

Efficient boron removal by using mesoporous matrices grafted with saccharides

Gertrudis Rodríguez-López,^a M. Dolores Marcos,^{*a} Ramón Martínez-Máñez,^{*a} Félix Sancenón,^a Juan Soto,^a Luis A. Villaescusa,^a Danile Beltrán^b and Pedro Amorós^b

^aGDDS, Departamento de Química, Universidad Politécnica de Valencia, Camino Vera s/n 46071, Valencia, Spain. E-mail: rmaez@qim.upv.es; Fax: +34 963879349; Tel: +34 963877340

^bInstitut de Ciència dels Materials de la Universitat de València (ICMUV), P.O. Box 2085, 46071-València, Spain

Received (in Cambridge, UK) 5th May 2004, Accepted 24th June 2004

First published as an Advance Article on the web 19th August 2004

Highly efficient boron removal from water was achieved by using mesoporous silica materials functionalised with saccharides.

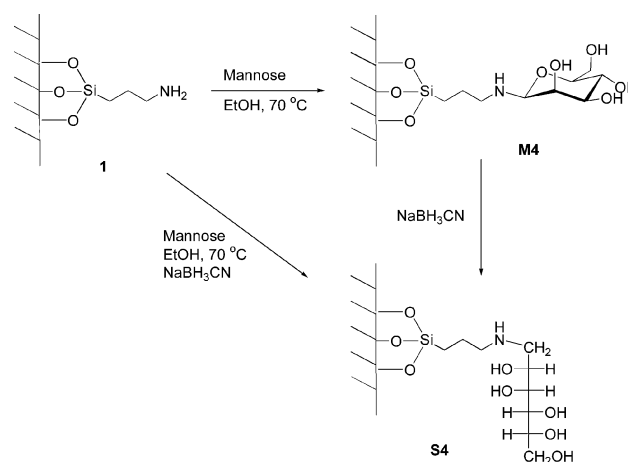
Although boron is an essential plant nutrient, the range between deficiency and toxicity is very narrow and it has been found to be toxic for both plants and animals. For instance, it is known to be phytotoxic in small amounts and can induce serious damage such as stunted growth, chlorosis and necrosis.¹ In potable water it is generally admitted that its level should be less than 500 ppb. Boron contamination is in great part due to anthropogenic sources as it is present in many household (cosmetics, insecticides, medicines *etc.*) and industrial products (coal-fired steam power plants, chemical plants, rockets, fertilizers, *etc.*) and by-products. Especially, wastewaters from certain ceramic factories contain a high level of boron and, in regions with a high concentration of such industries, the contamination of ground and subsoil by boron is considered of maximum environmental concern. In this respect, an important aspect of pollutant management is the development of new useful environmental boron remediation agents for its application in a wide range of situations.

Boron is mainly present in water as borate which is very soluble and hence difficult to remove from aqueous environments. Basically, the only method utilised to separate boron from liquid media has been the use of ion exchange resins. An alternative would be the design of novel systems using a new generation of adsorption materials such as those based on mesoporous silica. Some recent work dealing with the use of mesoporous functionalised MCM-41 materials for toxic metal cations removal has been reported.² In contrast, the use of hybrid mesoporous solids as adsorbents for anions from water is very rare and has only been applied to the removal of the toxic oxyanions arsenate and chromate.³

The design approach we have followed in the synthesis of boron adsorbents was inspired by the attractive properties of mesoporous solids (very large specific surface, capacity of functionalisation, *etc.*) for their use as matrices in anion remediation protocols, and by the ability of borate to react with non-acidic polyalcohols. Based on these ideas, it was envisaged that the grafting of mesoporous scaffolds with saccharides could yield highly efficient boron removal systems.

The starting mesoporous material⁴ was first reacted with 3-aminopropyltriethoxysilane to yield **1**. Synthesis of the intermediate solids **M1** to **M4** was accomplished by reaction of **1** with the saccharides glucose, fructose, galactose or mannose, respectively in MeOH at 70 °C for 12 h (see Scheme 1 where the solid with mannose **M4** is shown).⁵ To avoid possible leaching of active sites (due to a potential hydrolysis of the "saccharides" groups) the final solids **S1** (glucose), **S2** (fructose), **S3** (galactose) and **S4** (mannose) were prepared by reaction of the corresponding solid **M1** to **M4** with sodium cyanoborohydride or by direct reductive amination of the corresponding sugar with **1** and NaBH₃CN,⁶ see Scheme 1.

Fig. 1 shows the powder X-ray pattern of **S4**. The main feature of a UVM-7 phase is clearly shown, suggesting that the structural



Scheme 1 Reaction scheme for the synthesis of the functionalised mesoporous solid **S4**.

ordering of the small channels has not changed after the functionalisation. Fig. 1 also shows a representative SEM image of **S4** where the particular topography of these types of solids, consisting of nanometric particles joined together into micrometric conglomerates, is observed.⁴ From TG and elemental analysis it was found that, in **1**, about 16% of the silica was functionalised with the 3-aminopropyl groups from which about 75% of the amines reacted further with the corresponding saccharide to give the functionalised **S** solids. That gave an overall saccharide functionalisation of near 12% in terms of moles of silica. Table 1 summarises these results.

Solids **S1**, **S2**, **S3** and **S4** were tested as boron adsorbent agents.

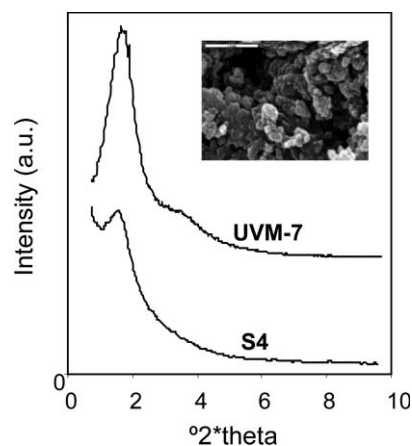


Fig. 1 X-ray pattern of **S4** and the starting mesoporous UVM-7 materials. The inset shows a representative SEM image of **S4** (the white bar is equivalent to 1 μ m) for solid **S4**.

Table 1 Characteristics of the saccharide-functionalised mesoporous adsorbents

Solid	Saccharide/ SiO ₂ (mol/mol)	Max. boron uptake/ "saccharide" (mol/mol)	Boron adsorption capacity (mmol g ⁻¹)
S1	0.135	0.53	0.67
S2	0.092	0.61	0.76
S3	0.127	0.39	0.49
S4	0.129	1.49	1.85

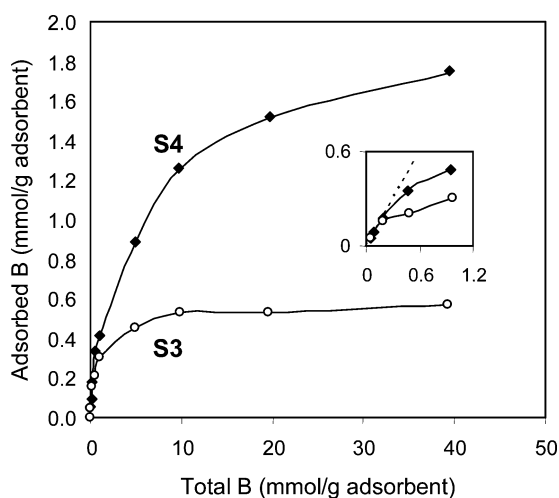


Fig. 2 Boron adsorption isotherms at 25 °C for functionalised solids **S4** and **S3**. The inset shows the same curve at low boron concentrations (dashed line corresponds to the theoretical maximum loading (100% removal efficiency of boron)).

In a typical assay the corresponding solid (22.5 mg) was mixed with a certain volume of water containing borate (pH *ca.* 8) at a certain concentration (usually from 0.4 to 400 ppm). The mixture was filtered and the boron concentration in the solution analysed by plasma-atomic emission spectroscopy. Table 1 shows the maximum boron loading reached for these materials. Most of the solids prepared have medium adsorption capacity (around 0.6 mol g⁻¹). These values in general contrast with the results obtained for the solid **S4** containing "mannose" for which a remarkable boron adsorption per gram of material of near 2 mmol g⁻¹ was observed.

Fig. 2 shows the adsorption isotherms of boron by using the solid **S4**. The inset shows the adsorption isotherm at low boron concentrations. From these data for instance, removal efficiencies larger than 80% were observed for solutions containing 4 ppm of boron using solid **S4**. In contrast to the high adsorption behaviour of **S4** (see Table 1) no detectable boron adsorption was found using both the non-functionalised starting mesoporous material and solid **1**. It was also confirmed that the boron-loaded material **S1** to **S4** can be regenerated by washing the solid with acidic aqueous solutions (*ca.* pH 3.5). For instance, regenerated solids **S3** and **S4** showed a maximum boron adsorption capacity corresponding to about 85% of the original.

Boron removal in functionalised solids is due to the formation of complexes between the borate and polyol groups. The large boron uptake of solid **S4** is in agreement with the usually large affinity of boron for "mannitol" derivatives with respect to other polyols.⁷

The solids that we have prepared show several remarkable characteristics. Specially, solid **S4** showed a very noteworthy boron adsorption capacity which is comparable to conventional boron remediation technologies.⁸ These solids also showed a suitable

durability because of the stable inorganic nature of the mesoporous material, and because the active sites are shielded in nanoporous cavities making them protected against degradation including that by bacteria. The adsorbent solids were designed following a "zero waste" approach. Thus, waste materials which are finally exhausted (after several regeneration cycles) can be recycled by calcination and re-functionalisation or can finally be used as raw material (source of silica or silica and boron) in other processes.

In summary, the functionalisation of mesoporous solids with "saccharides" has resulted in new hybrid systems suitable for boron adsorption procedures. The high loading capacity found for **S4** and the possibility of obtaining these solids with a controlled macrostructure (by formation of monoliths)⁴ in order to minimize pressure drop, make them promising candidates as new materials for boron remediation.

We thank the Ministerio de Ciencia y Tecnología (MCyT) (MAT2003-08568-C03 and REN2002-04237-C02-01) and the Generalitat Valenciana (GRUPOS03/035 and GRUPOS03/099) for support. L.A.V. thanks the MCyT for a Ramón y Cajal contract. We also thank the Servicio de Microscopía of the Universidad Politécnica de Valencia for SEM analysis.

Notes and references

- See for instance: I. Novozámsky, V. J. G. R. Houba, J. J. Vanderlee, R. Vaneck and M. D. Mignorance, *Commun. Soil Sci. Plant Anal.*, 1993, **24**, 2595; R. E. Chapin and W. W. Ku, *Environ. Health Perspect. Suppl.*, 1994, **102**, 87.
- X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923; L. Mercier and T. J. Pinnavaia, *Adv. Mater.*, 1997, **9**, 500.
- As far as we know functionalised MCM-41 solids have only been used as anion adsorbents for the arsenate and chromate oxyanions. See for instance: G. E. Fryxell, J. Liu, T. A. Hauser, Z. Nie, K. F. Ferris, S. Mattigod, M. Gong and R. T. Hallen, *Chem. Mater.*, 1999, **11**, 2148; H. Yoshitake, T. Yokoi and T. Tatsumi, *Chem. Mater.*, 2002, **14**, 4603; H. Yoshitake, T. Yokoi and T. Tatsumi, *Chem. Mater.*, 2003, **15**, 1713.
- We have chosen as mesoporous inorganic matrix the solid UVM-7 that consists of MCM-41-like mesoporous nano-sized particles (average mesopore size of 35 Å) tied together in micrometric conglomerates. It provides a solid with a noteworthy textural porosity in the range of 20 to 70 nm that might facilitate the migration of the active species (borate) through the solid. Typically, the UVM-7 solid shows a surface of 1100 m² g⁻¹ (*ca.* 900 and 200 m² g⁻¹ for internal and external surface, respectively). For more details see: J. El Haskouri, D. Ortiz de Zárate, C. Guillem, J. Latorre, M. Caldés, A. Beltrán, D. Beltrán, A. B. Descalzo, G. Rodríguez-López, R. Martínez-Mañez, M. D. Marcos and P. Amorós, *Chem. Commun.*, 2002, 330.
- Synthesis of **2**: Solid **1** was dried at 110 °C overnight. Then 0.5 g of **1** (containing *ca.* 1.93 mmol of 3-aminopropyl groups) was suspended in dry methanol (175 mL). 3.48 g of glucose (19.3 mmol) were added and the mixture refluxed for 12 hours. The obtained solid was filtered, scrupulously washed with methanol and water and dried at 70 °C. The same procedure was followed for fructose, galactose and mannose.
- Synthesis of **S1**: Solid **1** was dried at 110 °C overnight. Then 0.5 g of **1** (containing *ca.* 1.93 mmol of 3-aminopropyl groups) was suspended in dry methanol (175 mL). 3.48 g of glucose (19.3 mmol) were added and once the sugar was dissolved, 34.6 mg of NH₄Cl (0.648 mmol) and 1.4 g of NaBH₃CN (22.2 mmol) were added. The mixture was refluxed during 16 hours and the resulting solid was filtered, scrupulously washed with methanol and acidic water until no trace of boron (from the use of the NaBH₃CN reactive) in the washing waters was observed. The solid was finally dried at 70 °C. The same procedure was followed for fructose (**S2**), galactose (**S3**) and mannose (**S4**).
- See for instance: G. Sprinsteen and B. Wang, *Tetrahedron*, 2002, **58**, 5291.
- A theoretical boron capacity of 0.93 mmol g⁻¹ has been described for AMBERLITE IRA743 (Rohm and Haas, macroporous polystyrene resin).