Efficient boron removal by using mesoporous matrices grafted with saccharides

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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 (coaled 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 material 4 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 and 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 NaBH4.6 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 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. 7 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.
Table 1 Characteristics of the saccharide-functionalised mesoporous adsorbents

<table>
<thead>
<tr>
<th>Solid</th>
<th>Saccharide/ Solid</th>
<th>Max. boron uptake/ “saccharide”</th>
<th>Boron adsorption capacity (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.135</td>
<td>0.53</td>
<td>0.67</td>
</tr>
<tr>
<td>S2</td>
<td>0.092</td>
<td>0.61</td>
<td>0.76</td>
</tr>
<tr>
<td>S3</td>
<td>0.127</td>
<td>0.39</td>
<td>0.49</td>
</tr>
<tr>
<td>S4</td>
<td>0.129</td>
<td>1.49</td>
<td>1.85</td>
</tr>
</tbody>
</table>

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 the solid S1 to S3. 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.

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. 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) in order to minimize pressure drop, make them promising candidates as new materials for boron remediation.

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Notes and references

4. 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 Zarate, C. Guilem, J. Latorre, M. Calle, A. Beltran, D. Beltran, A. B. Desalado, G. Rodriguez-Lopez, R. Martinez-Maibet, M. D. Marcos and P. Amoros, Chem. Commun., 2002, 330.
5. Synthesis of S1. Solid 1 was dried at 110 °C overnight. Then 0.5 g of 1 (containing ca. 1.93 mmol of 3-amino propyl 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.
6. Synthesis of S1. Solid 1 was dried at 110 °C overnight. Then 0.5 g of 1 (containing ca. 1.93 mmol of 3-amino propyl groups) was suspended in dry methanol (175 mL). 3.48 g of glucose (19.3 mmol) were added and then the sugar was dissolved, 34.6 mg of NH₄Cl (0.648 mmol) and 1.4 g of NaBH₄/CN (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 NaBH₄/CN 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).
8. A theoretical boron capacity of 0.93 mmol g⁻¹ has been described for AMBERLITE IRA743 (Rohn and Haas, macroporous polystyrene resin).