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A novel fine-tuning mesoporous adsorbent for simultaneous lead(II) detection and removal from wastewater

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ABSTRACT

The functionalized mesoporous silica based fine-tuning mesoporous adsorbent was developed for ultra-trace lead (Pb(II)) detection and removal from wastewater. The mesoporous adsorbent was fabricated by direct immobilization of 1E,1‘E,1“E,1“‘E(tetrakis(3-carboxysalicylidene)) naphthalene–1,2,5,5–tetramine (TSNT) onto mesoporous silica monoliths. The design of the ligand into ordered pore-based mesoporous adsorbent transformed the Pb(II) detection and removal systems into smart and stable assemblies. The ability of the mesoporous adsorbent to detect and remove Pb(II) from aqueous solutions has been studied and discussed with different optimized conditions of concentrations, the amount of mesoporous adsorbent, concentration of coexisting electrolyte and pH. The design of such a tunable mesoporous adsorbent offered a simple procedure in such toxic Pb(II) ions removal without using high-tech, sophisticated instruments. The mesoporous adsorbent was able to detect the ultra-trace Pb(II) ions with high sensitivity and selectivity based on charge transfer ((intense π–π transition) transduction. Therefore, the mesoporous adsorbent proved to have an efficient ability for continuous monitoring of toxic Pb(II) ions even on-site and in situ chemical analyses. The removal data revealed that mesoporous adsorbent has high sorption capacity (184.32 mg/g) based on sorption isotherms measurements. The major advantage of the tunable design mesoporous adsorbent was that the mesoporous adsorbent retained highly efficient sensitive selectivity without a significant kinetic hindrance, despite the slight decrease of sorption after several regeneration/reuse cycles. Uptake of Pb(II) onto mesoporous adsorbent to equilibrium occurred quickly and the mesoporous adsorbent could be regenerated for reuse with diluted HCl. Therefore, the mesoporous adsorbent has been shown to have the potential to be used as an effective adsorbent for ultra–trace Pb(II) ions detection and removal from wastewater.

1. Introduction

Tons of heavy metals are generated annually by industrial activity that has contaminated water bodies all over the world. Therefore, heavy metal pollution has received much attention in the media and scientific literature due to the severe toxic effects on human health and the environment [1]. However, lead (Pb(II)) is generated from the paints, pigments and printing industries, petroleum refining industry, use of storage batteries and electrodes in electrochemistry and chemical industries [2–4]. Lead is the second top priority hazardous substance according to ATSDR [5]. Lead is non-biodegradable and has a tendency to accumulate in blood, soft tissues and as lead triophosphate in bones. Long-term consumption of water containing Pb(II), even in low concentration, can cause many chronic or acute diseases such as brain damage, kidney damage, and gastrointestinal distress to humans, as well as damage to the central nervous center, renal system, convulsions possibly resulting in death and mental retardation in children [6–8]. Therefore, the maximal permissible limit is set to 0.015 mg/L (15 ppb) [9]. This concentration value is considered as the threshold for the safeguard of public health and maintenance of an ecological equilibrium. Thus, monitoring of lead from the environment with high sensitivity and the removal of excess lead ions from wastewater is important and essential to safeguarding the public health and maintaining water quality.

Recent attention to the impact of low level Pb(II) on public health has encouraged a major research effort to develop effective means to detect and remove toxic Pb(II) from drinking water and wastewater. There are several techniques widely-used for Pb(II) detection such as atomic absorption spectrometry (AAS),

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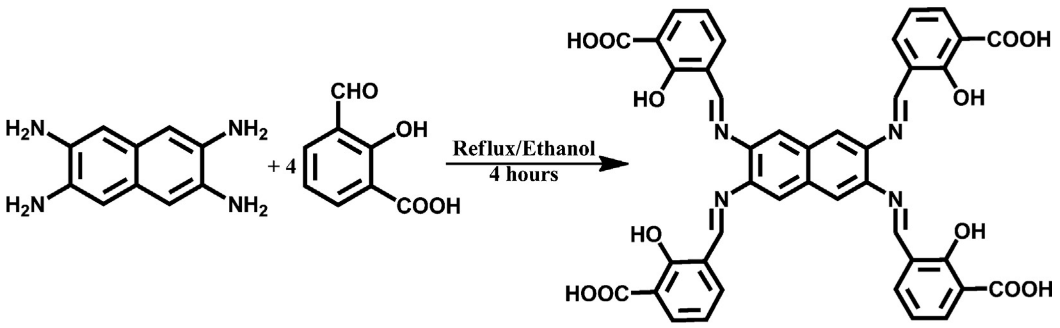

Scheme 1. Synthetic route for the preparation of 1E,1‘E,1“E,1“‘E (tetrakis(3-carboxysalicylidene))naphthalene-1,2,5,5-tetramine (TSNT) ligand.

colorimetric assay, atomic emission spectrometry (AES), electrochemistry methods, biosensors, nuclear magnet resonance, and inductively coupled plasma mass spectrometry (ICP-MS) [10–13]. However, most traditional analytical techniques do not allow direct analysis of Pb(II) especially in complex media and their sophisticated instrumentation and/or complicated sample preparation hamper their application for in-field studies. For this reason, interest in innovative methods to monitor contaminated water has been increasing based on simple, robust, easy-to-use and efficient sensitivity. Therefore, a variety of chemosensors [12] have been developed to detect Pb(II) in wastewater. However, colorimetric methods [13] are attractive and able to be directly read with naked-eye observation. The colorimetric methods are quite sensitive, however, these are not specific for Pb(II) and form color complexes with other metal ions [14–16]. Therefore, an effective method for technological diversity is the optical mesoporous adsorbent model based on generating the analytical signal as a response to binding with Pb(II) ions.

Several technological methods such as chemical precipitation, coagulation, complexions, ion exchange, solvent extraction, reverse osmosis, distillation and adsorption have been used to remove Pb(II) from wastewater [17–23]. Many of them suffer from incomplete Pb(II) removal, high reagent and energy requirements and generation of toxic waste sludge products that require proper disposal and further treatment. In the last few decades, the adsorption process has received much attention and represents an effective process for the removal of pollutant contaminants [24,25]. Moreover, adsorption of solid adsorbents is more effective at low concentrations of harmful pollutants removal. However, the high price of adsorbents increases the cost of treatment methods. Therefore, several research efforts have been performed in order to develop new sensitive, selective and cost-effective adsorbents.

Recently, nanomaterials based nanotechnology is gaining considerable public interest for ultra-trace toxic metal ions removal due to the high surface-area-to-volume ratio that makes them a suitable and cost-effective treatment method [26–28]. So, the present work is aimed at developing ligand supported mesoporous adsorbent for simultaneous low-level Pb(II) detection and removal from water. The conventional ligands are slow metal-ion capturing and lack selectivity toward a particular metal ion. So the specific and fast complexation of the metal ions with ligand immobilized mesoporous adsorbent was investigated for selective removal of heavy-metal ions from wastewater.

In this study, we developed mesoporous adsorbent by successful immobilization of synthesized 1E,1‘E,1“E,1“‘E (tetrakis(3-carboxysalicylidene))naphthalene-1,2,5,5-tetramine (TSNT) ligand (Scheme 1) onto large cage mesostructures silica for the detection and removal of Pb(II) ions. The ligand onto mesoporous silica was associated based on non-covalent interactions, Van der Waals forces and reversible covalent bonds. Several parameters such as pH, limit of detection, adsorbent dosage, contact time, and sorption capacity were systematically investigated and discussed. This paper is concerned with operational parameters for optimum detection and removal of Pb(II) from water by fine tunable mesoporous adsorbent. A complete laboratory investigation of this process would generally consist of three parts such as (i) preparation of mesoporous adsorbent, (ii) demonstration the detection operation and feasibility low detection limit and (iii) optimum removal operation to obtain data to be used in designing the full-scale plant.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (TMOS) and the triblock copolymers of poly(ethylene oxide–b–propylene oxide–b–ethylene oxide) as Pluronic F108, designated as F108 ($EO_{141}PO_{44}EO_{141}$) were obtained from Sigma–Aldrich Company Ltd. USA. The standard Pb(II) and other metal ions solutions were prepared from their corresponding AAS grade (1000 μg/mL) solutions and purchased from Wako Pure Chemicals, Osaka, Japan. For pH adjustments in detection operation, buffer solutions of 3–morpholinopropane sulfonic acid (MOPS) and 2–(cyclohexylamino)ethane sulfonic acid (CHES) were procured from Dojindo Chemicals, Japan, and KCl, HCl, NaOH from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Milli–Q Elix Advant 3 was used throughout this work.

2.2. Synthesis and characterization of the TSNT ligand

The preparation of major steps for the 1E,1‘E,1“E,1“‘E (tetrakis(3-carboxysalicylidene)) naphthalene-1,2,5,5-tetramine (TSNT) are shown in Scheme 1. The TSNT was prepared by the reaction of naphthalene-1,2,5,6-tetraamine (0.25 moles) and 3-formyl-2-hydroxybenzoic acid (one mole) in ethanol and small amount of acetic acid was added. The resultant mixture was then heated under reflux for 4 h and left to cool at room temperature. The solid formed upon cooling was collected by suction filtration. The separated product was recrystallized from the system dichloromethane/methanol 1/1 and the purpose product was dried at 50 °C for 24 h. The purity of the TSNT was analyzed by CHNS elemental analyses as follows: C, 64.59%; H, 3.56%; N, 7.15% as consistent with the $C_{42}H_{28}N_4O_{12}$ molecular formula, which requires C, 64.62%; H, 3.59%; N, 7.17%. The product was characterized by ^1H NMR spectroscopy. The ^1H NMR (400 MHz in $CDCl_3$) data of BSBAE are as follows: δ 5.35 (4H, Ph—OH), 7.29 (4H, p, Ph—OH), 8.0 (4H, o, Ph—OH), 8.01 (4H, naphthalene), 8.2 (4H, m, Ph—OH), 8.87 (4H, CH-imine), 11 (4H, carboxylic acid). ^{13}C NMR (400 MHz, $CDCl_3$): δ 113.4 (4 C, Ph, Ph—COOH), 118.4 (4 C, Ph, Ph—CH=N), 121.3(4CH,