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Sulphonic acid functionalized periodic mesoporous organosilica with the bridged bissilylated urea groups for high selective adsorption of cobalt ion from artificial seawater

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ABSTRACT

Bissilylated urea-bridged periodic mesoporous organosilicas (DUP-PMOs) were synthesized by the co-condensation of N,N′-diureylenepyridine-bis-[(3-propyl)triethoxysilane)] (DUP) and tetraethyl orthosilicate (TEOS) using a triblock copolymer (Pluronic P123) as a structure-directing agent at various DUP to TEOS ratios. Sulphonic acid-functionalized PMOs (SUP-PMOs) were prepared based on a reaction between amine groups of DUP-PMO with chlorosulphonic acid in chloroform under mild reaction conditions. These PMOs were well characterized by small angle X-ray scattering, N_2 adsorption–desorption measurements, Fourier-transform infrared spectroscopy, solid state ^{29}Si magic angle spinning (MAS) and ^{13}C cross polarisation-MAS nuclear magnetic resonance spectroscopy, transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The DUP-PMOs and SUP-PMOs had an ordered mesostructure, high to low surface area (ranging from 637 to 38 m^2 g^{-1}), medium pore volume (0.69–0.05 cm^3 g^{-1}) and uniform pore sizes (4.3–5.2 nm). The functionalized PMOs were used effectively for the adsorption of Co^{2+} ions with high selectivity from artificial seawater. Owing to the presence of highly hydrophilic sulphonic acid moieties as pendent functional groups in the 1 and 3 positions of the urea nitrogen atoms, the materials were found to be highly suitable for the adsorption of Co^{2+} ions from artificial seawater at pH 8 with 96.1% selectivity, even in the presence of several interfering metal ions, such as Cr^{3+}, Cu^{2+}, Ni^{2+}, and Li^{+}. The adsorption experiments showed that the selectivity towards Co^{2+} depended heavily on the sulphonic acid loading on the surface nitrogen of diureylenepyridine-bridged PMO and the time of contact with metal ions in the artificial seawater.

1. Introduction

Periodic mesoporous organosilica (PMO) is considered an interesting subcategory of mesoporous silica materials, which can be obtained by the condensation of organo-bridged silsesquioxane precursors in the presence of organic soft templates [1–3]. These materials have attracted considerable interest in materials science not only because of the homogeneous distribution of organic groups inside the framework, but also because of their attractive features, such as amazing morphology, large surface area, pore volumes, affordable pore diameter, and mechanical and hydrothermal stability [4–10]. Significant progress has been made in controlling the framework composition of PMOs through the successful integration of various bridging and non-bridging functional organic groups (amino, sulphonyl, carbonyl, acid, amido, ether, aromatic, etc.) into a siliceous pore wall to create structurally-controlled functional PMOs [11–16].

Over the last few decades, the adsorption of heavy metal ions is a topic of intense study as the sewage from many sources includes large concentrations of organic or inorganic contaminants, which are deleterious to human health. A range of harmful materials are generated in line with the development and rapid growth of an industrial society, and the problems concerning environmental contamination become intensified. Accordingly, the demand for environmentally benign and effective heterogeneous systems to remove metal ions from such water sources to protect the environment is increasing. A series of new PMO materials have been synthesized using commercial and new synthetic silylating agents

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for the effective removal of various metals, such as magnesium, nickel [17–20], aluminium [21,22], copper [23], zinc [24], and calcium [25]. Currently, there is increasing demand for the recovery of rare metals that can be applied in computers, displays, secondary batteries, hybrid cars, cameras, semiconductors, electric components, liquid crystal display (LCD), and light emitting devices (LED). In particular, the recovery of rare metals from seawater has been an important research topic in Korea because the country is on a peninsular surrounded by sea, and seawater is known to contain an abundance of rare metals including Co^{2+} (1.3×10^8 ton) or Li^+ (2.3×10^{11} ton), etc. Despite this, it is difficult to separate rare metals from seawater because their concentrations are too low to be detected with the instruments currently available. Furthermore, the seasonal variability in the quality of natural seawater is another problem. Therefore, in the preliminary studies of rare metal adsorption from seawater, artificial seawater has been commonly tested as the solvent rather than natural seawater to overcome the problems of analysis and the seasonal variability in the quality of natural seawater as well as to prepare reproducible solutions of known compositions.

Cobalt has recently become an important metal in the area of secondary batteries. Metal ion removal and recovery were carried out mainly using adsorption, ion exchange, precipitation, membrane separation, and solvent-extraction methods. Among these, adsorption is generally preferred for the removal or recovery of heavy metal ions because of the availability of various adsorbents, high efficiency, easy handling, and cost effectiveness [26]. Obviously among the many materials used for the selective removal of metal ions, such as Mn(II), Co(II), Ni(II), Cu(II), Hg(II), Cr(III), Zn(II), Pd(II), and Li(II), urea-derived heterogeneous silica based materials have attracted considerable attention because of their ease of synthesis and hydrophilic nature. Bhattacharyya et al. evaluated cobalt adsorption using montmorillonite [27] but there was no adsorption selectivity in a specific artificial solution. The separation and condensation of cobalt has been performed using metal oxide, such as TiO_2, as the adsorbing agent [28–31]. The structure of the metal oxide, however, may collapse, resulting in a decrease in the efficiency of the adsorbing agent [32]. SBA-15 modified with (3-aminopropyl)triethoxysilane and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) was used successfully for the removal of heavy metal ions, such as cobalt, copper and zinc, from aqueous solutions [17,33–35]. Recently, Awual and coworkers reported the studies on the selective detection and removal of Co(II) from waste water with mesoporous silica materials including various organic functional groups such as (N,N′-di(3-carboxysalicylidene)-3,4-diamino-5-hydroxypyrazole, 6-((2-(2-hydroxy-1-naphthoyl)hydrazono) methyl)benzoic acid, and N,N(octane-1,8-diylidene)di(2-hydroxyl-3,5-dimethylaniline) [36–38]. They also reported the novel ligand based dual conjugate adsorbent for cobalt(II) and copper(II) ions capturing from water [39]. El-Safty and coworkers reported on the simultaneous optical detection and extraction of cobalt(II) from lithium ion batteries using mesoporous silica monoliths including optical organic ligands (2-nitroso-1-naphthol, bis[N,N-bis(carboxymethyl)aminomethyl]fluorescein and pyrogallol red) [40]. On the other hand, there are few reports of the selective and efficient removal of cobalt ions using sulphonic acid functionality.

In the present investigation, sulphonic acid functionalized N,N′-diureylene pyridine PMO was synthesized via a co-condensation pathway. The obtained materials were characterized using several spectroscopic techniques to determine the successful functionalization and textural properties. The bridged silane precursor was synthesized in a homogeneous manner, followed by the preparation of homogeneously-distributed N,N′-diureylene pyridine containing PMO. The secondary amine present in the urea moieties was used for the functionalization of sulphonic acid under mild reaction conditions. Both urea and sulphonic acid are hydrophilic in nature. Accordingly, in this study, the synergetic effect of hydrophilicity and the coordination ability of sulphonic acid were combined for the efficient removal of cobalt ion from artificial seawater. Both the effects of the sulphonic acid loading and adsorption time were investigated under the same experimental conditions from artificial seawater.

2. Experimental

2.1. Materials

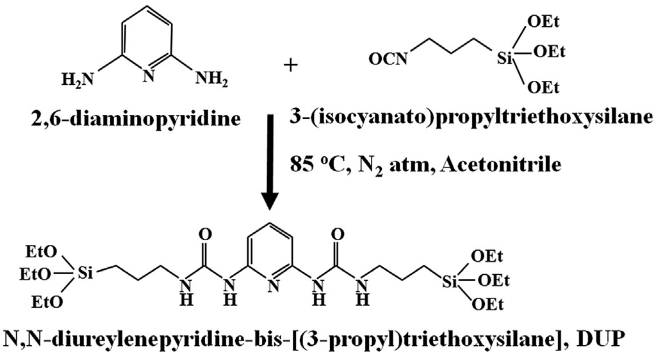
2,6-Diaminopyridine (98%), 3-(triethoxysilyl)propyl isocyanate (95%), poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123, $EO_{20}PO_{70}EO_{20}$, MW = 5800 g/mol), tetraethyl orthosilicate (TEOS; reagent grade, 98%), chlorosulphonic acid (99%), triethylamine (99%), cobalt nitrate, chromium nitrate nonahydrate, copper nitrate trihydrate, lithium chloride, and nickel nitrate hexahydrate were purchased from Aldrich Chemicals. All chemicals were used as received. Water used in all syntheses was distilled and deionised.

2.2. Preparation of organic–inorganic hybrid silica precursor, N,N′-diureylenepyridine-bis-[(3-propyl)triethoxysilane)] (DUP)

2,6-Diamino pyridine (1.1 g, 10 mmol) and 3-(triethoxysilyl) propyl isocyanate (5.0 g, 20 mmol) were dissolved in 80 ml of dry acetonitrile under a nitrogen atmosphere (Scheme 1). The mixture was heated to 85 °C under reflux for 24 h under inert conditions. The progress of the reaction was monitored by thin layer chromatography (TLC). The solvent was evaporated, followed by the production of a white precipitate, which was dispersed in dry hexane for 5 h. The swelled white product was filtered, washed with hexane and dried under vacuum. The product was called DUP.

2.3. Synthesis of N,N′-diureylenepyridine-bridged periodic mesoporous organosilica (DUP-PMO)

N,N′-diureylenepyridine bridged mesoporous materials were prepared [41] using TEOS as the parent silica source, DUP as the source of bridging organic groups and P123 as the structure-directing agent. The molar ratio of TEOS:DUP:P123:HCl:H_2O was $(1 - x)$:x:0.017:4.79:185, where $x = 0.03$, 0.06, 0.12, and 0.18. The materials synthesized were called as DUP-PMO-3, DUP-PMO-6, DUP-PMO-12, and DUP-PMO-18, respectively. In a typical procedure, a solution of P123, HCl and water was prepared at 35 °C. To this solution, a mixture of TEOS and DUP was added slowly with



Scheme 1. Preparation of N,N′-diureylenepyridine-bis-[(3-propyl)triethoxysilane).