**Detailed Understanding of Transport Mechanisms during Sr2+ and Cs+ Adsorption onto Cryogels via Application of Rigorous Diffusion Models**

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**1. Introduction**

The removal of heavy metals and radioactive elements from wastewaters is nowadays imperative to reach the goals of a sustainable development. In this context, adsorption is a consolidated purification technology characterized by generally low costs and high operating flexibility. In particular, polymeric cryogels are emerging adsorbents with high potentiality for the removal of different classes of adsorbates from liquid phase thanks to their tunable chemico-physical and microstructural properties [1]. Limited rigorous analyses on the complex transport mechanisms occurring along adsorption in porous sorbents are currently available in the literature (and, in particular, for cryogels), and most of the adopted dynamic models rely on empirical expressions [2].

In this work we investigate the batch adsorption dynamics of strontium and cesium ions onto two cryogels, and a detailed analysis of kinetic results was attained by adopting a rigorous diffusional model accounting for fluid film, pore volume and surface transport mechanisms coupled with a time-dependent expression for surface diffusivity.

**2. Methods**

Two kinds of cryogels (termed as AAC and SAC) were synthesized by means of free-radical polymerization performed at sub-zero temperatures [3]. Batch kinetic adsorption tests were performed at room temperature and by fixing both the initial concentration of Sr2+ and Cs+ ions (100 mg L−1) and the sorbent mass/solution volume ratio (0.7 g L−1). The time trend of the sorbent specific adsorption capacity $\overbar{q(t)}$ was evaluated by monitoring the evolution of each metal ion concentration in the liquid phase via ICP-MS technique. Kinetic data were analyzed by means of the rigorous Pore Volume Surface Diffusion model (abbreviated as PVSDM [4]), in which we adopt our recently proposed fractal-like expression for surface diffusivity [5] (model named PVSDM−MBI):

$\frac{1}{D\_{s}(t)} = \frac{1}{D\_{s0}}\left[\frac{β}{\left(t+1\right)^{-h}}+\frac{(1-β)}{\left(t+1\right)^{α}}\right]$ (1)

where *Ds*(*t*) and *Ds0* are the time-dependent and zero-loading surface diffusion coefficient, respectively; **, *h* and ** represent the fractional contribution of the fractal diffusion resistance, the fractal and hopping exponent, respectively. The resolution of ordinary and partial differential equations was carried out in the MATLAB R2019b numerical environment by adopting the method of lines.

**3. Results and discussion**

Figure 1a) reports, as an example, a comparison between experimentally and theoretically determined dynamic adsorption profiles for strontium capture onto AAC cryogel. In general, the PVSDM (with constant surface diffusivity) and PVSDM−MBI did not provide significant differences in the interpretation of $\overbar{q(t)}$ vs. *t* trends, with the latter model providing a slightly better fitting accuracy, in particular when Cs+ and Sr2+ adsorption onto AAC is considered. Dynamic results highlighted that, for each adsorbent material, the capture rate for cesium is greater than in the case of strontium, which can be ascribed to the greater value of the molecular diffusivity for the former ion. A comparison of the adsorbent materials, at fixed adsorbate species, revealed that the adsorption dynamics is faster for AAC when compared to SAC cryogels, due to more rapid fluid film, pore, and surface transport mechanisms. For instance, in the case of cesium capture onto AAC, the mean integral value of the fractal-like surface diffusivity is 5.43×10−11 m2 s−1, a figure about 1.3 times greater than the value retrieved for SAC. Modelling results according to the PVSDM−MBI also allowed to observe that, for all the investigated systems, the surface diffusivity exhibits a non-monotonic pattern in time with the occurrence of a maximum (see Figure 1b)). This demonstrates that the hopping contribution (increasing term of *Ds*(*t*) in Eq. (1)) to surface transport prevails in the first stages of the adsorption process, whereas the fractal contribution (the time-diminishing term associated with hindered surface transport) rules thereafter. An analysis of results based on the average Biot number $\overline{Bi(t)}$ values (cf. [2]), witnessed that both fluid film and intraparticle transport resistances regulates the adsorption dynamics (the latter with a comparatively higher relevance) for the systems AAC-Sr2+, SAC-Cs+ and SAC-Sr2+ (with $\overline{Bi(t)}$ varying from 14 to 20). In the case of cesium adsorption onto AAC, intraparticle diffusion is significantly slower than the transport of the adsorbate in the fluid film ($\overline{Bi(t)}$ equals to 167). Finally, both surface and pores diffusion resistances are relevant for the intraparticle transport of Cs+ and Sr2+ ions.



**Figure 1.** a) Comparison between experimental and theoretical kinetic adsorption patterns for the system AAC-Sr2+; b) Surface diffusivity ratio as a function of the adsorption time predicted by PVSDM−MBI for AAC-Sr2+.

**4. Conclusions**

In this work, the removal of strontium and cesium ions from liquid phase by adsorption onto two cryogels (named AAC and SAC) was investigated. Batch adsorption tests showed that the equilibrium removal efficiency of Sr2+ was 86% and 48%, for AAC and SAC, respectively. In the case of cesium, AAC attained a final removal efficiency of 58%, while 63% was reached for SAC sorbent. Mathematical modelling of dynamic capture results, according to a rigorous diffusional model accounting for all transport resistances, highlighted that the inclusion of a fractal-based expression for surface diffusivity is able to provide a very satisfying fitting accuracy. Moreover, surface diffusivity exhibits a non-monotonic pattern with the occurrence of a maximum in the time domain. Finally, the analysis of the average Biot number revealed that, in general, both external and intraparticle transport resistances are important, with the latter being comparatively more limiting in the capture process.

**References**

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