



Ceramic foam supported active materials for boron remediation in water



Cristina Sanfeliu^{a,b,c}, Ramón Martínez-Mañez^{a,b,c}, Félix Sancenón^{a,b,c}, Juan Soto^{a,b,c}, Pedro Amorós^d, M. Dolores Marcos^{a,b,c,*}

^a Centro de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Unidad Mixta Universitat Politècnica de València, Universitat de València, Spain

^b Departamento de Química, Universitat Politècnica de València, Camino de Vera s/n E-46022 Valencia, Spain

^c CIBER de Bioingeniería Biomateriales y Nanomedicina (CIBER-BBN), Spain

^d Institut de Ciència del Materials (ICMUV), Universitat de València, P.O. Box 22085, E-46071 Valencia, Spain

HIGHLIGHTS

- We show ceramic monoliths acting as proper supporting matrices for boron mesoporous adsorbent.
- Ceramic-Foam-mesoporous adsorbent shows total adsorption capacity comparable with the parent mesoporous adsorbent.
- Ceramic-Foam-mesoporous adsorbent can be recycled for new uses.

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ABSTRACT

Due to the narrow range between boron necessities and toxicity in the environment, there is a high interest in the design of effective boron remediation procedures. We have previously reported a promising boron adsorption material based on the affinity of boron aqueous species for cis-diol groups that were anchored on different mesoporous silica matrices. However, the small particle size of these systems makes them difficult to be applied on real remediation situations. In this context we report herein a novel system for boron adsorption from aqueous solutions in which the high boron affinity for functionalized mesoporous materials is combined with the mechanical properties of ceramic foams as macroscopic supports. The efficiency of these new composites for boron removal is very high and comparable with the parent microparticulated adsorbent.

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1. Introduction

Boron is widely distributed in the environment, mainly in the form of borate salts which are very soluble and hence difficult to remove from water. The principal boron contamination is due to industrial wastewater discharge as for example the ceramic industry. In regions with a high concentration of such industries the contamination of ground and subsoil by boron is considered of maximum environmental concern [1].

Boron is an important micronutrient for plants, animals and humans. It has a marked effect on plants in terms of both nutrition and toxicity, even 1–2 ppm in irrigation water can cause stunting of plant growth. Boron also has virulence for reproduction and causes disease in the nervous system of animals and humans [2,3]. Therefore, removal of boron from water is crucial for boron environmental protection.

The World Health Organization (WHO) guidelines for water quality recommend a 2.4 mg l^{-1} standard for boron in drinking water [4]. In the case of the European Union (EU) a standard of 1 mg l^{-1} for drinking water [5] for boron has been adopted, though in some countries derogations have been made due to a higher boron concentration in natural fresh water [6].

There is no universal method for the removal of boron from water [7]. The main processes for boron removal include adsorption [8,9], coagulation [10], reverse osmosis [11–14], electrodialysis [15], etc. The adsorption process is extensively used [16,17]. Therefore, novel materials and methods are being developed [18].

Previously, we presented an alternative system: a new generation of boron adsorption materials based on functionalized mesoporous silica [19]. This method was developed taking advantage, in one side, of the boron ability to produce esters with chemical compounds containing multiple hydroxyl groups (polyols) [20,21] and, on the other, of the attractive properties of mesoporous solids such as very large capacity of functionalization and very high specific surface [22,23]. Based on these ideas, it was envisaged that the grafting of

* Corresponding author at: Centro de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Unidad Mixta Universitat Politècnica de València, Universitat de València, Spain.

E-mail address: mmarcos@qim.upv.es (M.D. Marcos).

mesoporous scaffolds with saccharides could yield highly efficient boron removal systems. Several of these mesoporous scaffolds with different porous structures have been obtained and compared with non-porous inorganic materials and though the best adsorption result was obtained for highly homogeneous scaffolds, other cheap matrices showed also a good performance [24].

However, thinking on real applications, the relatively small particle size of these functionalized mesoporous materials constitutes a significant disadvantage. At this point, we will pointed out that the grain size of the inorganic silicas we have used (50–300 nm) is significantly lower than the size of other materials used for boron remediation such as Dianion or Dowex ion exchange resins (in the micrometric–millimetric range) [25–27]. The solid–liquid separation process becomes hard and difficult when nanometric particles are involved. This drawback can be solved by the incorporation of the active species onto a macroscopically structured support. In this context, ceramic foams (CF) represent an emerging category of hosts that possess a unique combination of physicochemical (high porosity and chemical stability) and mechanical (low thermal-expansion coefficients and high specific strength) properties [28–30]. In addition, CF can be easily manufactured by impregnation of organic template foams with inorganic particles or by in situ polymerization followed by calcination [31].

Preparation and characterization of “CF-mesoporous silica” composites in the form of rigid large monoliths having trimodal pore systems (small meso-, large meso-, and macroporous) has been described [32]. The monoliths have been synthesized by using preformed mesoporous nanoparticles and a CF as support. The surfactant-assisted synthesis of the silica-based nanoparticulate mesoporous materials, denoted as **UVM-7** (a nanometric version of the MCM-41 silicas), has been reported elsewhere [33]. These **UVM-7** materials show very open architectures consisting of micrometric aggregates of mesoporous nanoparticles connected through covalent bonds.

In this study, we present a novel system for boron adsorption from aqueous solutions in which the high accessibility of the **UVM-7** mesoporous materials has been combined with the boron affinity towards diols and the mechanical properties of the ceramic foams as macroscopic supports. The efficiency of this new system in boron removal is also presented.

2. Experimental

2.1. Synthesis of the adsorbents

The synthesis of the ceramic foam (CF) was carried out through a typical organic foam replication, a technique that allows good control of the monolith shape and dimensions [34]. Commercially available inexpensive polyurethane foam (PUF) without cell forming membranes (average pore diameters around 600 μm (30 ppi)) was used as macro-scale template. The foam was impregnated with an optimally deflocculated casting slip for porcelain bodies prepared with two different kaolins, feldspar and quartz, which contained 67% of solid materials (19.4% kaolin A, 18.1% kaolin B, 10.7% quartz, 18.8% feldspar), and 33% of water, which included the deflocculant (0.45% with respect to solid kaolins), to give a slip density of 1.6 g/cm^3 . As deflocculant, a mixture of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and sodium silicate (aqueous solution with a density of 1.36) in a weight ratio of 2:1 was used. The green body obtained with this slip had the following chemical composition: SiO_2 , 68.0%; Al_2O_3 , 21.5%; Na_2O , 0.8%; K_2O , 4.1%; ignition loss, 5.6%; distributed as kaolinite, quartz, and feldspar minerals. The impregnated PUF was passed through rollers preset at 80% compression to expel the excessive slurry and dried at room temperature to obtain a coated PUF. Then, the monolith was calcined in a two-step process (at 500 $^\circ\text{C}$ for 2 h, and later at 1200 $^\circ\text{C}$ for 5 h) to provoke PUF evolution and ceramic vitrification. The corresponding porcelain body contains two crystalline

phases, mullite and quartz, and a vitreous phase containing sodium and potassium aluminosilicates.

The nanosized mesoporous **UVM-7** silica was synthesized through a one-pot surfactant-assisted procedure using a homogeneous hydroalcoholic reaction medium (water/triethanolamine). The general procedure, a modification of the so-called atrane route [35], has been described in detail elsewhere. It is based on the use of a simple structural directing agent ((CTABr) cetyltrimethylammonium bromide) and a complexing polyalcohol (triethanolamine), which originates silatrane complexes (relatively inert complexes that include triethanolamine-related ligand species) as hydrolytic precursors. Together with its complexing ability, the presence of the cosolvent (triethanolamine) was a key in order to favor the formation of nanoparticulated materials. To open the intranoparticle mesopores, the surfactant was extracted from the as-synthesized mesostructured solid by chemical exchange using an HCl/ethanol solution (CTA^+/H^+ exchange). Thus, 1 g of mesostructured **UVM-7** powder was suspended in a solution containing 16 ml of HCl (37%) and 130 ml of ethanol (99%), and this mixture was heated at reflux (60 $^\circ\text{C}$) for 2 h while stirring. Later, after renewal of the HCl/ethanol solution, and to complete the extraction process, the suspension was heated again at 60 $^\circ\text{C}$ for 16 h while stirring. The resulting mesoporous solid **UVM-7-e** was collected by filtration, washed with ethanol, and air-dried at 100 $^\circ\text{C}$.

The large aggregates of **UVM-7-e** material were transformed into submicrometric or nanometric aggregates by means of high power ultrasound treatment (using a Branson instrument). In a typical preparation, a suspension containing 3 g of **UVM-7-e** in 100 ml of distilled water (3% in weight) was irradiated for 15 min at a nominal power of 350 W. After irradiation, the suspension has colloidal character showing the Tyndall effect. The CF coating was performed by successive impregnation cycles. In each cycle an immersion of the ceramic foam into an aqueous **UVM-7-e** colloidal suspension (ca. 3% in weight) was firstly performed, and afterwards, a soft thermal treatment (150 $^\circ\text{C}$ for 16 h) to favor water evolution and nanoparticles adhesion (formation of covalent Si–O–Si bonds with the CF surface). The solid **CF-UVM-7-e** was hence obtained. Mesoporous material anchored to the monolith was functionalized in order to build the active sites on the materials surface [36]. **CF-UVM-7-e** monoliths were immersed in anhydrous acetonitrile (500 ml) and heated at 120 $^\circ\text{C}$ in a Dean-Stark apparatus to remove the adsorbed water by azeotropic distillation under an inert atmosphere (Ar gas). After this, 25.6 mmol (6 ml) of APTES ((3-aminopropyl)-triethoxysilane), were added and the solution was stirred for 16 h. Then, the monoliths (**CF-UVM-7-N**) were washed with acetonitrile, and ethanol. Finally, 0.5 l of a 0.07 M solution of gluconolactone in methanol was added to the former mixture, and after stirring for 48 h at room temperature the fully functionalized monoliths, named **CF-G** (–a, –b, –c for those used for adsorption essays and –d, –f, –g, to be used in the different analytical techniques), were achieved.

In order to compare the adsorption capacity of the supported active materials, a non-supported **UVM-7-e** material was also functionalized. Hence, 2 g of **UVM-7-e** was suspended in 70 ml of acetonitrile and heated at 120 $^\circ\text{C}$ in a dean-stark apparatus. Then, 3.4 mmol of APTES was added at room temperature following the same conditions as those described above for the **CF-UVM-7-e**. After 16 h., the solid was filtered and washed with acetonitrile and water reaching to **UVM-7-N**. Finally, in order to achieve the active sites **UVM-7-N** material was reacted with 6.8 mmol of gluconolactone in 100 ml of methanol. The mixture was stirred during 48 h at room temperature. After that, the obtained **S1** solid was filtered, washed with water and dried. A summary of the codes used for naming the prepared materials and composites is shown in Table 1.

2.2. Boron adsorption assays

Adsorption studies of boron on **CF-G** were carried out dipping each monolith in 25 ml of distilled water while stirring. After 2 h, an aliquot

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