**Two approaches for fluoride removal from natural waters: adsorption on a new titanium oxide material and transport through a polymer inclusion membrane**

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The presence of fluoride can be either beneficial or harmful for human health depending on the fluoride concentration in drinking water. Lower concentration of fluoride in drinking water is determined as an essential micronutrient to prevent dental caries and facilitate the mineralization of hard tissues, while at higher levels, fluoride can have adverse impact on human health, causing dental or skeletal fluorosis. The standard level of fluoride in drinking water is 1.5 mg L-1 according to the WHO.

Extensive and widespread use of fluoride in different industries including aluminum refining, fertilizer and semiconductor manufacturing, glass and ceramic production has been found to be a reason for releasing large quantities of fluoride in the environment.

Among the different technologies developed for inorganic species removal, the adsorption process is a well-established technology that can be used for fluoride removal from groundwater, especially for small communities, because of the ease of handling, sludge-free operation, and possibility of regeneration. It is well-known that fluoride is adsorbed by ferric and aluminum (hydr)oxides through the formation of inner-sphere surface complexes with the surface hydroxyl sites (Quiao 2014). When the surface complexes are formed, the surface hydroxyl groups, which are considered as the most abundant and active adsorption sites for adsorption of anions, will be replaced by the adsorbed anions.

Recently, a new adsorbent based on titanium dioxide (Adsorbsia As600, from Dow) is commercially available and specially designed for As removal. In our work we have characterized this material by different techniques such as X-ray diffraction and XPS. Moreover, this new solid has been explored for the first time as a fluoride adsorbent and all the parameters affecting the system have been evaluated such as adsorption isotherms, possible interferences, and effect of pH, among others. The good performance of this adsorbent for fluoride has been demonstrated achieving high removal efficiency values using different polluted waters, and allowing, after its use, the fulfillment of the limits established by the WHO.

Moreover, the same problem has been investigated using a membrane system developed specifically for fluoride treatment. In this particular case, we have prepared different polymer inclusion membranes based on cellulose triacetate (CTA) as a base polymer and Aliquat 336 and tributyl phosphate (TBP) as the organic phase. The use of a separation system based on a chemically functionalized membrane allows the extraction and elution in one single-step and avoids the saturation of the active sites, as it happens in the case of the adsorbents. Moreover, the high operation and high consumption of electrical energy associated to membrane technology is here avoided since the separation process is based on a chemical pumping instead of a physical rejection. The PIM system developed allowed the removal of fluoride at different level concentration from natural waters bearing different chemical characteristics.

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