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New type mesoporous conjugate material for selective optical copper(II) ions monitoring & removal from polluted waters

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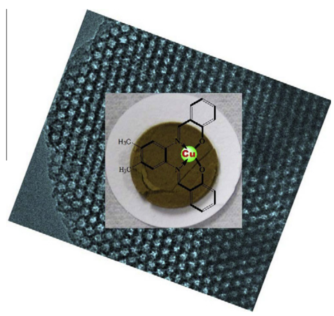
HIGHLIGHTS

- New type conjugate nanomaterials were fabricated for Cu(II) capturing.
- The porosity engaged as the auxiliary for enhancing the adsorption & selectivity.
- The stable complexation made the materials potentiality for Cu(II) ion remediation.

GRAPHICAL ABSTRACT



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ABSTRACT

The main objective of this work is to evaluate the effectiveness of the ligand supported mesoporous silica as conjugate nanomaterials for the copper (Cu(II)) ions detection and removal from environmental samples. The ligand synthesization, characterization, silica substrate preparation and their conjugation were presented. The absorbance spectra of the conjugate nanomaterials was changed when it was corroded by Cu(II) ions. The prepared nanomaterials was exhibited an obvious color change from yellowish to dark red in the presence of Cu(II) ions, which was visualized through naked-eye. The concentration-dependent colorimetric response with the nanomaterials was matched well with the exponential linear curve under color optimization conditions, where the linear range was observed in the low level of Cu(II) ions, and the detection limit were measured to be 0.37 μg/L. The solution pH, adsorption isotherms, initial concentration, contact time and foreign ions were investigated. The pH-dependent adsorption capability of the nanomaterials was much higher efficiency under weak acidic pH conditions. More attractively, the adsorption equilibrium was achieved within a short-time, which showed superior properties among various materials. The modification of silica by functional ligand not only increase the adsorption sites, but also cause chelation with Cu(II) ions for improving the adsorption capacity. The adsorption isotherm results showed that the maximum adsorption capacity of Cu(II) ion was 183.81 mg/g with monolayer coverage as judged from the Langmuir adsorption model. Continuous adsorption-elution-regeneration cyclic results demonstrated that Cu(II)-loaded conjugate nanomaterials was effectively regenerated by HCl acid, and the regenerated nanomaterials was employed for repeated use without significant capacity loss, indicating the good stability of the materials. Therefore, the fabricated conjugate nanomaterials could be readily applied to environmental samples for Cu(II) ions remediation.

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1. Introduction

Clean water is important due to the environmental ecosystem, human health and industrial developments. However, increasing industrial growth is a great concern for the diverse heavy-metal ions introduction for water pollution [1]. Therefore, the heavy-metal ions contamination is a great environmental problem in nowadays [2]. Copper (Cu(II)) ions is the third most abundant metal ions in the life system and playing a vital role in the electron transfer processes during the biological reactions system in the human body [3,4]. In addition, the lack of Cu(II) ions in the human body can adversely affect the enzyme activity and causing neurological problems [5]. On the other hand, excess of Cu(II) ion has detrimental effects to human and animal health and can cause neurodegenerative diseases including, Alzheimer's, Parkinson's, Menkes, Wilson's, and prion diseases [6–8]. Therefore, Cu(II) ions is recognized as one of the most harmful pollutants in the environment from the aspect of its bioaccumulation, non-biodegradability and toxicity [9]. Then the World Health Organization (WHO) has recommended the maximum permissible limit of Cu(II) ions in drinking water is 2.0 mg/L, while the United States of Environmental Protection Agency (USEPA) restricted the allowable level at 1.3 mg/L [10,11]. Therefore, a reliable material is always welcome for the detection and removal of trace Cu(II) ions in environmental samples.

Several strategies have been developed for Cu(II) ions detection, including atomic absorption/emission spectroscopy (AAS/AES), ICP-MS, surface plasmon resonance (SPR), ion chromatography, electrochemistry, and colorimetry [12–15]. These are promising but exhibited high-cost, which is difficult for developing countries. Over the past few years, several articles are reported for the constructive Cu(II) ions detection with cost-effective and visualization by colorimetric methods [16,17]. The colorimetric sensors have advantages such as good sensitivity and able to recognize by naked-eyes. However, many of them are suffered from low detection limits, low ion selectivity and long response times [18,19]. To overcome these previous drawbacks, we have developed ligand based nanomaterials solid optical materials for selective target metal ions detection under optimum conditions [20–22]. It is also noted that the naked-eye detection was achieved due to the devised molecule was equipped with functional groups scaffold as chromogenic signaling subunit. To date, various sensors have been synthesized for the detection of diverse metal ions [23,24]. Despite the good performance of relevant sensors, it is still a big challenge for the researchers to achieve the colorimetric detection of trace Cu(II) ions with extreme selectivity as the practical application is usually beyond capability for the efficient colorimetric assessment. Therefore, a new type of ligand functionalized silica conjugate nanomaterials for efficient Cu(II) ion detection with naked-eye. In our earlier report, we have prepared mesoporous silica based conjugate nanomaterials for detecting and separating Cu (II) ions at optimum conditions [25]. In this study, novel conjugate nanomaterials by ligand conjugation onto the mesoporous silica composite was fabricated for the improvement of the detection sensitivity, adsorption capacity for potential application in the onsite analysis.

Over the past decades, a number of methods, including precipitation, coagulation/flocculation, reverse osmosis, electrodialysis, membrane separation, ion-exchange adsorption, ultrafiltration, electrochemical operation and biological treatments have been developed for metal ions separation and removal [26–28]. Precipitation is a common method; however, the uses of chemicals with a long process with the possibility of sample contamination make this method unsuitable [29]. Therefore, many of these have limitations due to high-energy requirements, complex operations, unable to remove trace level metals, production of high amounts of sludge, and high-cost [30]. However, the adsorption is one of the most recommended processes because of high adsorption capacity, high efficiency, simple operation, fast response and cost-effective [31,32]. In this connection, a number of adsorbent materials have been reported, including activated carbon, activated alumina, zeolite, carbon nanotubes and nanostructure titanium oxide/alumina from waste waters [30,33–35]. However, these materials encountered some drawbacks that limit their application from the low adsorption capacity and separation inconvenience [36]. Nano-adsorbents are an alternative choice due to some porous materials as supports to solve these problems. In addition, this porosity engaged as the auxiliary adsorbents in enhancing the adsorption capacity [37,38]. Therefore, nanomaterials have received great attentions from the researchers because of the special properties of high adsorption capacity, simple operations, rapid responses, high surface to volume ratios and able to remove ultra-trace levels. Also the nanoparticles have exhibited the high number of unsaturated atoms on their surfaces and easily take part in chemical bonding to other atoms in the case of high adsorption and trace level sensitivity [34,39,40]. In this connection, the highly porous mesoporous silica has fabricated and then immobilized with the organic ligand. The present work describes the investigations of the detection and removal of Cu(II) ions in colorimetric methods. Then the designing of robust technology that can remove the contaminants from wastewater with rapid environmental analysis and low-cost is highly demanded [41–43].

In the present study, functional ligand of *N*,*N*-disalicylidene-4, 5-dimethyl-phenylenedene (DDPD) was prepared and successfully anchored onto the mesoporous silica to use as effective conjugate nanomaterials for ultra-trace Cu(II) ions detection and removal from waste waters. Because of the ligand functional groups supported by porous silica making complexation with Cu(II) ions, the removal efficiency of Cu(II) ions was certainly enhanced with sensitivity [25]. A range of experiments were carried out to evaluate the adsorption abilities of the conjugate nanomaterials to Cu(II) ions in water solutions. The high sensitivity and selectivity of the conjugated materials for Cu(II) ions were achieved by the naked-eye with color optimization, resulting from the formation of a strong charge-transfer upon complexation with Cu(II) ions. The objectives of this work were (a) prepare and characterize of the organic ligand; (b) evaluate the detection and adsorption capacity of Cu(II) ions; (c) investigate the effects of pH, color optimization, limit of detection, reaction time and ionic strength on the detection and adsorption processes.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as it was. Tetramethylorthosilicate (TMOS), F108 ($EO_{141}PO_{44}EO_{141}$), Al $(NO_3)_3{\cdot}9H_2O$, 4,5-dimethyl-1,2-phenylenediamine, salicylaldehyde and 3-formyl-4-hydroxybenzoic acid were purchased from Sigma–Aldrich Company Ltd. USA. The standard Cu(II) ions solutions, and metal salts for the source of metal ions were purchased from Wako Pure Chemicals, Osaka, Japan. The buffer solutions of 3–morpholinopropane sulfonic acid (MOPS) and sodium acetate were procured from Dojindo Chemicals, Japan, and KCl, HCl and NaOH from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Millipore Elix Advant 3 was used throughout in this work.