HYDROTHERMAL SYNTHESIS OF A HYBRID ADSORBENT Ce:Mn-CARBON FOR FLUORIDE REMOVAL FROM WATER

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Introduction
Fluorine can be present in drinking water and is considered beneficial human being at levels of around 0.8 to 1.0 mg L⁻¹, but it is dangerous if it exceeds 1.5 mg L⁻¹, which is the maximum limit recommended by the World Health Organization (WHO). Exposure to high concentrations of fluoride can cause dental and skeletal fluorosis or neurological damage, and in severe cases, increased susceptibility to kidney disease and cancer. Fluoride concentrations of up to 30 mg L⁻¹ can be found in groundwater in many parts of the world and are present in at least 25 countries. Due to the above, it is necessary to develop new technologies and highly efficient materials for the fluoride removal from water. In recent years, bimetallic oxides as Ce-Mn; Fe-Ti; Ce-Ti and Al-Mn have had a great interest in the fluoride removal and/or other contaminants. However, these bimetallic oxides have been studied in colloidal or nanoparticles form, which makes their application quite difficult in continuous systems. Therefore, it is desirable to anchor these nanoparticles on a support to allow their application. Activated carbon is a poor adsorbent for fluoride, but this can provide a stable support to achieve a high dispersion of metallic phases that have a high fluoride adsorption capacity. Therefore, the objective of this research is to improve the adsorption capacity of fluorides of granular activated carbon by anchoring Ce-Mn oxyhydroxides on its surface by means of hydrothermal synthesis assisted by a microwave oven.

Materials and Methods
Modification of GAC was performed by using the following method: 0.1 g of granular activated carbon F-400 (GAC) were contacted with a Ce:Mn solution for 12 h at 25 °C and 130 rpm. Subsequently the impregnated GAC was synthesized in a microwave oven for 30 min at 110 °C. Adsorption isotherm was determined for both the GAC and GAC-Ce:Mn as follows: 30 mL of fluoride solutions at different concentrations (1 to 80 mg L⁻¹) were added to 0.03 g of the adsorbent at 25 °C. The pH sample was adjusted to 7 ± 0.2. The fluoride concentration was measured by selective ion electrode (Thermo Electron Corp). Surface charge distribution and point of zero charge (pHₚZC) of each adsorbent were obtained by an automatic titrator (Mettler-Toledo T70). 0.03 g were dispersed in 25 mL of 0.1 M NaCl and next stirred for 12 h. Then, a titration with 0.1 N NaOH was carried out in a nitrogen atmosphere. The pKₐ distribution was obtained by using the SAEIUS-pK-Dist© (1994) program.

Results and Discussion
Figure 1A shows the arsenic adsorption isotherms of GAC and Ce:Mn-GAC. The Langmuir and Freundlich models adjusted the adsorption equilibrium data. The Langmuir model presented the best mathematical fit by better describing the adsorption experimental data of all materials, based
on the highest correlation coefficient ($R^2$). This indicates the formation of a monolayer of fluoride ions on the surface of GAC and (Fe:Ce)-GAC. The presence of this monolayer is due to the electrostatic interaction between $F^-$ and surface of adsorbent, and through the exchange of ligands. In addition, the $q_{\text{max}}$ parameter of Langmuir can be interpreted as the maximum coverage for the formation of this monolayer. The GAC fluoride adsorption capacity is related to its metal oxides contain, such as Al, Si, Mn and Fe. The Ce:Mn-GAC showed an adsorption capacity ($q_{\text{max}}$) of 8.6 mg g$^{-1}$, which can be associated with a higher content of hydroxide groups provided by the bimetallic oxyhydroxides anchored on the GAC surface. From the adsorption isotherm, it was determined that the material Ce:Mn-GAC had the maximum adsorption capacity, at pH 7, 25 ºC and $C_e = 5$ mg L$^{-1}$, with a $q$ value of 6.4 mg g$^{-1}$ while GAC only reached 0.33 mg g$^{-1}$. On the other hand, the intensity and $pK_a$'s distribution are presented in Figure 1B, where the chemical changes in the surface of commercial and modified GAC are illustrated. It can be seen that the Ce:Mn-GAC showed an increase in the phenolic groups ($8<pK_a<11$) of 0.12 mmol g$^{-1}$. The above can be attributed to the increase of $OH^-$ groups of Ce (oxy)hydroxides anchored on the GAC surface. In addition, the acidic conditions present during the synthesis process generated carboxyl groups ($3<pK_a<6$). The peaks of high intensity in $7<pK_a<8$ of the Ce:Mn-GAC are attributed to the presence of cerium hydroxide. Due to the high density of $OH^-$ groups on the surface of the hybrid material, the fluorides adsorption capacity of Ce:Mn-GAC was 4.3 times higher than GAC. According to the adsorption kinetics, 30 min are required to remove 80% of the maximum capacity and about 2 h to achieve equilibrium.

**Figure 1.** A) Adsorption isotherms at pH 7 and 25 ºC. B) pK$_a$'s distribution of GAC and Ce:Mn-GAC

**Conclusions**
The hydrothermal synthesis process assisted by microwave oven allows to anchor Ce:Mn oxyhydroxides on the GAC surface at a synthesis time of 30 min. The improved adsorbent material has a higher density of hydroxyl groups, which is reflected in a high fluoride adsorption capacity, up to 8.6 mg g$^{-1}$, 4.3 times greater than the commercial GAC.

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References

