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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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ABSTRACT

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 L_4 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, hydrogencarbonate was found to be the main competitor for the active sites of CMPNS during the fluoride removal process.

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, electrodialysis, 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 coconout 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 ($Ca_5(PO_4)_3(OH)$) [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

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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 $KMnO_4$-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 illinoinensis*) 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 L_4 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 Aguascalientes (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 designed 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 and level 2: 100%, 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). 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

$$\frac{S}{N} = -10 \log \frac{\sum_i (1/{Y_i}^2)}{n} \quad (1)$$

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:

$$SS_T = \left[\sum_{i=1}^{N} Y_i^2\right] - \frac{T^2}{N} \quad (2)$$

$$SS_A = \left[\sum_{i=1}^{k_A} \left(\frac{A_i^2}{n_{A_i}}\right)\right] - \frac{T^2}{N} \quad (3)$$

$$\sigma_A = \frac{SS_A}{\nu_A} \quad (4)$$

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_{Ai} is the number of observations under the i level, k_A 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), ν_T is the total degrees of freedom (i.e., $N-1$), ν_A is the factor A degrees of freedom (i.e., $k_A - 1$), and σ_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
Experimental layout for the modification of pecan nut shell with a calcium solution extracted from egg shells, following a L_4 orthogonal array of the Taguchi method, and results obtained for fluoride removal.

Experiment	Factors			Carbon name	Fluoride removal (%)		
	A: Concentration of activating agent (%, v/v)	B: Impregnation temperature (°C)	C: Particle size of nut shell (mm)		[a]R1	[b]R2	S/N ratio
1	25	25	1.0	CMPNS-1	60.8	61.1	35.7
2	25	100	1.7	CMPNS-2	52.3	52.8	34.4
3	100	25	1.7	CMPNS-3	49.4	50.0	33.9
4	100	100	1.0	CMPNS-4	83.9	84.4	38.5

[a]Fluoride removal in replica 1.
[b]Fluoride removal in replica 2.