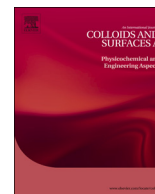




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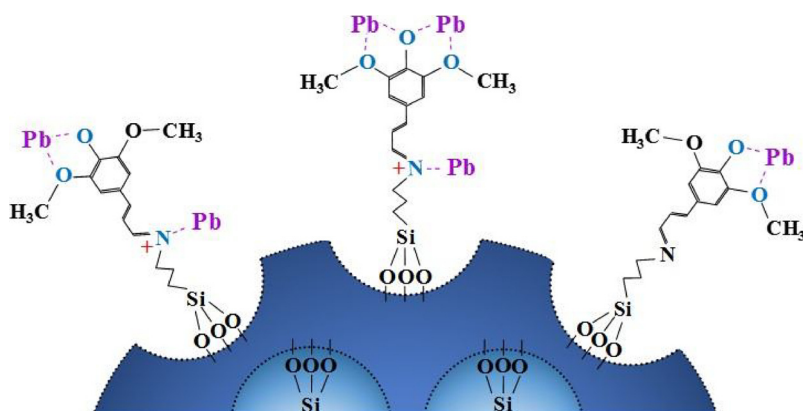
Distinguishing surface sites involved in the adsorption of lead onto sinapinaldehyde-functionalised mesocellular foam mesoporous silica

Veronica B. Cashin, Daniel S. Eldridge*, Peter Kingshott, Aimin Yu*

Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, VIC, 3122, Australia



GRAPHICAL ABSTRACT



Lead binding configurations on SA-MCF adsorbent

ARTICLE INFO

Keywords:

MCF
Sinapinaldehyde
Lead adsorption
Surface functionalisation
XPS
Mesoporous silica

ABSTRACT

X-ray photoelectron spectroscopy (XPS) has been used to distinguish specific sites involved in the removal of Pb^{2+} by the novel adsorbent sinapinaldehyde functionalised mesocellular foam, denoted SA-MCF. Adsorption capacity experiments combined with thorough XPS analysis of the material both before and after lead adsorption provide a detailed representation of the interactions occurring at the surface. We report the formation of strong, multidentate chelates between the cationic water pollutant and terminal, electron-rich O atoms of the organic SA ligand, yielding a high Pb^{2+} adsorption capacity of 48.3 mg g^{-1} . This binding site determination was distinguished from Pb-O bonding at residual surface silanol sites by interpretation of several survey spectra obtained for both the modified and unmodified materials. Additionally, it was found that tertiary amino groups of SA-MCF remained sufficiently reactive to bind Pb^{2+} ions, and that the adsorbent exhibited a preference for binding lead at the external aspect of the surface, which is likely due to steric factors despite the ultra-large mesopores (18.6 nm) of the material. This study both highlights the advantages of modifying the beneficial morphology of MCF mesoporous silica, and presents a simple approach to distinguishing between chemically similar surface sites involved in the removal of pollutants onto functionalised adsorbents.

Abbreviations: MCF, Mesocellular Foam; SBA-15, Santa Barbara Amorphous; SA, Sinapinaldehyde; APTES, 3-aminopropyltriethoxysilane; TEOS, Tetraethylorthosilicate; BET, Brunauer-Emmett-Teller; BJH, Barrett-Joyner-Halenda; SEM, Scanning Electron Microscopy; FTIR, Fourier Transform Infrared Spectroscopy; XPS, X-ray Photoelectron Spectroscopy

* Corresponding authors.

E-mail addresses: vcashin@swin.edu.au (V.B. Cashin), deldridge@swin.edu.au (D.S. Eldridge), pkingshott@swin.edu.au (P. Kingshott), aiminyu@swin.edu.au (A. Yu).

<https://doi.org/10.1016/j.colsurfa.2018.05.021>

Received 16 March 2018; Received in revised form 8 May 2018; Accepted 8 May 2018

Available online 08 May 2018

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1. Introduction

Adsorption, using materials such as activated carbon and metal oxides, is an established technique for the removal of heavy metal pollutants from contaminated water [1]. Silica has been studied extensively in recent literature and is particularly promising as an adsorbent due to the control of variation in morphology, particle size and surface functionality that can be achieved depending upon the synthesis method [2–9]. Mesoporous silica (MS), defined by the possession of pores in the range of 2–50 nm, is an excellent adsorbent due to its potential for high surface areas (up to 2370 m² g⁻¹) and variable pore sizes [8]. Mesocellular foam (MCF), one of many varieties of mesoporous silica, is structurally unlike other more common morphologies such as SBA-15 (Santa Barbara Amorphous), in that it possesses much larger pores due to the inclusion of organic swelling agents such as trimethylbenzene (TMB) in the synthesis, which expands the pores before being removed, leaving behind ultra-large mesopores [10,11].

The functionalisation of SBA-15 mesoporous silica for pollutant adsorption has been thoroughly investigated, and considerable improvements to its adsorption capacity for a variety of pollutants have been achieved [2,12–14]. In our previous work, the surface of SBA-15 was modified with the organic molecule sinapinaldehyde (SA) (shown in Fig. 1) to produce SA-SBA-15 [15], achieving a Pb²⁺ adsorption capacity of 33.6 mg g⁻¹ at a pH of 4. While this SA modification was successful in improving the Pb²⁺ loading capacity, the proposed chelation mechanism was not verified. Further, it is possible that the small diameter of the SBA-15 pores limited the performance of the material, as a result of steric obstruction which could restrict the effective surface area of the pores. It therefore follows that the transfer of this successful functionalisation to an adsorbent with substantially larger pores, such as MCF, could yield a higher adsorption capacity.

The aim of this research is to combine the beneficial geometry of MCF silica with SA functionalisation, in order to further improve the Pb²⁺ adsorption capacity of MS. It is expected that this will increase the access of Pb²⁺ ions to potential binding sites and allow more physical entrapment of the metal within the pores. Further, it is predicted that the pendant structure of SA will enable strong, covalent bonding as well

as multidentate chelation of the metal to occur both at the inner surface of the pores as well as on the external walls of MCF. Lastly, this research aims to conclusively identify the binding sites (and subsequent mechanisms) involved in the removal of Pb²⁺ by this modified material, in order to guide future novel adsorbent design and functionalisation for the removal of heavy metal wastewater pollutants.

2. Experimental

2.1. Chemicals and materials

Tetraethylorthosilicate (TEOS), trimethylbenzene (TMB), Pluronic 123, 3-aminopropyltriethoxysilane (APTES), sinapinaldehyde (SA), and NH₄F were purchased from Sigma-Aldrich. Pb(NO₃)₂ and NaNO₃ were from Ajax Chemicals. All other chemicals were analytical grade reagents and were used without further purification. Milli-Q water (18.2 MΩ cm) was used throughout the experiments.

2.2. Synthesis and functionalisation of adsorbents

MCF was prepared following the surfactant template-directed synthesis method outlined by Subagyono et al. [11]. HCl activation and amine-functionalisation with APTES was performed as described previously [15]. Sinapinaldehyde functionalisation involved refluxing 2 g of the as-prepared NH₂-MCF at 85 °C for 12 h in 35 mL of ethanol containing 1.2 g of SA. The functionalised product was washed with diethyl ether and ethanol and dried under vacuum, producing a fine brick-red powder, denoted SA-MCF.

2.3. Characterisation

Scanning electron microscopy (SEM) was conducted on a Zeiss SUPRA 40 V P field emission Scanning Electron Microscope (Germany) under vacuum. Samples were sputter-coated with Au by an EMITECH K975X Sputter-Coater. Fourier transform infrared spectroscopy (FTIR) analyses were performed on the dry powder samples in the range of 525–4000 cm⁻¹, using a Thermo Scientific Nicolet iS5 iD5 with a diamond

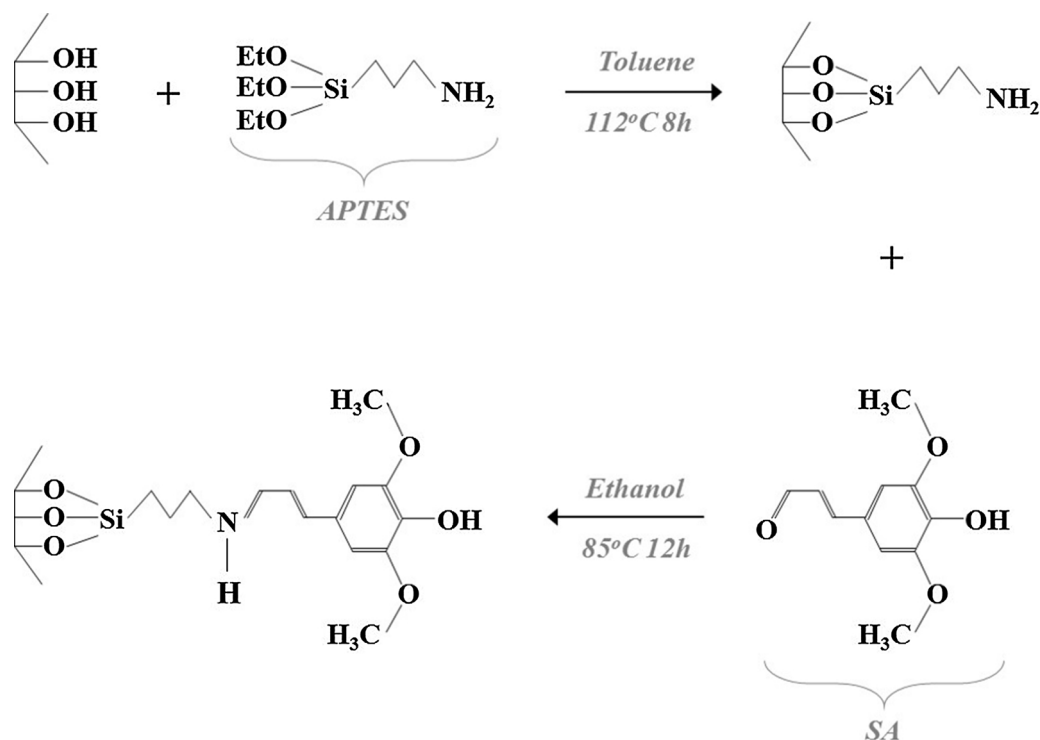


Fig. 1. Schematic representation of the synthesis of SA-MCF.

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