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LTA zeolite monoliths with hierarchical trimodal porosity as highly efficient microreactors for strontium capture in continuous flow

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ABSTRACT

LTA zeolite monoliths (6 mm diameter, 3 cm length) featuring a hierarchical trimodal network of micro-/meso- and macropores (obtained by either controlling the nucleation step of LTA crystallization into nanocrystals or by creating mesopores into micronic crystals by using organosilane surfactant) were used for strontium capture in aqueous medium. LTA monoliths were compared to other LTA zeolite architectures: LTA microcrystals, commercial LTA beads and bimodal micro-/macroporous LTA zeolite monoliths. In batch mode, the presence of mesopores allowed to increase remarkably by a factor 15 the diffusion of ions, whereas macropores had no influence on ions transport. In flow mode, only LTA monoliths featuring flow-through macropores proved suitable as microreactors. The trimodal LTA monoliths were 1000 times more efficient than packed-beds of LTA beads, and 4 times than bimodal (micro-/macroporous) LTA monoliths due to higher rates of diffusion. Trimodal LTA monoliths were able to treat efficiently 4 L of Sr^{2+} solution (10 mg L^{-1}) with 1 mL of material at a flow rate of 0.5 mL min^{-1} (or 1 m h^{-1}); *ie.* 4200 bed volumes (BV) were efficiently treated at a flow rate of 34 BV h^{-1}, with no Sr^{2+} detectable by ionic-chromatography in the effluent. This result highlights the fact that the multiscale pore architecture engineering of an adsorbent is crucial for process intensification: macropores allow uniform mass transport of solutions with low pressure drop while the generation of mesopores in zeolites leads to faster ionic transport and more efficient crystal use in cation-exchange processes, both in batch and flow modes.

1. Introduction

Our approach foresees developments in the use of nanozeolites in microreactor design and their impact as continuous flow devices for the purification of wastewater. Shaping LTA in a single piece as monolith for flow applications and process intensification is a veritable challenge. Na-LTA ($Na_{12}Si_{12}Al_{12}O_{48}.27H_2O$) with a molar ratio of Si/Al ratio of 1 features the highest aluminum content possible in tetrahedral aluminosilicate frameworks. LTA zeolite contains the maximum number of cation-exchange sites, and thus the highest exchange capacity attainable for a zeolite (5.4 meq g^{-1}). Cation-exchange properties of LTA zeolite are mainly industrially exploited in water softening to trap Ca^{2+} and Mg^{2+} cations. The largest use for LTA zeolite is the laundry detergent market. By removing the Ca^{2+} and Mg^{2+} cations, LTA zeolite enhances detergents efficiency and avoids the ecosystem damage caused by polyphosphates, which were formerly used [1]. The unique ion-exchange properties of LTA can be used for cleaning up wastewater coming from different industrial activities such as in oil extraction and its subsequent refining processes by removing the heavy metal ions Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} present in this type of wastewater. LTA zeolites can also serve to traces determination of the same heavy metals as preliminary preconcentration systems [2]. LTA has been also used for desalination purposes of aqueous solutions containing Cs^{+}, Sr^{2+} [3].

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LTA zeolites have also great potentiality to clean wastewater of nuclear industry and decontaminate radioactive effluents. The challenge in nuclear wastewater treatment or radioactive water decontamination is to develop an inorganic material, stable under irradiation, easy to handle, able to trap selectively, efficiently and rapidly in continuous flow radioactive species in low concentration (10–100 ng L^{-1}) contained in wastewaters of different compositions, including seawater. Sandbags of zeolites were dropped into the seawater near the power plant to adsorb radioactive Sr^{2+} and Cs^{+} present in high levels after the Fukushima nuclear disaster (March 11, 2011). The alumino-silicate structures of these zeolites are extremely durable and resistant to radiation. Additionally, once they are loaded with trapped nuclear products, the zeolite-waste combination can be hot pressed into an extremely durable ceramic form, that greatly reduces its hazard compared to conventional reprocessing systems. Na-LTA zeolite is one of the most promising materials for radioactive ^{90}Sr removal without pH adjustement, as it possesses a high ion-exchange capacity of 5.4 meq g^{-1} for Sr^{2+} (236 mg g^{-1}), and a high Sr^{2+} selectivity: $Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^{+} > Na^{+}$, and LTA zeolites maintain their cation-exchange capacity over a larger range of pH ($6 < pH < 13$). However, cation-exchange capacity of Na-LTA decreases with an increase of Na^{+} concentrations [4].

Besides zeolites promising materials have been developed to trap ^{90}Sr as SrTreat® based on layered sodium nonatitanate ($Na_4Ti_9O_{20}$,x H_2O) [5,6] and sodium titanosilicate [7], all of them demonstrating advantages and drawbacks as shown below. Sodium titanosilicates feature a high exchange capacity for Sr^{2+} over a wide range of pH ($2 < pH < 12$), but it has been shown that it is most effective at high Sr^{2+} concentration (>500 mg Sr L^{-1}) with a capacity of 1.8 and 4 meq g^{-1} for Sr^{2+} concentration of 500 and 2000 mg L^{-1}, respectively [7]. SrTreat® has a high cation-exchange capacity (4.1 meq g^{-1}) and maintains its activity in the presence of high amounts of Na^{+} (2 mol/L), but is less effective at pH below 10–11 and requires pH adjustement. Nonatitanates are sensitive to the presence of Ca^{2+} cations with a selectivity: $H^{+} > Ca^{2+}, Sr^{2+} \gg Mg^{2+}, NH_4^{+} > K^{+} > Li^{+} \gg Cs^{+}$. LTA zeolites and sodium nonatitanates appear therefore as the best materials to treat nuclear effluents featuring low Sr concentrations.

Performances of LTA zeolites and sodium nonatitanates [4] (previously synthesized by some of us) have been compared in batch. For a Sr^{2+} solution of 100 mg L^{-1}, the Sr^{2+} adsorption capacity at pH 9 of sodium nonatitanate was equivalent to that of Na-LTA zeolite (4.2 meq g^{-1}) and decreased similarly from 4.2 to 1 meq g^{-1} when Na^{+} concentration was increased from 0 to 1 mol L^{-1}, respectively. A capacity of 2 meq g^{-1} for both materials was obtained at a Na^{+} concentration of 0.4 mol L^{-1}, as usually encountered in seawater. For low Sr^{2+} concentration of 10 ng L^{-1} (66 kBq L^{-1}), both materials absorb selectively ^{90}Sr radionuclides in low-saline concentration (0.1 mol L^{-1} Na^{+}). Then Na^{+} concentration was increased, the uptake capacity of Na-LTA decreased, whereas nonatitanate showed a constant uptake until 0.5 mol L^{-1} Na^{+}. However, in presence of Ca^{2+} (0.067 g L^{-1}), Na-LTA zeolite was more selective towards ^{90}Sr than sodium nonatitanate with a decrease of radioactivity from 77 kBq L^{-1} to 3.4 and 8.5 kBq L^{-1} for Na-LTA and nonatitanate, respectively. LTA zeolites and nonatitanates are therefore both suitable for Sr^{2+} capture in low concentrations, but with different specificities for both materials: LTA for low Na^{+} concentration in a wide range of pH ($6 < pH < 13$) and nonatitanates for low Ca^{2+} concentration with pH > 9.

Both materials are commonly present as powders or pellets formed by aggregation of micronic crystals, which give rise to diffusion limitations in continuous flow processes. Beads of SrTreat® are used in industrial columns. In the lab scale, packed-bed columns of SrTreat® (bed volume 0.5 mL, bed height 2.5 cm, 0.30–0.85 mm particle size) were able to treat 1000 bed volumes (BV) at flow rate 16–26 BV h^{-1} for the removal of ^{90}Sr (7.4 GBq L^{-1}, pH 10, 2.4 mol L^{-1} $NaNO_3$) [5]. However a decrease of decontamination was noticed within time due to ions diffusion limitations [5]. Packed-bed columns of LTA (bed volume 3.5 mL, bed height 4.5 cm, 0.25–0.38 mm particle size, Sr^{2+} 100 mg L^{-1}) have shown an ions uptake decrease with the increase of flow rate (89 BV treated at 40 BV h^{-1} and 42 BV treated at 82 BV h^{-1}) revealing a system dominated by external diffusion limitation [8]. As an alternative to powders or pellets, we have previously developed hierarchical LTA zeolite monoliths (micro-/macropores), synthesized by pseudomorphic transformation of silica monoliths, which feature flow through macropores to allow effective aqueous solution transport. These LTA monoliths (first generation) featured a skeleton built by an aggregation of micronic crystals (1 μm) [9]. LTA monoliths (bed volume 0.7 mL, bed height 2.6 cm) were able to treat 2700 bed volumes (BV) at flow rate 12 BV h^{-1} (Sr^{2+} 10 mg L^{-1}) and 1500 BV at 57 BV h^{-1}. The decrease in BV efficiently treated then increasing flow rate revealed some diffusion limitations. It is therefore of prime importance to enhance cations diffusion into these promising materials to increase their efficiency of ions capture in flow processes.

In the case of molecules, it has been shown that the creation of mesoporosity in zeolites, leading to hierarchical zeolites, increases the diffusion of molecules [10,11]. To examine the role of mesoporosity on cations diffusion in continuous flow, we have devoted large efforts to succeed in the synthesis of trimodal hierarchical LTA monoliths (micro-/meso-/macroporous) by controlling aging and crystallization steps of the zeolite during the pseudomorphic transformation [12].

In the present study, two of these LTA monoliths (second generation) featuring a hierarchical trimodal porosity (micro-/meso-/macropores), so an additional mesoporosity (either generated by an aggregation of nanocrystals or by organic-templated micronic crystals) in comparison to LTA monoliths (first generation) were studied in batch and flow processes for Sr^{2+} removal, in order to evaluate the role of materials architecture on ions diffusion. The size of the monoliths (6 mm diameter, 3 cm length) was chosen in accordance to catalysis results to prevent external diffusion limitation [13]. Their performances were compared with those of different materials: Na-LTA micronic crystals (5 μm), commercial Na-LTA (500 nm crystals aggregated with binders into 3 mm beads or crushed into 100–300 μm particles), LTA-monolith (first generation) (with no mesoporosity) and mesoporous silico-aluminate monolith (with no microporosity).

2. Experimental

2.1. Silica monolith synthesis

First, tetraethylorthosilicate (TEOS, Aldrich) (20 g) is left at −19 °C for 1 h. In parallel, water (24.560 g) and then (2.313 g) nitric acid (68%) are added in a 100 mL Erlenmeyer. The mixture is stirred for 5 min at room temperature. Polyethylene oxide (PEO 20 kDa) (2.534 g) is added to the mixture and stirred at room temperature until having complete dissolution of the polymer. The mixture is left 10 min at −19 °C in the freezer to cool down the solution without freezing. The flask is then placed in an ice bath and stirred. TEOS (coming from the freezer) is directly added to the slurry and the solution is stirred for 30 min. The final composition of the mixture in molar ratio is: 1 Si/0.60 EO unit/0.26 HNO_3/14.21 H_2O. Polyvinyl chloride (PVC) tubes of 8 mm diameter and 10 cm length are closed on one side with a cap, sealed with parafilm and kept at −19 °C in the freezer. The tubes are taken from the freezer and filled with the mixture of the ice bath. The tubes are then closed by caps