there is a growing interest in looking for alternative precursors (i.e., wastes) in AC production. Nowadays, some lignocellulosic wastes such as mango pit and coconut shell have been used as precursors of ACs [12,13]. Despite of availability of these general purpose adsorbents, specific carbons are required for the removal of some toxic pollutants such as fluorides. According to the literature, “bone carbon” is the most suitable material for F⁻ abatement due to its particular chemical composition, which is rich in hydroxyapatite (Ca₅(PO₄)₃(OH)) [5,14]. The superior performance of this type of carbons has been understood in terms of an anionic exchange mechanism between the hydroxyl or the phosphate ion of the hydroxyapatite and the fluoride of the water [15]. A significant disadvantage of bone carbons is their high price. As a consequence, the implementation of adsorption technologies for removal of F⁻ from drinking water is seriously restricted in some areas of Mexico and other developing
countries. In this context, recent studies have been focused in the synthesis or modification of carbons with tailored surface chemistry for fluoride removal. Carbons from Scandinavia spruce wood containing dispersed aluminum oxide or calcium compounds [16,17], adsorbents prepared from steam pyrolysis of rice straw and KMO3-modified [18], a composite of manganese oxide with granular activated carbon and aluminum-impregnated carbon are some relevant examples [19,20].

The purpose of this study was to prepare low cost carbons from two common wastes in Mexico: pecan nut (Carya illinoinsis) shells that would be used as carbon precursor [21,22] and egg shell employed as a source of calcium that was added to the pecan nut shells before their carbonization. Specifically, modified carbons were prepared following a Taguchi L4 orthogonal array. Samples were characterized and tested for fluoride removal from both synthetic fluoride solutions and groundwater from one of the most polluted wells in Agualascalientes (Mexico) [23].

2. Materials and methods

2.1. Materials

2.1.1. Preparation of activated carbons

Pecan nut shells were collected from a nut processing facility located in Nuevo León, Mexico. They were milled and sieved to obtain a particle size of 1 mm. They were then washed with deionized water at 25 °C until pH was constant and, finally, dried at 70 °C for 24 h. The resulting sample, labeled PNS, was used to prepare activated carbons for fluoride removal from water.

For the synthesis of the activated carbons, PNS were impregnated with a calcium solution extracted from egg shell. The extraction procedure comprises a digestion of 50 g of egg shells using one liter of acetic acid (25%, v/v). The resulting solution (100%, v/v) was rich in calcium (12604 mg l\(^{-1}\)). An additional solution (25%, v/v) was prepared by dilution (1:4) of the previous one with deionized water. Both solutions (labeled: 100 and 25%, v/v) were used for the impregnation of PNS according with the experimental design shown in Table 1 (see below). Typical impregnation ratios were 2 ml of solution per gram of PNS.

After impregnation of PNS, samples were dried at room temperature for 24 h prior their thermal treatment. Pyrolysis experiments were performed in a ceramic tubular furnace (Carbolite Eurotherm 2416CC, model CTF 12/65/550). Approximately, 15 g of the dried samples were put into an alumina crucible and heated under 500 ml min\(^{-1}\) of flowing nitrogen from room temperature to 110 °C at 5 °C min\(^{-1}\) and from 110 to 800 °C at 5 °C min\(^{-1}\). In each heating step, the maximum temperature was held for 60 min. Samples were then allowed to cool down to room temperature in N\(_2\) atmosphere. The obtained chars were washed with hydrochloric acid 1 M during 1 h at 150 rpm and, finally, with deionized water at 25 °C until constant pH was attained.

2.2. Methods

2.2.1. Taguchi method used for the optimization of fluoride removal

A L\(_4\) Taguchi orthogonal array experimental design was followed to explore the effect of different variables related to the impregnation process on the final performance of the carbons. Accordingly, three factors were considered at two different levels: concentration of the modifier agent (Factor A) (level 1: 25%, v/v and level 2: 100%, v/v), impregnation temperature (Factor B) (level 1: 25 °C and level 2: 100 °C), and particle size of PNS (Factor C) (level 1: 1 mm and level 2: 1.7 mm). Fluoride adsorption at 30 °C was used as response variable (Y\(_i\)), using an initial concentration of 20 mg l\(^{-1}\) and a mass to volume ratio of 8 g l\(^{-1}\) (see Section 2.2.3). The Taguchi recommends the analysis of the mean response for each run in the inner array as well as the variation using an appropriately chosen signal-to-noise ratio (S/N), which is derived from a quadratic loss function [24] and can be calculated by the following equation:

\[
S/N = -10 \log \left( \frac{1}{N} \sum_{i=1}^{N} \frac{1}{Y_i^2} \right)
\]

where Y\(_i\) is the response variable and N is the replication number of the experiment. The S/N ratios are different according to the type of characteristics used in the experimental design. Note that the larger the characteristic property, the better the result [25].

An analysis of variance (ANOVA) was applied to the data obtained from the statistical design in order to perform a systematic analysis of the relative importance of each factor onto the fluoride adsorption capacity of carbons obtained from PNS and calcium modification. This analysis is based on the following equations:

\[
SS_T = \frac{1}{N} \sum_{i=1}^{N} Y_i^2 - \frac{T^2}{N} \tag{2}
\]

\[
SS_A = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{A_i^2}{n_i} \right) - \frac{T^2}{N} \tag{3}
\]

\[
\sigma_A = \frac{SS_A}{V_A} \tag{4}
\]

where T is the sum of all observations, N the total number of observations (in this case (3)), A\(_i\) is the sum of observations under the i level, n\(_i\) is the number of observations under the i level, k\(_i\) is the number of levels of the factor A, SS\(_T\) is the total sum of squares, SS\(_A\) is the sum of squares for factor A (note that this equation is similar for the factors B and C), V\(_i\) is the total degrees of freedom (i.e., N − 1), v\(_i\) is the factor degrees of freedom (i.e., k\(_i\) − 1), and \(\sigma_A\) is the variance for factor A [24]. Similar equations are used to analyze the remaining factors of the experimental design.

In addition to the four samples prepared following the Taguchi method, namely CMPNS-1, CMPNS-2, CMPNS-3 and CMPNS-4 (Table 1), a reference material (sample CPNS-0) was also considered. CPNS-0 was obtained by a direct carbonization of PNS.

Table 1

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Factors</th>
<th>Carbon name</th>
<th>Fluoride removal (%)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>25</td>
<td>1.0</td>
<td>CMPNS-1</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>25</td>
<td>1.7</td>
<td>CMPNS-2</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>25</td>
<td>1.7</td>
<td>CMPNS-3</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>100</td>
<td>1.0</td>
<td>CMPNS-4</td>
</tr>
</tbody>
</table>

\(^a\)Fluoride removal in replica 1.

\(^b\)Fluoride removal in replica 2.
i.e., without any previous modification using the calcium solution extracted from egg shell.

2.2.2. Physicochemical characterization of carbons

The content of carbon, hydrogen, nitrogen and sulfur of the carbons was obtained with a LECO CHNS-932 elemental analyzer and the oxygen content with a LECO VTF-900. The samples were observed under a SEM (DSM-942, Zeiss, Germany) equipped with an EDX detector (Link-Isis II, Oxford, UK). Solid particles were dispersed on a graphite adhesive tab placed on an aluminum stub. No further coating was required and a semi-quantitative analysis of the principal elements was made by integration of the peaks identified by EDX. The textural parameters were calculated from the adsorption isotherms of nitrogen at −196 °C. An automated adsorption apparatus Micromeritics ASAP 2420 was used. Prior to measurement, samples were outgassed overnight by heating at 523 K under vacuum. The experimental points of the nitrogen isotherms were analyzed with suitable methods for microporous and mesoporous materials.

To determine the percentages of inorganic fraction (i.e., ash content) of the carbons, samples were heated at 815 °C under air atmosphere for 1 h (UNE 32004 standard). The ashes obtained were analyzed by X-ray diffraction. Diffraction patterns of ashes were recorded in a Bruker D8 Advance diffractometer equipped with a Cu Kα X-ray source operated at 40 kV and 40 mA. A single Gölbel mirror configuration was used to monochromate and focus the X-rays on the sample, attaining highly efficient parallel beam geometry. Diffraction data were collected by step scanning with a step size of 0.02° 2θ and a scan step time of 5 s.

2.2.3. Fluoride adsorption tests

Fluoride adsorption tests were performed at 30 °C in batch systems with constant agitation (200 rpm) using polycarbonate bakers covered with a lid. The mass to volume ratio was 8 g l−1 and three types of adsorption experiments were made. The first type of adsorption tests were performed using a 20 mg l−1 synthetic fluoride solution to obtain the response variable values for the Taguchi method (fluoride removal, Section 2.2.1).

A second adsorption study was devoted to obtain fluoride adsorption isotherms in order to determine the maximum F− adsorption capacity of the prepared carbons. In this case, synthetic fluoride solutions of increasing concentration (5–40 mg l−1) were used.

Finally, comparative studies were performed using ground water and synthetic fluoride solutions of similar concentration (14.10 mg l−1). The groundwater was obtained from a polluted well located in the community of Palo Alto in the municipality of Calvillo (21°50′ N, 102°43′ W). Additionally, other ions that were also present in the groundwater in relevant concentrations were identified and the adsorption of these ions was carried out to determine the selectivity of the prepared carbons.

A common methodology was used in the three types of adsorption experiments; after stirring for 36 h at 200 rpm, the sorbent was extracted from the fluoride solution or groundwater. An ion-selective electrode (Denver Instruments model UP-25) was used to determine the fluoride concentration in the solution [26]. At least three experiments for each carbon under similar conditions were conducted, and average results are reported in this study. The amount of adsorbed fluoride was calculated from Eq. (5)

\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

where \( q_e \) is the equilibrium adsorption capacity (mg g−1), \( C_0 \) and \( C_e \) are the initial and the equilibrium fluoride concentrations (mg l−1), \( V \) is the volume of aqueous solution (l) and \( W \) is the adsorbent mass (g).

### Table 2

Ultimate analysis and yield of the activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content (wt%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>CPNS-0</td>
<td>86.9</td>
<td>1.2</td>
</tr>
<tr>
<td>CPNS-1</td>
<td>86.4</td>
<td>1.4</td>
</tr>
<tr>
<td>CPNS-2</td>
<td>84.1</td>
<td>1.4</td>
</tr>
<tr>
<td>CPNS-3</td>
<td>82.6</td>
<td>1.4</td>
</tr>
<tr>
<td>CPNS-4</td>
<td>81.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Aiming at elucidating the adsorption mechanism, the concentration of different ions was also quantified in the equilibrium solution (i.e., after the fluoride adsorption process) with an 850 Professional ionic chromatograph (Metrohm) provided with a conductivity detector and using a standard anionic column (Metrosep A Supp7 250/4 mm) and sodium carbonate (3.6 mM) as mobile phase.

### 3. Results and discussion

3.1. Characterization of the carbon samples modified with calcium solution

Yields and elemental compositions of the studied carbons are shown in Table 2. The carbon content of CPNS-1, CPNS-2, CPNS-3 and CPNS-4 was lower than that of CPNS-0. This has been related to an increase in the ash content of the CPNSs (1–4) materials due to the calcium modification of PNS.

In general, all PNS derived carbons preserved the original shape and size of the precursor. With illustrative purposes, Fig. 1b shows SEM images of CPNS-4 having a particle size of 1 mm. When the particles were milled (<200 μm), some deposits of calcium were observed only in the samples of carbon obtained by modification of PNS with the calcium solution (bright particles in Fig. 1c). A semi-quantitative analysis was performed using EDX results (Fig. 1a).

Table 3 shows the relative areas of the EDX peaks corresponding to the main elements detected in the carbon materials. It is clear that the calcium content was higher for CPNS-1, CPNS-2, CPNS-3 and CPNS-4 carbons than that obtained for CPNS-0. Additionally, the Ca/C ratio was higher in samples CPNS-2 and CPNS-4, i.e., the materials in which a temperature of 100 °C was used during the modification process of PNS (see Table 1). This is an indication of the decisive role of the impregnation temperature in the incorporation of calcium onto PNS.

X-ray diffraction results of the ashes obtained from the modified carbons are reported in Fig. 2. Main reflections corresponding to calcium oxide (CaO) were detected (Fig. 2a). Minor crystalline phases (CaCO₃, CaClOH, KCl) were also found (Fig. 2b). Whereas Ca and Cl species should be present in the carbons due to the modification process, K salts are reported to be constituents of the PNS precursor [27]. KCl is expected to be formed after neutralization of those basic K salts with HCl. Although KCl is very soluble in water, residual amounts are likely to remain on the surface of the chars after successive washings. In that sense, it should be remained here that KCl is only observed in minimum quantities when analyzing the ashes of the modified carbons, i.e., after concentration of the inorganic matter. Calcium hydroxychloride was an interesting compound detected by DRX. According to [28] CaClOH is the first product formed when HCl is absorbed by limestone (at high temperatures), thus suggesting that the modification process designed in this study for the carbons led initially to the formation of calcium carbonate which would be subsequently transformed to CaClOH during the ashing process. Alternatively, CaClOH has been also detected after the thermal dehydration of CaCl₂·2H₂O, which could be therefore present on the carbons after partial neutralization of the calcium salts with HCl. It seems clear from the
XRD analysis of the carbon ashes and the textural parameters that such neutralization has been limited to the most accessible calcium deposits of the carbon materials. As a consequence, the bright spots corresponding to calcium rich particles of Fig. 1c were only noticeable after crushing the original particles.

3.2. Fluoride adsorption studies

3.2.1. Statistical analysis of the Taguchi method

The fluoride adsorption capacity of carbons, which was measured at 30 °C using an adsorbent/solution ratio of 8 g l⁻¹ and an initial F⁻ concentration of 20 mg l⁻¹, has been selected in this study as the response variable to evaluate the effect of the three different factors considered in the Taguchi method. Fluoride adsorption results are reported in Table 1. The combination of factors selected in the experiment 4 provides the better results in terms of fluoride removal with almost an efficiency of 84%. In contrast, the reference sample was systematically outperformed by the modified carbons: only removal efficiencies of 29% were found when using CPNS-0.

Table 4 shows the values of S/N response for the modification of PNS using a calcium solution from egg shell. These results revealed that the optimal conditions for the modification of PNS when looking for selective carbons for fluoride removal are: A (concentration of the modifier agent) at level 2 (100%, v), B (impregnation temperature) at level 2 (100 °C) and C (particle size of PNS) at level 1 (1 mm). Under these conditions, the obtained carbon may remove up to 90% of fluoride present in the solution. Results of the analysis of the variance (ANOVA) are shown in Table 4. The most influential factor was the particle size of PNS because the variance (σ²) was higher (8.59) in comparison with the other factors. The impregnation temperature was the second factor and, finally, the concentration of activating agent (i.e., calcium solution extracted from egg shells).

3.2.2. Fluoride adsorption isotherms and modeling

Fluoride adsorption isotherms on the studied carbons were obtained in order to determine their maximum adsorption capacity (qₑ) [Fig. 3a]. Sample CMPNS-4 showed the highest adsorption capacity (2.3 mg g⁻¹) in spite of its very low S_{BET} (17 m² g⁻¹). This result suggests that the surface moieties incorporated during the preparation of the modified carbons are playing a more important role in the adsorption process than the textural parameters. Moreover, the fact that sample CPNS-0 showed a relatively low fluoride adsorption capacity remarks the relevance of the presence of calcium on the carbon samples for fluoride removal.

The equilibrium solutions of these particular fluoride adsorption experiments for carbons CMPNS-(1–4) were analyzed by ion chromatography. A considerable chloride concentration was found in the equilibrium solutions after fluoride removal. For example, in an adsorption experiment carried out with CMPNS-4, in which the initial fluoride and chloride concentrations were 30 mg l⁻¹ and

---

**Table 3**

EDX semi-quantitative analysis results and textural parameters of the carbons under study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratios of selected EDX peaks</th>
<th>Textural parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/C</td>
<td>CI/C</td>
</tr>
<tr>
<td>CPNS-0</td>
<td>0.395</td>
<td>0.413</td>
</tr>
<tr>
<td>CMPNS-1</td>
<td>0.474</td>
<td>0.784</td>
</tr>
<tr>
<td>CMPNS-2</td>
<td>0.798</td>
<td>0.677</td>
</tr>
<tr>
<td>CMPNS-3</td>
<td>0.595</td>
<td>0.809</td>
</tr>
<tr>
<td>CMPNS-4</td>
<td>0.816</td>
<td>1.666</td>
</tr>
</tbody>
</table>

---

![Fig. 1. EDX analysis (a) and SEM images of CMPNS-4 with a particle size of 1 mm (b) and after grinding (<200 µm) sample (c).](image)

![Fig. 2. XRD pattern of the ashes of CMPNS-4 (a) and zoom of the scale (b).](image)
Table 4
Statistical parameters for the Taguchi method and analysis of the variance related to the fluoride removal using carbons modified with a calcium solution extracted from egg shells.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Mean S/N ratio Level 1</th>
<th>Mean S/N ratio Level 2</th>
<th>Degrees of freedom (1)</th>
<th>Sum of squares (SS)</th>
<th>Variance (σ²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Concentration of activating agent (% v)</td>
<td>35.05</td>
<td>36.21</td>
<td>1</td>
<td>1.34</td>
<td>1.34</td>
</tr>
<tr>
<td>B: Impregnation temperature (° C)</td>
<td>34.81</td>
<td>36.46</td>
<td>1</td>
<td>2.69</td>
<td>2.69</td>
</tr>
<tr>
<td>C: Particle size of nutshell (mm)</td>
<td>37.10</td>
<td>34.17</td>
<td>1</td>
<td>8.59</td>
<td>8.59</td>
</tr>
<tr>
<td>Error</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>3</td>
<td>12.634</td>
<td>3.05</td>
<td>3.05</td>
<td></td>
</tr>
</tbody>
</table>

0.05 mg l⁻¹, respectively, the final concentration of fluoride and chloride was 18 mg l⁻¹ and 11.5 mg l⁻¹, respectively. In contrast, only residual amounts of Cl⁻ (<1 mg l⁻¹) were found when CMPNS samples were submerged in deionized water only (i.e., with a virtual F⁻ concentration of 0 mg l⁻¹). This would suggest that chloride plays an important role in the adsorption of fluoride using CMPNS as adsorbents. The relevance of Cl⁻ in fluoride removal has been just recently reported [16].

In the present work, it should be borne in mind that it is not only chloride that favors the F⁻ adsorption process. The role of calcium is crucial in the light of the results of Table 3, i.e., differences in Cl/C contents cannot explain the overall performance of the materials under consideration. According to the previous observations, the following fluoride adsorption mechanism on CMPNS is suggested:

\[
\text{C–Cl(aq) + H}_2\text{O} \rightarrow \text{C–OH(aq) + H}^+ + \text{Cl}^-(aq) \tag{6}
\]

\[
\text{C–OH(aq) + F}^-(aq) \rightarrow \text{C}^\circ \text{F}^- + \text{OH}^- \tag{7}
\]

where C represents the carbon rich surfaces modified with calcium compounds [16]. In addition to this, the possibility of fluoride removal by precipitation with calcium cannot be discarded. This precipitative mechanism would be limited to the inner porous structure of the carbons, since insignificant amounts of Ca (less than 0.1 mg l⁻¹) were detected in suspensions of CMPNS in pure deionized water.

Fluoride adsorption isotherms were fitted to both the Langmuir and Freundlich equations. Specifically, Langmuir isotherm assumes that adsorption occurs in a monolayer where the active sites are identical and energetically equivalent. This isotherm is given by

\[
q_i = \frac{q_m K_C}{1 + K_C C_a} \tag{8}
\]

where \(q_i\) and \(C_a\) are the fluoride adsorption capacity (mg g⁻¹) and concentration (mg l⁻¹) at equilibrium, \(q_m\) is the theoretical maximum adsorption capacity (mg g⁻¹), and \(K\) (L mg⁻¹) represents the Langmuir equilibrium constant, respectively. On the other hand, Freundlich model is an empirical expression used to describe a heterogeneous system and is defined as

\[
q_i = K_f C_a^{1/\nu} \tag{9}
\]

where \(K_f\) (mg⁻¹ / l¹/ν g⁻¹) and \(n_f\) are parameters characteristic of the adsorbent-adsorbate system. Data correlation of our experimental results was performed using a nonlinear regression approach based on the minimization of the following objective function

\[
F_{obj} = \frac{\sum_{i=1}^{ndat} \left( \frac{q_i^{exp} - q_i^{calc}}{q_i^{exp}} \right)^2}{ndat} \tag{10}
\]

where \(q_i^{exp}\) and \(q_i^{calc}\) are the experimental and predicted fluoride adsorption capacity and \(ndat\) is the overall number of experimental data, respectively. The stochastic optimization method Simulated Annealing was used for the minimization of Eq. (10). In this study, the criterions used to measure the goodness of the fittings of adsorption isotherm models were the correlation coefficient \((R^2)\), the behavior of the relative residuals, the objective function value \((F_{obj})\), and the mean absolute percentage deviation \((E)\) between calculated and experimental fluoride adsorption capacities, where

\[
E = \frac{100 \sum_{i=1}^{ndat} \left| \frac{q_i^{exp} - q_i^{calc}}{q_i^{exp}} \right|}{ndat} \tag{11}
\]

Results of data fitting for both isotherms are given in Table 5. Overall, the values of the parameters of both isotherms indicate a favorable fluoride adsorption by the modified carbons. However, the fluoride adsorption data are better described by the Langmuir model. Specifically, this isotherm model showed a mean absolute error of 15%.
Table 5
Parameters of Langmuir and Freundlich isotherm models for fluoride adsorption from aqueous solution using carbons modified with a calcium solution extracted from egg shell.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$</td>
<td>$K$</td>
</tr>
<tr>
<td>CPNS-0</td>
<td>0.81</td>
<td>0.49</td>
</tr>
<tr>
<td>CPNS-1</td>
<td>1.61</td>
<td>1.96</td>
</tr>
<tr>
<td>CPNS-2</td>
<td>1.27</td>
<td>2.88</td>
</tr>
<tr>
<td>CPNS-3</td>
<td>1.29</td>
<td>1.99</td>
</tr>
<tr>
<td>CPNS-4</td>
<td>2.51</td>
<td>1.06</td>
</tr>
</tbody>
</table>

percentage deviation ($E$) from 3.5% to 13.4% and correlation coefficients ($R^2$) from 0.90 to 0.96.

Finally, the fluoride adsorption capacities ($q_m$) of the carbons tested in this work are higher than that obtained for the carbon prepared from cashew nut shell impregnated with zincium (1.83 mg g$^{-1}$) [29], but very similar to the adsorption capacities of some commercial bone carbons such as the Fija fluor (2.65 mg g$^{-1}$) or the bone carbons prepared from raw bones of cow, pig, chicken and fish (<2 mg g$^{-1}$) [15,30].

3.2.3. Fluoride adsorption from groundwater

The drinking water used in this section was obtained from a well located in Palo Alto Calvillo, Aguascalientes, Mexico. A complete water characterization was made in an external certified lab and the results confirm that the fluoride concentration was very high (Table 6), when compared with the concentration limits established by Mexican regulation (1.5 mg l$^{-1}$). Fig. 3b shows the results of fluoride removal using synthetic and ground water with the same initial concentration (14.10 mg l$^{-1}$). Fluoride removal was less efficient from the groundwater than from the synthetic solutions due to competition with other ions such as sulfate and hydrogencarbonate. The performance of the original precursor (PNS) as biosorbent is very limited when treating groundwater. On the other hand, sample CMPNS-4 (with rather low specific surface area and the highest amount of calcium) remains also in real water as the most effective carbon for fluoride removal, although the percentage was very low (~20%) due to the complex composition of the groundwater studied in this work. In order to explain better the important decrease observed in the ability of the tested carbons when treating groundwater, additional adsorption tests were performed with this groundwater and the adsorption of sodium, potassium, calcium, magnesium, hydrogencarbonate, sulfate, chloride and phosphate was determined. Results obtained for CMPNS-4 are shown in Fig. 4. This carbon is also effective in removing hydrogencarbonate (5.8 mg g$^{-1}$), which constitutes then the main competitor and limits the selectivity of CMPNS-4 toward fluoride. This result agrees with previous findings [17]. Sulfate is also adsorbed on CMPNS-4 but to a lower extent (0.048 mg g$^{-1}$).

4. Conclusion

It is possible to obtain low cost carbons, selective for fluoride removal, employing pecan nut shell as a precursor and using a calcium solution extracted from egg shell as a modifier agent during the carbon preparation. Additionally, it has been demonstrated that the use of the L$_4$ orthogonal array of the Taguchi method is a good alternative to optimize the carbon synthesis for this purpose. The best sample for fluoride removal in synthetic solutions was also effective when treating real groundwater, although a significant drop in the adsorbent performance was nevertheless observed due to competitive adsorption. Specifically, hydrogencarbonate is the main competitor for the fluoride active sites present on CMPNS.

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