

Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/greenchem

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Starch-derived carbonaceous mesoporous materials (Starbon®) for the selective adsorption and recovery of critical metals

Andrea Muñoz García,^a Andrew J. Hunt,^{a*} Vitaly L. Budarin,^a Helen L. Parker,^a Peter S. Shuttleworth,^b Gary J. Ellis^b and James. H. Clark^a

The formation, characterization and application of starch-derived carbonaceous mesoporous materials (Starbon®) for the selective adsorption and recovery of critical metals (Au³⁺, Pt²⁺ and Pd²⁺) has been described. Starbon® successfully separated these critical metals from a mixture containing earth abundant elements (Ni²⁺, Cu²⁺ and Zn²⁺) with the consequent formation of metal nanoparticles.

Recent development of low carbon technologies has led to increased use of precious metals.¹ Many products reaching their end of life result in the dispersion of metals into the “technosphere”, making elemental recovery technically challenging.² The EU has identified a list of elements deemed to be ‘critical’ based on their economic importance and risk of supply.³ Thus, the development of effective recycling processes and recovery strategies for these finite resources is essential. With the move towards a low carbon (and highly metal dependent) future, the risk of metal supply shortages will increase and new technologies for metal recovery must be developed.⁴

Several methods for metal recovery are available,⁵ for example, adsorption on activated carbons.⁶ However, highly microporous materials, such as these, can be very unfavorable as they can lead to unselective, irreversible adsorption due to high surface energy within the small pores.⁷ Mesoporous carbonaceous materials demonstrate selective and reversible adsorption of different metals, though production costs have limited their use.⁸ Recently, carbonaceous mesoporous materials (Starbon®) derived from waste polysaccharides have been used for dye adsorption, in a low cost process requiring no templates or hazardous chemicals.⁹ Herein, Starbons® are demonstrated as effective materials for the selective adsorption and separation of Platinum Group Metals (PGM) from mixtures containing earth abundant elements, with the consequent formation of precious metal nanoparticles.

The principal methodology to produce Starbon® comprises five main steps: (1) microwave gelation of the polysaccharide and subsequent retrogradation, (2) water exchange with ethanol, (3) drying, using CO₂ under supercritical conditions (scCO₂), (4)

doping with an organic acid and (5) carbonisation, under vacuum, up to 800 °C. The textural properties of the Starbon® were investigated by N₂ sorption porosimetry. Starbon® prepared at 800 °C displayed a type IV isotherm, typical for mesoporous materials, and BET surface area and pore volume of 631 m²·g⁻¹ and 0.48 cm³·g⁻¹ respectively (see Table S1 in Supplementary Information†). Textural properties of Starbon® were compared to those values previously reported in the literature (BET surface area 535 m²·g⁻¹ and pore volume 0.75 cm³·g⁻¹).¹⁰ Differences in these values are attributed to a lower starch:water ratio employed during gelation, to reduce solvent requirements during the exchange process and drying.

XPS analysis was employed to understand the surface chemistry of Starbon® carbonised at 800 °C. Deconvolution of C 1s showed peaks at 284.5 and 289.2, corresponding to graphitic carbon, and O=C-O respectively.¹¹ These peaks are in good agreement with previous results for Starbon® powder carbonised at 800 °C (S800).^{9c} The presence of a third peak at 285.3 eV could be caused by defects or non-conductive areas on the material.¹² Other sources attribute this peak to β-carbons.¹³ The O=C-O group may be a residue from an earlier stage of carbonisation. Its presence is supported by the peak at 531.8 (C=O) and 533.4 eV (C-O-C) after deconvolution of the O 1s region. A third peak seen in the O 1s spectra at 536.2 eV indicates that chemisorbed H₂O is also present within the sample.¹⁴ This phenomena has been previously reported for similar materials.¹⁵

In order to investigate the use of Starbon® in metal recovery and separation, a solution of Ni²⁺, Cu²⁺, Zn²⁺, Ir²⁺, Au³⁺, Pd²⁺ and Pt²⁺ in HCl was employed as a model system to mimic those elements that are found in PGM mine tailings. Starbon removed >99% of Au³⁺, >90% of Pd²⁺ and >80% of Pt²⁺ from solution. Starbon® demonstrate significantly higher adsorption capacity of gold (>3800 mg·g⁻¹) than other similar materials described in the literature (i.e. >100 mg·g⁻¹ and 73 mg·g⁻¹ of coconut shell and peach stone activated carbons respectively).¹⁶ Conversely, the adsorption of Ni²⁺ and Zn²⁺ did not exceed 5% and therefore can be considered limited. Cu²⁺ and Ir³⁺ were partially adsorbed, 9%

and 31% respectively (Figure 1). The variation of Starbon® loading (5 to 50 mg) in 30 mL of solution was also investigated (see Fig. S1 in Supplementary Information†).

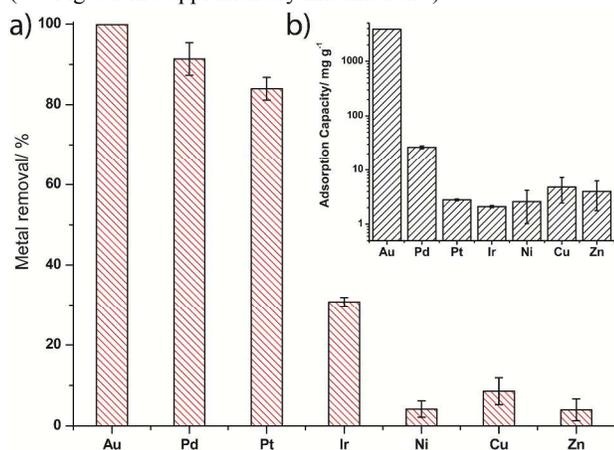


Fig. 1 a) Metal removed from 30 ml of a solution in HCl when 50 mg of adsorbent were added (%) and b) adsorption capacity for each metal ($\text{mg}\cdot\text{g}^{-1}$) (See Experimental in Supplementary Information†).

A further study was conducted where the initial concentration of precious metals in the mixture was lowered 100 times with respect to the other metals, in order to better represent real waste metal concentrations. Results showed that Starbon® removed >85% of the PGM from solution, leaving the other metals unaltered, despite this vast difference in concentration. Therefore a preferential adsorption of PGM was demonstrated regardless of the starting concentration. Demonstrating the commercial potential of the Starbon® for the recovery PGM, present in low concentration wastes or potentially when leached from catalysts.

In order to clarify the adsorption mechanism, analysis by XPS was undertaken of Starbon® samples before and after adsorption. It was found that before the adsorption of metals, the Starbon® materials had low oxygen content (C 1s 97% and O 1s 3%). After adsorption, a higher percentage of oxygen was detected suggesting that surface oxidation occurred during adsorption (see Table S2 in Supplementary Information†). Deconvolution of the O 1s XPS signals after adsorption indicated a greater O-C-O/C=O ratio than that prior to adsorption. This reflects an increase in the O-C-O groups at the material's surface, which may appear as a result of oxidation of the carbonaceous structure (see Fig. S2-3 in Supplementary Information†). The oxidation of Starbon® was associated with the reduction of the precious metals onto the surface (as observed by XPS). This phenomena has already been described in the literature, where activated carbon acted as reducing agent of certain metals.¹⁷ Metals with higher reduction potential were adsorbed and reduced first. This is in agreement with kinetic results, where saturation of the adsorbent was reached after 1 h for Au^{3+} ($\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}^0$, 1.50 V), 2 h for Pt^{2+} ($\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}^0$, 1.19 V) and 4 h for Pd^{2+} ($\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}^0$, 1.00 V). Cu^{2+} ($\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0$, 0.34 V) presents lower reduction potential and Ni^{2+} and Zn^{2+} both present negative reduction potentials ($\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}^0$, -0.25 and $\text{Zn}^{2+} + 2\text{e}^- \rightarrow$

Zn^0 , -0.76 V respectively) indicating why uptake was minimal. Starbon® presented remarkably high adsorption capacity for gold and the saturation point of the material was not reached.

Deconvolution of C 1s also provides further evidence in favour of the metal reduction mechanism for adsorption. A peak at 286.2 eV appearing post-adsorption may be related with the presence of C-OH (Figure 2).^{9c}

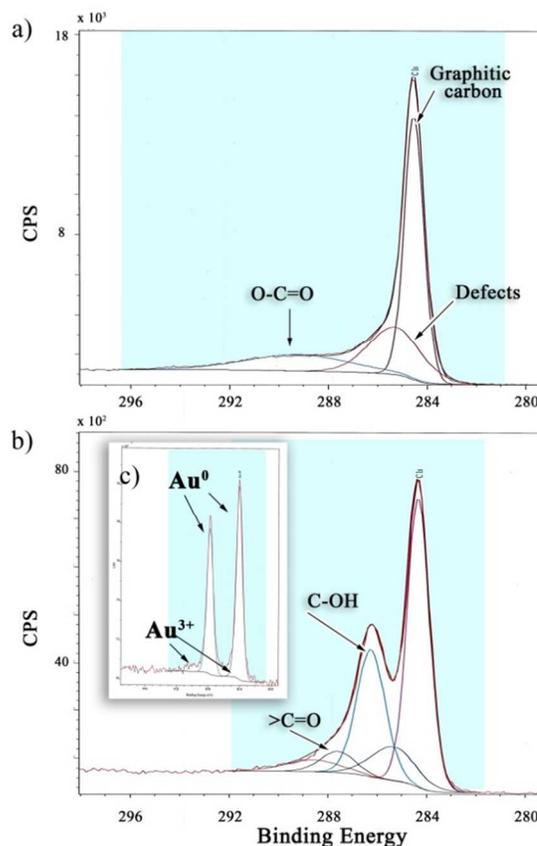


Fig. 2 XPS deconvolution peaks a) carbon before adsorption, b) carbon after adsorption, c) gold on surface of adsorbent.

XPS also detected Au and Pd on the material surface. Deconvolution of Au 4f showed that most of the gold was Au^0 (peaks at 84.0 and 87.6 eV), although traces of Au^{3+} (peaks at 85.9 and 89.6 eV) could be observed in the spectra (Figure 2).¹⁸ Deconvolution of Pd 3d exhibited Pd^0 (335.5 and 340.7 eV) and Pd^{2+} (337.7 and 343.0 eV)¹⁹ in a ratio 40/60 ($\text{Pd}^0/\text{Pd}^{2+}$). However, quantification was difficult due to the low intensity of the Pd peak (see Fig. S3-5 and Table 3 in Supplementary Information†). This indicates low concentration of Pd in the surface of the samples. XRD analysis of Starbon® samples was undertaken before and after adsorption (see Fig. S6-7 in Supplementary Information†). It was not possible to clearly observe the pattern of Au and Pd due to the low concentration of those metals on the surfaces established by XPS.

TEM images showed the presence of nanoparticles in the Starbon® after adsorption (Figure 3). The formation of nanoparticles during the adsorption also supports the proposed

reduction mechanism for adsorption. Based on the XPS results, nanoparticles are likely to be Au⁰ and Pd⁰. However, further analysis is required to clarify the nanoparticle composition. Metal-loaded bio-adsorbents have been recently used as catalysts in industrially relevant reactions, which shows potential for the metal-loaded Starbon® in such applications.²⁰ It has been recently discovered that Starbon® can be shaped during the production process. Optimisation of the supercritical drying process was a key step in the development of uniform and mesoporous Starbon® monoliths (see Fig. S8 in Supplementary Information†). For carbonaceous materials to be industrially relevant for metal adsorption, the ability to continuously separate is of vital importance. Monoliths presents greater chromatographic efficiency and lower back pressure drop than packed adsorbents.²¹ As such, the developed monolithic Starbon® could have the desired properties for adsorption under flow, albeit further work is required to confirm this.

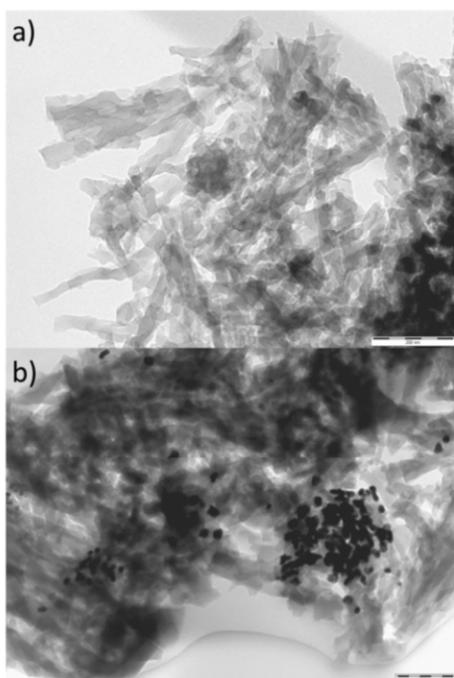


Fig. 3 TEM images of Starbon® a) before and b) after adsorption.

Conclusions

Carbonaceous mesoporous materials have been successfully produced from starch using greener techniques (MW heating and scCO₂ drying). These Starbon® materials have been effectively used in the selective adsorption and separation of precious metals from earth abundant elements, even when the concentration of PGM was lowered 100 times with respect to the earth abundant elements in solution. XPS and TEM suggest that the adsorption mechanism involves the reduction of metals by oxidation of the Starbon® to form metal nanoparticles. Simple and efficient routes to the production of Starbon® monoliths may lead to effective metal adsorption and separation in flow regimes.

Acknowledgements

The authors acknowledge the EPSRC (EP/P505178/1) and “G8 Research Councils Initiative on Multilateral Research Funding” (EP/K022482/1) and the Consejo Superior de Investigaciones Científicas for an international collaboration grant (i-LINK0636). PS gratefully acknowledges the Ministerio de Ciencia e Innovación for the concession of a Juan de la Cierva Postdoctoral Fellowship (JCI-2011-10836). The authors thank Meg Stark for assistance with microscopy, Dr. Kellye Curtis (EPRSC XPS service, University of Leeds) for assistance with XPS and Tengyao Jiang for assistance with XRD.

Notes and references

^a Department of Chemistry, The University of York, Heslington, York, YO10 5DD, UK. E-mail: andrew.hunt@york.ac.uk;

Fax: +44 (0)1904 432705; Tel: +44 (0)1904 324456

^b Departamento de Física de Polímeros, Elastómeros y Aplicaciones Energéticas, Instituto de Ciencia y Tecnología de Polímeros, CSIC, c/ Juan de la Cierva, 3, 28006, MADRID, Spain

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

1. M. Z. Jacobson and M. A. Delucchi, *Sci. Am.*, 2009, 301, 58-65.
2. A. Miller, *Strategically important metals: fifth report of session 2010-12, Vol. 1: Report, together with formal minutes, oral and written evidence*, The Stationery Office, 2011.
3. *Report on Critical Raw Materials For the EU, Report of the Ad hoc Working Group on defining critical raw materials*, EU Commission, Brussels, 2014.
4. a) J. R. Dodson, A. J. Hunt, H. L. Parker, Y. Yang and J. H. Clark, *Chem. Eng. Process.*, 2012, 51, 69-78; b) A. J. Hunt, T. J. Farmer and J. H. Clark, in *Element Recovery and Sustainability*, ed. A. J. Hunt, The Royal Society of Chemistry, 2013, pp. 1-28.
5. F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, 92, 407-418.
6. J. M. Dias, M. C. M. Alvim-Ferraz, M. F. Almeida, J. Rivera-Utrilla and M. Sánchez-Polo, *J. Environ. Manage.*, 2007, 85, 833-846.
7. C. F. Poole, *The essence of chromatography*, Elsevier, 2003.
8. S. Karabulut, A. Karabakan, A. Denizli and Y. Yürüm, *Sep. Purif. Technol.*, 2000, 18, 177-184.
9. a) R. J. White, V. L. Budarin and J. H. Clark, *ChemSusChem*, 2008, 1, 408-411; b) V. L. Budarin, J. H. Clark, J. J. E. Hardy, R. Luque, K. Milkowski, S. T. Tavener and A. J. Wilson, *Angew. Chem.*, 2006, 45, 3782-3786; c) H. L. Parker, A. J. Hunt, V. L. Budarin, P. S. Shuttlesworth, K. L. Miller and J. H. Clark, *RSC Adv.*, 2012, 2, 8992-8997.
10. H. L. Parker, V. Budarin, J. H. Clark and A. J. Hunt, *ACS Sus. Chem. Eng.*, 2013, 1, 1311-1318.
11. M.-W. Jung, K.-H. Ahn, Y. Lee, K.-P. Kim, J.-S. Rhee, J. Tae Park and K.-J. Paeng, *Microchem. J.*, 2001, 70, 123-131.
12. H. Estrade-Szwarckopf, *Carbon*, 2004, 42, 1713-1721.
13. E. Desimoni, G. I. Casella, A. Morone and A. M. Salvi, *Surf. Interface Anal.*, 1990, 15, 627-634.
14. S. D. Gardner, C. S. K. Singamsetty, G. L. Booth, G.-R. He and C. U. Pittman Jr, *Carbon*, 1995, 33, 587-595.
15. S. Biniak, G. Szymański, J. Siedlewski and A. Świątkowski, *Carbon*, 1997, 35, 1799-1810.
16. M. Yalcin and A. I. Arol, *Hydrometallurgy*, 2002, 63, 201-206.
17. R. Fu, H. Zeng and Y. Lu, *Carbon*, 1994, 33, 657-661.
18. a) K. Juodkazis, J. Juodkazyte, V. Jasulaitiene, A. Lukinskas and B. Šebeka, *Electrochem. Commun.*, 2000, 2, 503-507; b) M. Peuckert, F. P. Coenen and H. P. Bonzel, *Surf. Sci.*, 1984, 141, 515-532.
19. a) G. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddeman and M. M. Jones, *Inorg. Chem.*, 1972, 11, 296-300; b) C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg,

- Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Minnesota, 1st edn., 1979.
20. J. R. Dodson, H. L. Parker, A. Muñoz García, A. Hicken, K. Asemave, T. J. Farmer, H. He, J. H. Clark and A. J. Hunt, *Green Chem.*, 2015, DOI: 10.1039/C4GC02483D.
 21. T. Hara, H. Kobayashi, T. Ikegami, K. Nakanishi and N. Tanaka, *Anal. Chem.*, 2006, 78, 7632-7642.