# FLUORIDE REMOVAL FROM WATER USING NUTSHELL-BASED ADSORBENT

**ERGOVIĆ RAVANČIĆ M.[1] and HABUDA-STANIĆ M.[2]**

[1] Department of Food Technology, Polytechnic in Požega, Vukovarska 17, 34000 Požega, Croatia, [2]Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 20, 31000 Osijek, Croatia
E-mail: mirna.habuda-stanic@ptfos.hr

## ABSTRACT

Heightened fluoride concentration in drinking water can cause health problems such as immunological defects, dental and skeletal fluorosis, reproduction problems and induces birth. Several techniques have been worldwide used for fluoride removal from water: coagulation and precipitation, electrochemical treatments, ion-exchange, membrane filtration and adsorption. Among all above mentioned, adsorption technique is considered to be cheapest and efficient enough method for fluoride removal. In this study the batch tests were used to define efficiency of fluoride removal from aqueous solution using nutshell-based activated carbon, i.e. the effects of initial fluoride concentration (2-100 mg/l) and solution temperature (25-45°C) were examined. Up to 46% fluoride was removed. The obtained adsorption data were analyzed using the Langmuir and Freundlich isotherm models showing that fluoride adsorption onto nutshell-based activated carbon fits the Freundlich model well.

**Keywords**: fluoride removal, adsorption, water, activated carbon, nutshell

## 1. Introduction

Fluoride is a nutrient for human body at low concentration but due to fluoride ions high electronegativity continuous ingestion of food and water with high concentration of fluoride ions can cause toxic effect in human body such as dental fluorosis, teeth mottling, skeletal fluorosis and deformation of bones in children as well as in adults (WHO, 1984; Meenakshi and Maheshwari, 2006; Ozsvath, 2009). The maximum contaminant level (MCL) of fluoride concentration in drinking water proposed by World Health Organization, European Community Directive guidelines and Croatian Regulation is 1.5 mg/L (WHO, 2008; 98/83/EC; MZHR, NN 125/2013). Various technologies are used worldwide for fluoride removal such as coagulation and precipitation, membrane processes, electrolytic treatment, ion-exchange and adsorption (Meenakshi and Maheshwari, 2006). Adsorption is very often used technique for fluoride removal due to low cost, flexibility and simplicity of design, high efficiency, easy handling and high selectivity. Activated carbons are the most important commercial adsorbents whose large active surface and chemical structure allows to be used in a wide variety of industrial applications, and, among them, water purification and industrial wastewater cleaning. Different types of activated carbons, with animal, plant, or mineral origin, have been tested for water defluoridation. (Habuda-Stanić *et al*., 2014).

The objective of this study was to investigate the removal of fluoride by nutshell-based activated carbon and to determine the effect of initial fluoride concentration and solution temperature. The Langmuir and Freundlich isotherm models were used for determination of adsorption mechanism onto nutshell-based activated carbon.

## 2. Materials and methods

Activated carbon was obtained by carbonization of nutshells which primarily were grained using electric mill and sieved to obtained particle size ranged from 0.2 to 0.2 mm. Obtained nutshells particles were carbonized at 300°C for one hour, oxidized by sulfuric acid (1:1) during 24 hours at room temperature, and then rinsed by deionized water until neutral pH. Carbonized and

oxidized nutshell particles were then dried at 105°C during 3 hours, cooled and stored in desiccator.

A batch adsorption experiments were conducted using fluoride stock solution of 100 mgF/L prepared by dissolving 0.221 g of anhydrous NaF (Merck) in 1 liter of deionized water which has been further diluted with deionized water to subsequent concentrations (2-100 mg/L). pH of aqueous solutions were adjusted using 0.1 M HCl or 0.1 M NaOH. The pH values were measured by pH meter Seven Easy (Mettler Toledo).

Experiments were performed in using 100 ml conical flasks with 100 ml test fluoride solution at three different temperatures (25°C, 35°C and 45°C) using temperature-controlled shaker (Kottermann Labortechnik) at 120 rpm. After defined contact time, aqueous solutions were filtered through a 0.45 μm cellulose acetate membrane filters and fluoride concentrations were determined using fluoride ion selective electrode (Hach) and total ionic strength adjustment buffer (TISAB). All experiments were conducted in duplicate and average values are presented. The specific fluoride uptake $q_e$ (mg/g) was determined due to following equation:

$$q_e = \frac{(c_0 - c_e)}{m} \times V \tag{1}$$

where $c_0$ and $c_e$ are the initial and equilibrium fluoride concentrations in aqueous solutions (mg/L), respectively, $V$ is the solution volume (L), and $m$ (g) is the adsorbent mass.

The Langmuir and Freundlich isotherms were used for determination of adsorption mechanism onto nutshell-based activated carbon at temperatures of 25°C, 35°C and 45°C.

Langmuir adsorption isotherm is often applied in solid/liquid system to describe the saturated monolayer adsorption. It can be represented as (Dalifullah *et al*., 2007):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the amount of ion adsorbed (mg/g), $q_m$ is $q_e$ for a complete monolayer (mg/g) and $K_L$ is adsorption equilibrium constant (Lm/g). To evaluate the adsorption capacity for a particular range of adsorbate concentration, the before mentioned equation (Eq. 2) is usually used in a linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{3}$$

The constants $q_m$ and $K_L$ can be determined from a linearized form of Eq. 3 by the slope of the linear plot of $C_e/q_e$ versus $C_e$.

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface and suggests a multilayer adsorption. Adsorption energy exponentially decreases on completion of the adsorption centers of an adsorbent. The Freundlich isotherm was commonly presented as follows (Sepehr *et al*., 2013):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

or linearized as:

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \tag{5}$$

where $q_e$ is the amount of fluoride adsorbed per unit weight of the adsorbent at equilibrium (mg/g) and $C_e$ is the equilibrium concentration of fluoride solution (mg/L). The Freundlich constants $K_F$ and $n$ (as $1/n$) are measures of adsorption capacity (mg/g) and adsorption intensity

or surface heterogeneity. It is also consider that the value of 1/*n* represents a joint measure of both the relative magnitude and diversity of energies associated with a particular adsorption process.

## 3. Results and discusion

### 3.1. Effect of initial fluoride concentration and temperature onto fluoride removal

The effect of the initial fluoride concentration on the adsorption capacity of prepared nutshell-based activated carbon was tested using fluoride solutions with initial concentrations ranged from 2 to 100 mg/L under neutral pH and three temperature regimes (25°C, 35°C and 45°C). The adsorbent dosage was 10 g/L, contact time 120 min and obtained results are presented in Figure 1. Comparing percentages of fluoride removal it can be observed that highest efficiency of fluoride removals were obtained at 25°C and that higher temperatures did not enforced bonding of fluoride ions onto prepared nutshell-based activated carbon. The highest percentages of fluoride removals were achieved when nutshell-based activated carbon were used for fluoride adsorption at 25°C while the lowest fluoride removals were achieved at 35°C. The effect of initial fluoride concentration onto fluoride removal efficiency was also observed. The increase of initial fluoride concentration increased adsorption up to 25 mg/L while further increasing of fluoride concentration resulted with decreasing of percentage of fluoride removal at all temperature regime. The highest fluoride removal of 48% was obtained at 25°C using standard solution with 25 mgF/L, while the lowest fluoride removal of 7% was noted when experiment was conducted with 2 mgF/L at 35°C.

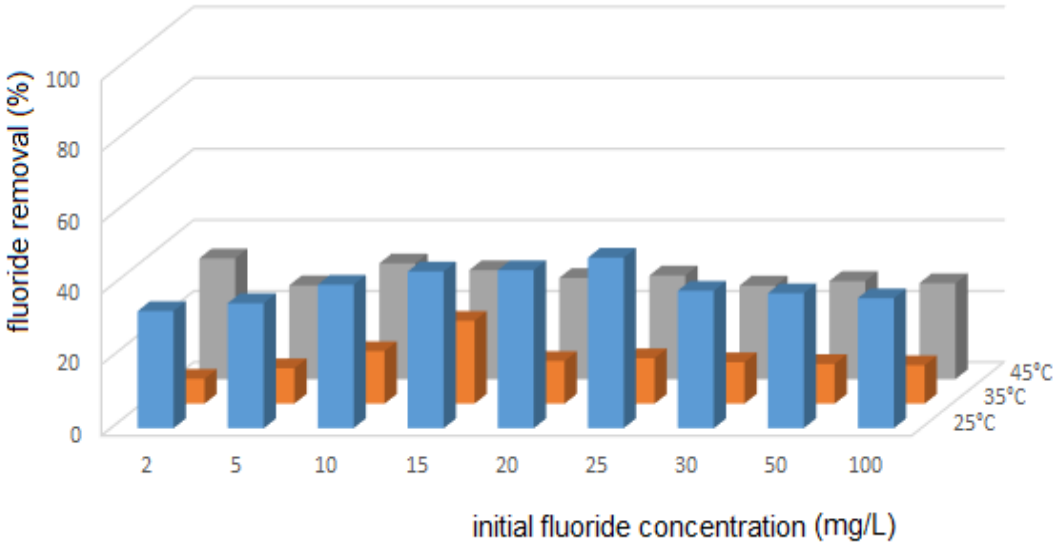


**Figure 1:** Effect of the initial fluoride concentration onto percentage of fluoride removal under three temperature regimes.

### 3.2. Adsorption Isotherms

The results obtained via batch adsorption tests were analyzed using previously described Langmuir and Freundlich adsorption isotherm models in order to define fluoride adsorption mechanism as well as to define maximum adsorption capacity of prepared nutshell-base activated carbon. Adsorption isotherms were obtained at three temperatures (25°C, 35°C and 45°C) and pH 7 at various fluoride concentrations. Figure 2 and 3 shows Langmuir and Freundlich isotherms while calculated values of Langmuir and Freudlich isotherm parameters are presented at Table 1.

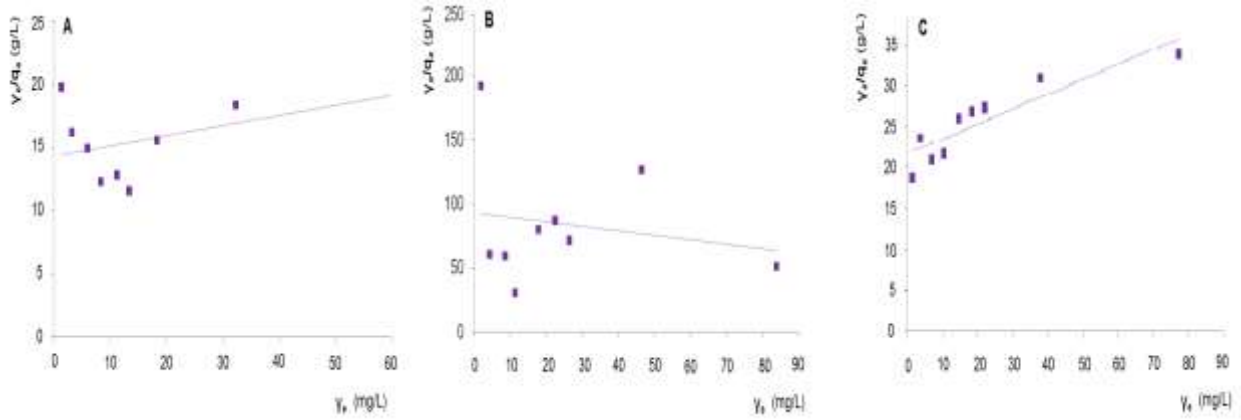


**Figure 2:** Langmuir isotherm of fluoride adsorption onto nutshell-base activated carbon at (A) 25°C, (B) 35°C and (C) 45°C.

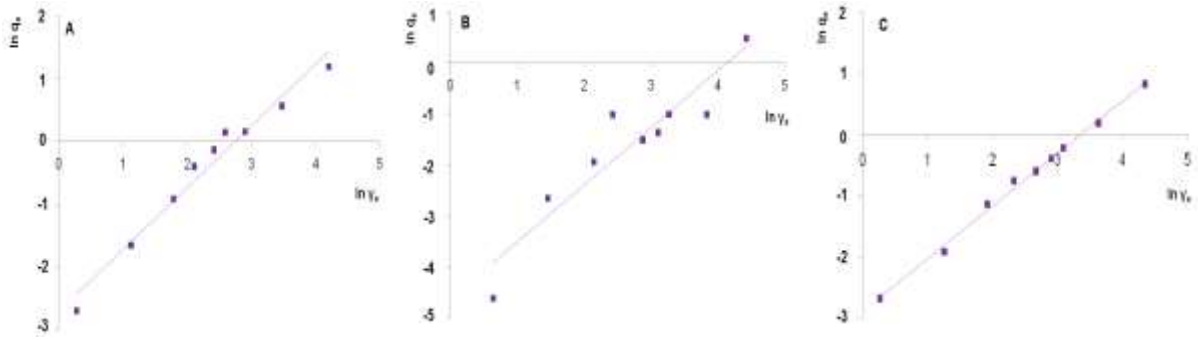


**Figure 3:** Freundlich isotherm of fluoride adsorption onto nutshell-base activated carbon at (A) 25°C, (B) 35°C and (C) 45°C.

Based on $R^2$ values, which are related to linear relationship between obtained data, for bought used isotherms models (Table 1) it can be observed that Freundlich model better fitted obtained results at all tested temperatures implicating the multilayer adsorption mechanism (Freundlich, 1906). The maximum adsorption capacity of nutshell-based activated carbon calculated from the linear form of Freundlich model was 0.066 g/g noted at 25°C. The 1/n value is related to intensity of adsorption and if value is higher than 1 adsorption of fluorides is unfavorable while the value of 1/n below 1 indicating favorable adsorption. The higher 1/n value also indicates more affinity and heterogeneity of adsorption sites for efficient adsorption. From Table 1 it can be observed that in this study, 1/n values ranged from 0.86 at 45°C to 1.12 at 35°C implying that at 25° and 45°C fluoride adsorption is favorable, while at 35°C due to value of 1/n of 1.12, fluoride adsorption is unfavorable.

**Table 1:** Langmuir and Freundlich constants for the fluoride adsorption onto nutshell-base activated carbon at pH 7 and 25°C.

| Temperature, °C | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $q_m$, mg/g | $K_L$, L/mg | $R^2$ | 1/n | $K_f$, g/g | $R^2$ |
| **25°C** | 12.56 | 0.006 | 0.26 | 0.99 | 0.066 | 0.97 |
| **35°C** | 2.85 | 0.008 | 0.03 | 1.12 | 0.009 | 0.87 |
| **45°C** | 5.48 | 0.009 | 0.80 | 0.86 | 0.057 | 0.99 |

## 4. Conclusions

This study investigated fluoride removal from aqueous solution using nutshell-based activated carbon. Adsorption tests were conducted in order to define the effects of initial fluoride concentration (2-100 mg/L) and solution temperature (25-45°C). It was observed that adsorption efficiency was increased when initial fluoride concentration increased up to 25 mg/L. Further increasing of initial concentration decreased efficiency of fluoride removal. The increasing of temperature did not increased amount of fluoride adsorbed onto nutshell-based activated carbon, and higher percentage of fluoride removal of 46% was observed at 25°. Analyzing obtained data with Langmuir and Freundlich isotherm models it was observed that adsorption mechanism of fluoride onto nutshell-based activated carbon followed Freundlich model i.e. multilayer adsorption with heterogeneous adsorption energy.

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