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# Large pore bi-functionalised mesoporous silica for metal ion pollution treatment

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ABSTRACT

Here we demonstrate aminopropyl and mercatopropyl functionalised and bi-functionalised large pore mesoporous silica spheres to extract various metal ions from aqueous solutions towards providing active sorbents for mitigation of metal ion pollution. Elemental analysis (EA) and FTIR techniques were used to quantify the attachment of the aminopropyl and mercatopropyl functional groups to the mesoporous silica pore wall. Functionalisation was achieved by post-synthesis reflux procedures. For all functionalised silicas the functionalisation refluxing does not alter particle morphology/agglomeration of the particles. It was found that sorptive capacities of the mesoporous silica towards the functional groups were unaffected by co-functionalisation. Powder X-ray diffraction (PXRD) and nitrogen adsorption techniques were used to establish the pore diameters, packing of the pores and specific surface areas of the modified mesoporous silica spheres. Atomic absorption (AA) spectroscopy and inductively coupled plasma-atomic emission spectrometry (ICP-AES) techniques were used to measure the extraction efficiencies of each metal ion species from solution at varying pHs. Maximum sorptive capacities (as metal ions) were determined to be 384 $\mu$mol g$^{-1}$ for Cr, 340 $\mu$mol g$^{-1}$ for Ni, 358 $\mu$mol g$^{-1}$ for Fe, 364 $\mu$mol g$^{-1}$ for Mn and 188 $\mu$mol g$^{-1}$ for Pd.

## 1. Introduction

Metal ions are the most significant environmental pollutants found in wastewater and long-term exposure to solvated metals ions and their effects on human health and natural ecosystems is a concern [1,2]. The metals of primary interest include chromium, nickel, manganese, iron and various heavy metals because of a combination of toxicity and exposure levels [1,3]. E.g. in 2004 the Irish Environmental Protection Agency released the following drinking water maximum contamination guidelines: chromium: 50 $\mu$g l$^{-1}$, nickel: 20 $\mu$g l$^{-1}$, manganese: 50 $\mu$g l$^{-1}$ and iron: 200 $\mu$g l$^{-1}$. Industrial wastewaters, especially mining and metallurgical wastewaters [4], are the major sources of heavy metal ion contamination and commensurate guidelines for metal concentration in industrial wastewaters are chromium: 0.5 mg l$^{-1}$ and nickel: 0.5 mg l$^{-1}$ [5]. Environmental pressures have resulted in a major focus on waste treatment and cleanup research to produce economic and effective methods for the removal of these metal ions.

Methods for metal ion removal include precipitation, coagulation/flocculation, ion exchange, reverse osmosis, complexation/sequestration, electrochemical operation and biological treatment. Some limitations of these are, e.g., high operating and energy costs. Sorbents such as activated charcoal, zeolites and clays have also been used as wastewater treatment systems [6,7]. However, disadvantages of these materials include relatively low and variable loading capacities and small metal ion-binding constants.

Ordered mesoporous materials (OMMs) are becoming established sorptives that may be exploited owing to their large surface areas (typically 200–1000 cm$^2$ g$^{-1}$) and large pore volumes. Functionalising OMMs with different chelating agents (or metal ion-specific ligands) allows specific metal ion pollutants to be selectively removed from aqueous or organic systems with correspondingly large uptakes. We refer to this uptake process as sorption in this text. Although the uptake is strictly an adsorp-

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tion process it sometimes described as absorption because the metal ions are taken into the bulk of the solid particle at interior surfaces. The choice of functionalisation agent can derive from the Irving-Williams stability series that associates particular ligands with particular metal ions to form the most stable complexes [8,9]. Accordingly, aminopropyl ligands (—NH) are identified as being attracted to 'hard' metal ions such as Ni, Cr, Mn and Fe while mercatopropyl ligands (—SH) are attracted to 'soft' metal ions such as Pd and Hg [10]. Most environmental samples will contain a mixture of metal ions, therefore, bi-functionalised (both aminopropyl and mercatopropyl) mesoporous silica would allow effective removal of a diverse range of both hard and soft metallic ions.

Many procedures for mono-functionalising mesoporous silica for metal ion extraction have been reported using a diverse assortment of ligands. For example, Fryxell et al. [11] and Mercier and Pinnavaia [12] have reported the functionalisation of mesoporous silica with mercatopropyl ligands for the extraction of mercury from aqueous solution. Functionalised mesoporous silicas for removal of various metal ions have been reported [13,14]. Here, we report a facile two-step synthesis method for bi-functionalising mesoporous silica spheres with both hard and soft ligand types. Although synthesis of mesoporous spheres offers a considerable challenge compared to routes to less well-defined particle shapes, they have considerable practical advantages in terms of sorbent packing and fluid flow through a packed bed that allow more rapid uptakes. Synthetic routes are now established [17–20].

## 2. Experimental

### 2.1. Materials and reagent

Copolymers F127 ($EO_{106}PO_{70}EO_{106}$) and P123 ($EO_{20}PO_{70}EO_{20}$) were purchased from BASF. Tetraethyl orthosilicate (TEOS, 98%) was purchased from Fluka, N-3-trimethoxysilylpropyldiethylenetriamine (TMSPA, $C_{10}H_{27}N_3O_3Si$), 3-mercaptopropyl-trimethoxysilane (MPTMS, $C_6H_{16}O_3SSi$), nickel, chromium, palladium, iron, and manganese salts, atomic absorption (AA) standard solution (1000 ppm) and atomic absorption pH buffers at pH of 4, 7 and 10 were all purchased from Sigma–Aldrich. ICP certified quality assurance metal standard containing a mix of the selected metals analysed was purchased from SPEX Certiprep Group, UK.

### 2.2. Synthesis of mesoporous silica spheres

Mesoporous silica spheres were synthesised using poly-(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymers as supramolecular templates based on the method of Kim et al. [15]. A mixture of copolymers F127 ($EO_{106}PO_{70}EO_{106}$) and P123 ($EO_{20}PO_{70}EO_{20}$) were dissolved in an aqueous solution of HCl (1.6 M). TEOS was then added to 280 ml, 1.6 M HCl solution and stirred at 35 °C. The mixture was stirred for 15 min and maintained under static conditions at 35 °C for 24 h and finally heated to 110 °C for 5 days. The starting molar composition of the mixture was 0.0037 F127:0.0032 P123:1 TEOS:4.2 HCl:144. The white precipitate was filtered without washing and dried at 60 °C. Subsequently, the product was calcined at 550 °C for 5 h to ensure complete template removal. It is important to note that the calcination temperature is somewhat higher than that used by Kim et al. [15] and we believe this has an important effect on mesopore structure because of instability of the cubic structure reported by these authors.

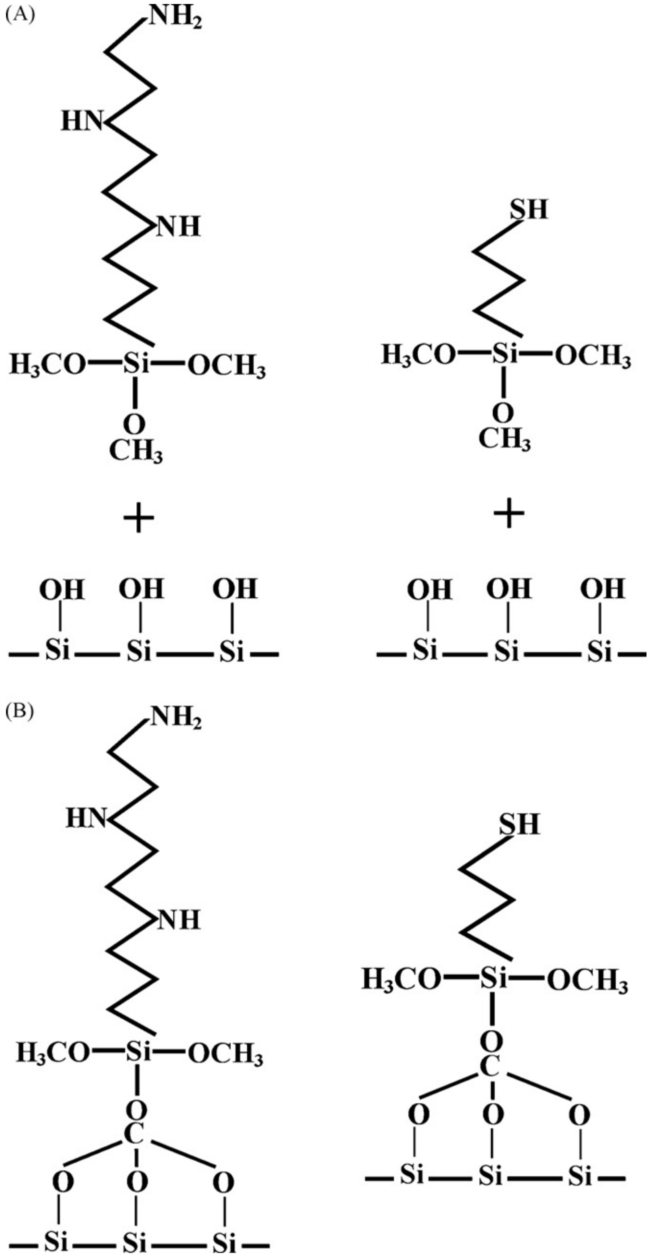

**Fig. 1.** Schematic representation of molecular species (A) and the functionalisation of a mesoporous silica surface (B) with aminopropyl groups (left) and mercatopropyl groups (right). Diagrams are indicative only and exact determination of bonding modes and sites is not implied.

### 2.3. Functionalisation procedure

Calcined mesoporous silica solid was modified with either amine or thiol groups. A sample of 5 g of the mesoporous silica material was dehydrated at 120 °C in a vacuum, and then stirred in 100 ml of dried toluene containing 5 ml of either TMSPA or MPTMS (illustrated in Fig. 1) under refluxing conditions for 6 h. Samples were then vacuum washed with dry toluene. Fig. 1 shows a schematic representation of the functionalising process which is thought to occur via reaction at surface hydroxyl sites. Bi-functionalisation followed the same procedure with the recovered sample following TMSAP treatment being refluxed in the MPTMS solution and recovery/thermal processing following the normal methodology.