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A sensitive ligand embedded nano-conjugate adsorbent for effective cobalt(II) ions capturing from contaminated water

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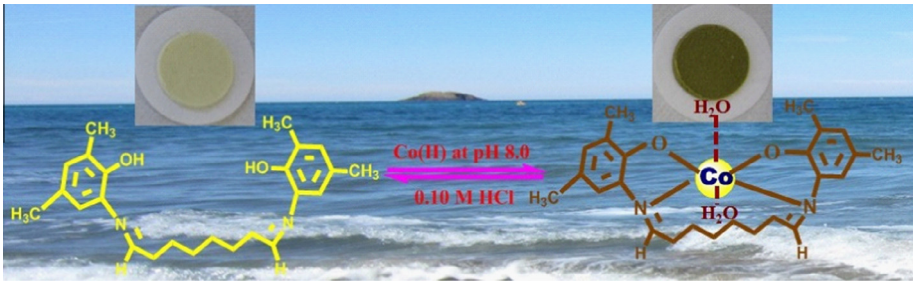
HIGHLIGHTS

- Nano-conjugate adsorbent (NCA) was based on organic-inorganic immobilization.
- The Co(II) capturing showed high functionality in terms of sensitivity/selectivity.
- The Co(II) ions can be detected without using of high-tech instruments.
- The NCA is efficient and eco-friendly for Co(II) treatment from water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, specific ligand embedded nano-conjugate adsorbent (NCA) was prepared and used for cobalt (Co(II)) monitoring and removal from wastewater. The organic ligand of *N*,*N*(octane-1,8-diylidene)di(2-hydroxyl-3,5-dimethylaniline) was synthesized and anchored onto inorganic mesoporous materials by direct immobilization method for Co(II) ions. The interaction of this material with various metal ions was evaluated, and it exhibited distinct color change (π–π transition) from whitish to green in the presence of Co(II) ions, detectable even to the naked-eye. The low detection limit for Co(II) was 0.19 μg/L and competitive monitoring studies revealed no significant interference from diverse metal ions. The effects of solution pH, contact time, competing ions and initial concentration on Co(II) sorption on NCA were investigated under optimum conditions. The NCA exhibited rapid sorption property for Co(II) ions, and the maximum sorption capability approached to 165.83 mg/g. The presence of other coexisting metal ions did not decrease the Co(II) sorption capacity and the NCA adsorbent had almost no sorption capacity to these coexisting metal ions, which suggested the high sorption selectivity of NCA to Co(II) ions at optimum conditions. The adsorbed Co(II) was eluted with 0.10 M HCl eluent and simultaneously regenerated into the original form for next operation without significant loss in its initial performances. The data also clarified that the NCA adsorbent is an efficient and eco-friendly adsorbent for Co(II) treatment. Therefore, the proposed adsorbent can be considered as a potential candidate for Co(II) ions monitoring and removal from wastewater in large-scale operations.

1. Introduction

Cobalt (Co(II)) is an essential element to humans, plants and animals for metabolic processes and a key constituent of cobalamin (vitamin B_{12}) [1,2]. Vitamin B_{12} is considered to contribute to the prevention of pernicious anemia, the production of red blood

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cells and enzymatic catalyzation reactions [3]. Therefore, the recommended allowance of vitamin B_{12} is 2.4 μg/day, which contains 0.1 μg of Co(II) ions [4]. Its deficiency may cause anemia, retarded growth and weight loss [5,6]. Similarly, Co(II) has been used in manufacturing process such as alloys, magnetic and stainless steels, batteries, catalysts and pigments. The permissible limits of cobalt in the irrigation water and live-stock watering are 0.05 and 1.0 mg/L, respectively (Environmental Bureau of Investigation, Canadian Water Quality Guidelines). In small amounts cobalt is essential for human health, because it is known to be an essential element at trace level in human beings, animals and plants for metabolic processes [7,8]. The radionuclide ^{60}Co is widely used for medical and industrial applications and may release from pressurized water nuclear power reactors [9,10]. Therefore, ^{60}Co is considered to be one of the most serious radionuclides in the environment to human beings [11]. The exposition to this element at high levels may induce toxic effects and causes nausea, reproductive problems, hypertension (high blood pressure), pulmonary diseases and hyperglycemia (high blood sugar), bone defects, and may also cause mutations (genetic changes) in living cells [12,13]. Therefore the detection of trace Co(II) in biological and environmental samples plays an important role in the fields of environmental analysis, process control and medicine. Since Co(II) has widespread occurrence in sea as well as in fresh water and the Earth's crust, the detection and removal of Co(II) is a critical endeavor.

Several analytical techniques have been reported for quantitative detection of cobalt in various samples such as electrothermal atomic absorption spectrometry (ETAAS) [14], flame atomic absorption spectrometry (FAAS) [15], inductively coupled plasma optical/atomic emission spectrometry (ICP-OES/AES) [16], neutron activation analysis (NAA) [17], inductively coupled plasma mass spectrometry (ICP-MS) [18], and gas chromatography mass spectrometry (GC-MS) [19]. The FAAS is one of the common analytical methods for the trace metal detection with low cost, operational facility and high sample throughput. However, lower levels of the heavy metals than the quantification limits of the technique and higher levels of the concomitant ions in the real samples make the techniques unsuitable for environmental samples [20]. The ETAAS and ICP-MS are very sensitive analytical techniques for detection of metal ions, but are still considered expensive by many laboratories, especially those in developing or less developed countries [8,21]. The long analysis time and complex sample pretreatment process restrict the GC-MS use as a routine analysis method for Co(II) detection [21]. As such, there is an increasing need to develop simple, selective and sensitive methods for a reliable analysis of Co(II) ions due to the coexisting matrices in complex samples and the low concentration of this element. As a consequence, it is still necessary to develop a simple, easy to use, cost-effective and sensitive analytical method for detection of ultra-trace Co(II) ions in environmental samples. Recently, the development of molecular sensing systems for transition metal ions has attracted intense attention for the scientists. The ligand decorated mesoporous particles attract much attention for colorimetric observation and simple operations [22–26]. They allow direct analysis of the specific elements by the naked eye without using high-tech instruments. In addition, the materials are cost-effective, easy to use and capable of being used in the field without a reference solution.

Many methods also have been reported for Co(II) removal from aqueous solutions such as liquid–liquid extraction, precipitation [27], cloud point extraction, reverse osmosis, ion-exchange, membrane electrolysis, oxidation, and adsorption [28–31]. However, many of them have some disadvantages such as low sorption capacity, weak chemical affinity, unsatisfactory enrichment factors, high time consumption, producing large secondary wastes or requiring rigorous conditions such as anaerobic and carbonate-free environments. Adsorption technology is one of the most effective alternatives for the removal of heavy metal ions from aqueous solutions. Different materials, such as iron oxide nanomaterials, clay minerals, zeolites, coal and chitosan and layered double hydroxides have been used as adsorbents [32,33]. However, there are still some problems that limit their practical application and thus, it is important to find a new adsorbent to solve these problems [34–36]. Recently, we have used different ligand immobilized silica based nanomaterials for various metal ions detection and removal from wastewater [37,38]. The functionalized nanomaterials have gained special attention due to the intrinsic properties such as high specific surface area, high mechanical stability, high sorption capacity and reusability.

In this study, we focused on the development of an efficient adsorbent based on organic–inorganic combination for the selective ultra-trace Co(II) detection and removal from aqueous solution. The novel ligand functionalized nano-conjugate adsorbent (NCA) was prepared through direct anchoring of *N*,*N*′-(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) onto mesoporous silica. The mesoporous silica exhibited highly ordered structure to use as an excellent carrier for combination with DHDM organic ligand. The DHDM was associated on mesoporous silica based on non-specific interaction via hydrogen bonding, Van der Waals forces and reversible covalent bonds. The performance of this NCA in colorimetric Co(II) ion sensing has been investigated without significant interference of diverse co-existing metal ions. The effect of different parameters affecting the Co(II) detection and removal efficiency including solution pH, initial Co(II) concentration, contact time, foreign ions effect, sorption capacity and regeneration were investigated and optimized systematically. The NCA responses can be triggered by Co(II) ions and transduced measurable signals at optimum pH conditions, enabling the removal even at trace-levels by stable complex formation. The developed adsorbent based on direct organic–inorganic composition is cost-effective and suitable to the large-scale treatment in the real field samples analysis.

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), the triblock copolymers of poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) designated as F108 ($EO_{141}PO_{44}EO_{141}$) and 1,8-octanedialdehyde were obtained from Sigma–Aldrich Company Ltd. USA. For pH adjustments in optical detection, 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. The standard Co(II) ions solutions, and metal salts for the source of metal ions were purchased from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Millipore Elix Advant 3 was used throughout in this work.

2.2. Synthesis and characterization of DHDM ligand

The structure and preparation of the *N*,*N*′-(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) is shown in Scheme 1. The DHDM was prepared by the reaction of 2-hydroxy-3,5-dimethylaniline (two moles) and 1,8-octanedialdehyde (one mole) in ethanol and a small amount of acetic acid was added.