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Colorimetric detection and removal of copper(II) ions from wastewater samples using tailor-made composite adsorbent

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ABSTRACT

The nitrogen donor ligand was functionalized with polarable mesoporous silica as composite adsorbent, by a cost-effective and environmentally friendly procedure, for highly selective copper (Cu(II)) ions detection and removal from water. The nitrogen donor ligand of *N*,*N*(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) was synthesized to be specific to Cu(II) ions. The composite adsorbent permitted fast and specific Cu(II) ions capturing via colorimetric naked-eye detection based on stable complexation $[\mathrm{Cu(II)–ligand}]^{n+}$ mechanism. The effect of pH value, interferential metal ions, initial Cu(II) concentration, and contact time on adsorption capability were investigated systematically. The adsorbent was selective toward Cu(II) as shown by a light yellow to green color change. This was characterized by UV–vis spectroscopy and the color change was observed for the visual detection of Cu(II) ions. The ions selectivity of the adsorbent toward Cu(II) was determined by changes in UV–vis reflectance spectra. However, the presence of competing ions showed no interference for the detection of Cu(II) ion by the composite adsorbent. The results demonstrated that the composite adsorbent exhibited excellent sorption performance for Cu(II) ions. The low detection limit and sorption capacity of the adsorbent were 0.10 μg/L and 200.80 mg/g, respectively. The adsorbed Cu(II) was eluted with suitable eluent and simultaneously regenerated into the initial form for next operation without significant deterioration in its nanostructure case cavities. The data also confirmed that the adsorbent is a cost-effective and environmentally friendly procedure for Cu(II) treatment. Therefore, the composite adsorbent can be considered as a potential adsorbent for Cu(II) ions monitoring and removal from wastewater.

1. Introduction

Heavy metal ions that exist in the environment and living systems directly or indirectly impact the biota and human beings. Therefore, simultaneous detection and removal of heavy metal ions in an aqueous solution is an important task related to protecting the environment. Copper (Cu(II)) ions are well known as the third essential transition metal in human bodies and play a critical role in the fundamental physiological process of organisms for a variety of metalloenzymes such as cytochrome oxidase, superoxide dismutase and tyrosinase [1,2]. However, excessive Cu(II) intake in the body causes liver and kidney damage, increased blood pressure and respiratory rates, damage to the central nervous system and imbalance in cellular processes resulting in pathogenesis such as amyotrophic lateral sclerosis, prion disease, Alzheimer's disease, Menkes syndrome, inflammatory disorders and Wilson's disease [3–7]. Therefore, it is necessary to design and develop a specific Cu(II) ion materials for selective and sensitive detection and removal from water.

Atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma absorption spectrometry, potentiometric techniques, X-ray fluorescence and anodic stripping voltammetry (ASV), chromatography, gravimetric detection or photometry and anodic stripping voltammetry have all been used for the detection and quantification of Cu(II) [8,9]. However, these are very sensitive but they are not easily and widely applied due to their rigid requirement of pre-processing. Moreover, the cost and complicated sample preparation hamper their application in in-field studies. Therefore, recent analytical interest has focused on developing optical adsorbents that can be reused and do not involve sample destruction. Colorimetric adsorbent based on decorated mesoporous particles attract much attention for their conveniences of visual observation and simple operations [11–14]. However, most of the sensors developed so far were kinetically slow with a limited selectivity for detection below the permissible level, indicating a

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lack of the possibility to control the remote sensing. Among the various detection methods, UV–vis and fluorescence spectroscopy still remains the most frequently used modes due to their high sensitivity and easy operational use. In recent years, development of suitable probes are emerging for monitoring of anions, cations or neutral molecules based on charge transfer mechanism [9,10,15–17]. They allow direct analysis of the samples by the naked eye without using highly sophisticated instruments. Moreover, they also have the advantages of size, cost-effectiveness, simplicity, no need for a reference solution, and can be used in the field.

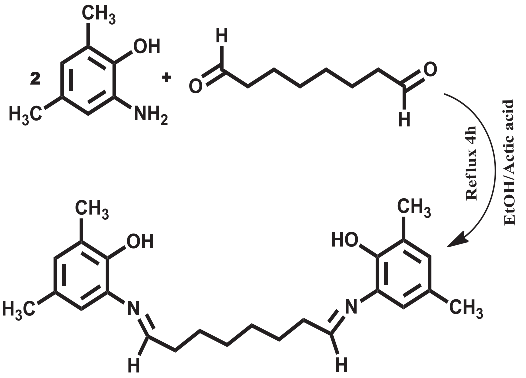
Ion exchange and adsorption, coagulation, chemical precipitation, solvent extraction, electrochemical techniques and membrane filtration are used as conventional methods [18–20]. The adsorption process is one of the simplest cost effective methods and extensively adopted nowadays. Adsorption performance of the different adsorbents strongly depends on its activated surface area and the quantity of surface activated sites for interaction with metal ions. Nanomaterials have shown remarkable potential because of their large surface area and tunable pore sizes [21–24]. Many adsorbents have drawbacks such as the low removal capacity, low selectivity and long equilibrium [25–27]. To overcome these, organic–inorganic mesoporous adsorbents have been developed for the removal of heavy metals. The mesoporous adsorbents modified by organic functional groups display higher adsorption capacity and selectivity than those of non-modified ones. We have reported different ligand functionalized nano-adsorbents for Cu(II) capturing from aqueous media [14,20]. However, there is room to development of selectivity, limit of detection and sorption capacity compared with the reported articles.

In a departure from conventional methods, we focused on the development of an optical adsorbent based on organic–inorganic combination for the selective determination and removal of Cu(II) in in an aqueous solution. Herein, novel ligand functionalized tailor-made composite adsorbent was fabricated through anchoring of *N*,*N*(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) on mesoporous inorganic silica. The DHDM exhibited the nitrogen donor atoms to make a stable complexation with Cu(II) ions in capturing under optimum condition. The mesoporous silica exhibited high ordered nanostructure and the pores were well arranged and homogeneous as nanocage structure to use as an excellent carrier for combination with DHDM organic ligand. It is noteworthy that the DHDM was associated on mesoporous silica based on non-specific interaction via hydrogen bonding, van der Waals forces and reversible covalent bonds. The sensing and removal studies revealed that the DHDM ligand immobilized composite adsorbent possess excellent detection and adsorption behavior of Cu(II) ions. The composite adsorbent responses can be triggered by Cu(II) ions and can transduce measurable signals at optimum pH conditions, enabling the sorption by stable complexation mechanism. The adsorbent displays high selectivity toward Cu(II) ions over competing metal ions and is capable of capturing Cu(II) directly due to the obvious colorimetric change seen by the naked eye. The developed adsorbent is cost-effective and suitable to the large-scale treatment of Cu(II) ions in environmental samples. The influence of various parameters such as solution pH, color optimization, Cu(II) sorption capacity, the presence of competing ions and elution or regeneration behavior was evaluated and discussed systematically.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (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-octanediol 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 Cu(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 this work.



Scheme 1. Preparation steps and structure of *N*,*N*′-(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) ligand.

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 1,8-octanediol (1 mol) and 2-hydroxy-3,5-dimethylaniline (2 mol) 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 using dichloromethane/methanol 1/1. Then the purpose materials were dried at 50 °C for 24 h. The purity of the DHDM was analyzed by CHN elemental analyses. The observed values ($C_{24}H_{34}N_2O_2$) were C, 75.32%; H, 8.88%; N, 7.31% and the calculated values were C, 75.39%; H, 8.90%; N, 7.33%. The product was characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (H, methylene), 1.52 (H, methylene), 2.15 (H, methyl), 2.34 (H, methyl), 5.34 (H, aromatic C–OH), 6.92 (H, benzene), 7.12 (H, benzene), 7.50 (H, aldimine). ^{13}C NMR (400 MHz, $CDCl_3$): δ 15.4 (CH, CH_3), 21.6 (CH, CH_3), 26.3 (CH, CH_2), 28.6 (CH, CH_2), 29.1 (CH, CH_2), 122.2 (CH, benzene), 129.3 (CH, benzene), 130.8 (CH, benzene), 132.2 (CH, benzene), 136.8 (CH, benzene), 149.1 (CH, benzene), 163.7 (CH, C–iminie).

2.3. Preparation of mesoporous inorganic silica and composite adsorbent

Mesoporous silica monoliths were synthesized following the reported methods with a slight modification [28]. The preparation of mesoporous silica monoliths procedure involved the addition of TMOS and triblock copolymers (F108, MW: 14,600) to obtain a homogenized sol–gel mixture based on the F108/TMOS mass ratio. The liquid crystal phase was achieved after quick addition of acidified aqueous solution and to promote hydrolysis of the TMOS around the liquid crystal phase assembly of the triblock copolymer surfactants. In typical conditions, the composition mass