



Investigation of ligand immobilized nano-composite adsorbent for efficient cerium(III) detection and recovery



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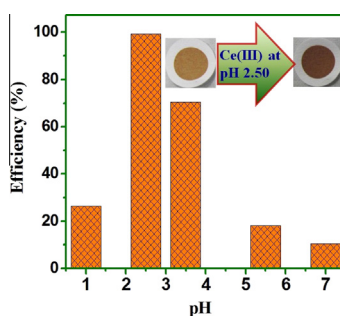
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HIGHLIGHTS

- Organic–inorganic nano-composite adsorbent was fabricated for Ce(III) recovery.
- The adsorbent exhibited nano-sized cavities and high functionality in the acidic media.
- The Ce(III) was captured by naked-eye observation with high sensitivity.
- The adsorbent was also highly selective to Ce(III) with fast kinetic performances.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the organic ligand of 4-dodecyl-6-((4-(hexyloxy)phenyl)diazanyl) benzene-1,3-diol (DPDB) and mesoporous silica have been used to prepare the nano-composite adsorbent. The nano-composite adsorbent was fabricated by indirect immobilization of DPDB onto the mesoporous silica. The adsorbent was applied as an efficient material for the detection and recovery of Ce(III) ions in aqueous solutions. The adsorbent was exhibited fast and specific capturing of Ce(III) ions observable to the naked eye and based on the stable complex formation between DPDB and Ce(III) ions. Several experimental parameters such as solution pH, color optimization with initial concentrations, contact time, foreign ions effect and regeneration studies were systematically performed. The experimental data clarified that the Ce(III) was detected and adsorbed by the adsorbent at pH 2.50. The limit of detection for Ce(III) ions by the adsorbent was 0.12 µg/L and the sorption capacity was 150.37 mg/g at optimum conditions. The co-existing ions did not affect the Ce(III) detection and sorption and sorption uptake on the adsorbent reached equilibrium with rapid kinetic performances. The adsorbed Ce(III) was completely eluted with 0.30 M HNO₃ and the adsorbent was regenerated into the initial form at the same time. In addition, the adsorbent was reused for several cycles without significant deterioration in its original functionality. Therefore, the proposed adsorbent allowed the sensitive, selective, easy to use, cost-effective, high efficiency, fast kinetics and stable capturing of Ce(III) ions even in the presence of diverse competing ions. In addition, there was no more secondary sludge produced in this operation and considered the adsorbent as the potential candidate in better replacement technology for capturing Ce(III) ions in a wide range of practical operations.

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1. Introduction

Cerium (Ce(III)) is one of the most important rare-earth elements because of its specific functional applications. Also Ce(III) is an important element in the lanthanum group, and it is abundant in the earth's crust with wide distribution among the most rare earths [1,2]. Ce(III) has many applications due to its specific properties in television, glass, metallurgy, ceramics, catalytic converters in vehicles, heterogeneous catalysts for selective oxidation of hydrocarbons, ductile iron, cast iron and aluminum alloys and some stainless steels [3,4]. In biological functions, Ce(III) affects the function of blood, the immune system, skin, bone organization, liver, heart and central nervous system [5]. On the other hand, it is toxic because the moisture and gasses can be inhaled with air and cause lung embolisms or threatens the liver [2,4]. Therefore, the determination and recovery of Ce(III) has great practical significance in research and establishment.

Many methods have been reported to determine the presence of Ce(III) such as X-ray fluorescence spectrometry, ICP-AES, ICP-MS and neutron activation analysis [6–9]. The detection limit by these instruments is low but these are costly, time consuming, several sample manipulations, require large infrastructure and are unsuitable in many laboratories, especially in developed countries. Several attempts have been made to determine the presence of Ce(III) by various materials [10–13]. However, these are not very fruitful due to the narrow working concentration range, long response times, costliness and poor reproducibility [14]. Different organic and inorganic based nano-composite materials are prepared for optical detection of several metals ions based on the advantages of speed and ease of preparation without requiring high-tech instrumentation, fast response, wide dynamic range, high sensitivity and selectivity at optimum conditions and cost-effectiveness [15–19]. This has led to the development of an optical detection and recovery of Ce(III) ions with nano-composite materials using functional group ligand immobilized mesoporous silica.

Separation of Ce(III) from aqueous solution has an interesting aspect, and several methods have been reported such as ion-exchange resins, organic solvents, precipitation, membrane separation, coagulation and flocculation, electrochemical treatment, and functionalized adsorbents [8,20–23]. The solvent extraction has a fast separation rate and high selectivity. However, it suffers from crud formation and created another problem. The ion-exchange resins are simple in equipment and operation; however, it suffers from a lower selectivity and mass transfer rate than the liquid-liquid extraction system [24]. The adsorption process is a potential candidate based on efficiency, ease-of-use and cost-effectiveness [25]. In this connection, we have used different ligand immobilized silica based materials for various metal ions' detection and recovery from aqueous solution [16,26,27]. The nanomaterials have high surface area and an absence of internal diffusion resistance, and they have excellent performance to adsorb metal ions at optimum conditions. Therefore, the present study was planned to develop ligand based functionalized nano-composite adsorbent for Ce(III) detection and recovery from acidic media.

In this work, we focused on preparing the organic ligand of 4-dodecyl-6-((4-(hexyloxy)phenyl)diazanyl)benzene-1,3-diol (DPDB) and then the ligand was successfully immobilized onto the mesoporous silica as nano-composite adsorbent. In DPDB, several functional groups, existed such as —OH and —N=N— containing N and O. It is noted that the —N=N— group itself can produce color and make a stable complex formation based on charge-transfer (π - π transition) transduction in the detection system. The prepared mesoporous silica also exhibited highly ordered mesostructure to use as a suitable carrier for combination with DPDB. The DPDB was associated onto the mesoporous silica by non-specific interaction via hydrogen bonding, van der Waals forces and reversible

covalent bonds. The performance of Ce(III) detection and recovery by the adsorbent was evaluated in batch approach. Several experimental parameters such as solution pH, initial Ce(III) concentration, contact time, competing ion effects, sorption capacity and regeneration were measured and optimized systematically. The adsorbent displays high selectivity toward Ce(III) ions over competing metal ions and is capable of Ce(III) capturing directly by naked-eye observation.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethyl orthosilicate (TMOS) and Pluronic F108 (EO₁₄₁PO₄₄EO₁₄₁) were obtained from Sigma–Aldrich Company Ltd., USA. The 4-(hexyloxy)aniline and 4-dodecylresorcinol were also purchased from Sigma–Aldrich Company Ltd., USA. The Ce(III) as the nitrate derivative (Ce(NO₃)₃·6H₂O) was purchased from Rare Metallic Co. Ltd., Japan and other metal ions solutions were prepared from their corresponding AAS grade and purchased from Wako Pure Chemicals, Osaka, Japan. For pH adjustments in the detection operation, buffer solutions of 3-morpholinopropane sulfonic acid (MOPS), 2-(cyclohexylamino)ethane sulfonic acid (CHES) and *N*-cyclohexyl-3-aminopropane sulfonic acids (CAPS) 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. Preparation and characterization of DPDB ligand

The structure and preparation steps of 4-dodecyl-6-((4-(hexyloxy)phenyl)diazanyl)benzene-1,3-diol (DPDB) is shown in Scheme 1. The 4-(hexyloxy)aniline (0.10 mol) was dissolved in 100 mL of 1 M HCl and the solution stirred for 1 h at 0 °C. To this homogeneous mixture, an ice-chilled 50 mL solution of NaNO₂ (0.10 mol) was added drop-wise, followed by vigorous stirring for 2 h under freezing conditions. Then, an equivalent quantity of 4-dodecylresorcinol (0.1 mol), dissolved in 50 mL of NaOH (0.25%) was added to the diazotate at 0 °C. The reaction mixture was stirred for 24 h and the desired product was obtained. The solid product was filtered and purified by washing with hot and cold water subsequently. The product was characterized by ¹H NMR spectroscopies. ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, 2H), 7.58 (s, H), 7.19 (d, 2H), 6.65 (s, H), 5.35 (s, 2H, C—OH), 4.06 (t, 2H, CH₂—O), 2.62 (t, 2H, CH₂), 1.76 (m, 2H, CH₂), 1.59 (m, 2H, CH₂), 1.43 (m, 2H, CH₂), 1.31 (m, 4H, CH₂), 1.29 (m, 12H, CH₂), 1.26 (m, 6H, CH₂), 0.88 (t, 6H, CH₃).

2.3. Analyses and instruments

The porosity of the calcined samples was characterized by TEM on a JEOL (JEM-2100F) instrument and operated at the accelerating voltage of the electron beam at 200 kV. SEM analysis was performed on Hitachi S-4300 operated at 16 keV. The N₂ adsorption–desorption isotherms were measured using the 3Flex analyzer (Micromeritics, USA) at 77 K. Before the N₂ isothermal analysis, mesoporous silica materials were pre-treated at 100 °C for 3 h under vacuum until the pressure was equilibrated to 10^{−3} Torr. The specific surface area (*S*_{BET}) was measured by using multi-point adsorption data from linear segments of the N₂ adsorption isotherms using Brunauer–Emmett–Teller (BET) theory. The NMR spectra were obtained using a Varian NMR System 400 MHz spectrometer. The absorbance spectrum was measured

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