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Schiff based ligand containing nano-composite adsorbent for optical copper(II) ions removal from aqueous solutions

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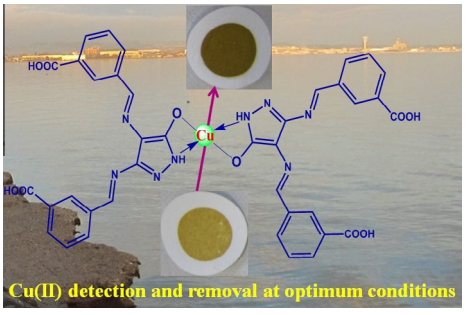
HIGHLIGHTS

- Schiff base ligand was synthesized and immobilized for nano-composite adsorbent.
- Nano-composite adsorbent (NCA) was used for optical Cu(II) ions detection/removal.
- The NCA exhibited the high sensitivity and selectivity for Cu(II) ions capturing.
- The NCA can easily be handled and able to use of industrial wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel Schiff base ligand based nano-composite adsorbent (NCA) was prepared for the detection and removal of copper (Cu(II)) ions in wastewater samples. Upon the addition of Cu(II) ions to NCA at optimum conditions, the clear color was visible to the naked-eye in the detection system. This NCA exhibited an obvious color change from yellowish to dark green in the presence of Cu(II) ions in aqueous solution. The limit of detection was found to be 0.16 μg/L by optical detection. The NCA could detect the Cu(II) ions over other foreign ions with high sensitivity and selectivity. For adsorption behavior, influences several factors such as solution pH, contact time, concentration for Cu(II) ion adsorption was investigated by batch experiment in detail. The results showed that neutral solution pH was suitable to get optimum Cu(II) ions adsorption. Also an extending contact time was favorable for improving adsorption efficiency. The adsorption process of Cu(II) ions by the NCA was followed the Langmuir adsorption isotherm model. The maximum adsorption capacity of Cu(II) ions by the NCA from the Langmuir isotherm model was 173.62 mg/g. The mesoporous NCA exhibited higher adsorption capacity compared with some other reported diverse materials. In the multi-component system, the competing ions did not significantly interfere in the adsorption of Cu(II) ions. The adsorbed Cu(II) ions was effectively eluted with 0.25 M HCl and remain the almost same functionality for many cycles use. Even in seven consecutive cycles, the NCA showed great potential in the optical Cu(II) ions removal from wastewater. Then the proposed NCA could be used a promising adsorbent for the clean-up of Cu(II) ions in wastewater treatment.

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1. Introduction

Copper ions (Cu(II)) are an essential element in living organisms and play an important role in body functions [1,2]. Most of the Cu(II) ions have been discharged into the environment and human body through the food chain from diverse manufacturing, mining and casting industries [3]. An excess intake of Cu(II) ion is adversely affected and associated with a number of diseases such as hepatitis, liver cirrhosis, kidney disease, anemia, bone disorders and Parkinson's diseases [4,5]. The maximum permissible limit in drinking water set by USEPA is 1.30 mg/L [6] while the WHO restricted for Cu(II) ions in drinking water is 0.05 mg/L [7]. Therefore, the detection and removal of Cu(II) ions is of great significance to keep control of water quality and human health.

Many sophisticated methods have been exploited for the determination of Cu(II) ions such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectroscopy, neutron activation analysis, voltammetry and electrothermal atomic absorption spectrometry [8–12]. These are highly sensitive and selective, however; these always require expensive instrumentation, laboratory setup, complicated sample preparation procedures, long detection period, skilled personnel and high operating cost, which make unsuitable for on-site or field monitoring [13]. Therefore, there is an increasing demand in the development of high sensitive, low cost, good selective and easily prepared colorimetric materials for Cu(II) ions detection that can be utilized for simple naked-eye detection without using highly sophisticated instruments and reliable for using in on-site real sample treatment [14,15]. There are numerous reports on colorimetric Cu(II) detection and most of them showed low sensitivity and poor selectivity over competing diverse ions [16–18]. In this connection, we have reported different functional group containing optical nanomaterials for diverse metal ions detection with rapid sensitivity and selectivity [19–21]. In this study, we have prepared different Schiff base ligand functionalized nanomaterial that has high selectivity for Cu(II) ions and can be applied to environmental samples treatment for efficient detection and removal operations.

In the past decades, several technologies have also been developed for the removal of heavy metal ions including ion exchange, reverse osmosis, chemical precipitation, co-precipitation, oxidation, electrochemical treatment and adsorption [22–25]. It is noted that adsorption is one of the most recommended physicochemical technologies due to the fast response, cost-effective, high efficiency and simple operation [26–31]. In addition, the adsorbents are easy to remove from a purified solution and reduce the overall costs of the processes. Compared with other forms of materials, functional nanomaterials are promising absorbents because of their high adsorption performance, low secondary pollution problem and operation simplicity [32]. A series of highly ordered mesoporous silica materials [33–35] has been developed for metal ions capturing due to their high surface area, good accessibility to active sites and rapid mass transport inside the nanostructures [36]. Recently, the design and synthesis of organic–inorganic mesoporous silica for removal and sensing of enormous metal ions has become drawn the scientific interest [37,38]. From the stand point of large surface area even after ligand immobilization, mesoporous structure materials exhibited the high stability and keep the open functionality of the functional ligand capable of reacting with metal ions to enhance the efficiency and high selectivity for the target metal ions [39]. Particularly interesting is the synthesis of Schiff bases ligand containing nanomaterials in their structure make an effective functional group for metal ions capturing. In addition, the Schiff bases which contained nitrogen and oxygen donor atoms and trend to high selectivity towards complexation of transition metal ions at optimum conditions. Also the Schiff bases containing additional donor groups to form stable metal ion complexation in the case of optical signaling for simultaneous metal ions detection and removal. Therefore, this study will focus the Schiff base ligand containing nano-composite adsorbent (NCA) for efficient Cu(II) ions detection and removal in water samples.

Ligand immobilization onto the mesoporous silica is a simple and versatile method to generate organic–inorganic based promising material [40,41]. The Schiff base ligand of N,N′di(3-carboxysalicylidene)-3,4diamino-5-hydroxypyrazole (DSDH) (Scheme 1) was successfully synthesized and then indirectly immobilized onto the mesoporous silica. The obtained NCA has potential advantages for detection and adsorption of Cu(II) ions from wastewater because of its number of interesting characteristics such as high surface area, high porosity, and high functionality at optimum conditions. Also the surface chemical properties of the NCA can be easily changed by chemical processes to improve its sensitivity and adsorption capacity. Moreover, the prepared NCA can easily be handled and eco-friendly and it can be used of industrial wastewater treatment. The morphology of the NCA was characterized by SEM, TEM and BET studies. The detection and adsorption performance toward Cu(II) has been investigated in the batch mode. The factors affecting the Cu(II) ions detection and adsorption sorption such as the solution pH, contact time, initial concentration, competition of the diverse metals and the adsorption behavior of Cu(II) ions with adsorption isotherm model were studied systematically.

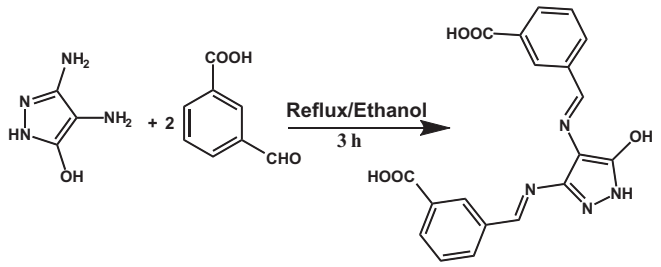
2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (TMOS), Pluronic F108 ($EO_{141}PO_{44}EO_{141}$) and 3-formylbenzoic acid were obtained from Sigma–Aldrich Company Ltd. USA. Dilauryl dimethyl ammonium bromide (DDAB) was purchased from Tokyo Chemical Industry Co. Ltd., Japan. 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 reagents of 3-morpholinopropane sulfonic acid (MOPS), 2-(cyclohexylamino) ethane sulfonic acid (CHES) and *N*-cyclohexyl-3-aminopropane sulfonic acid (CAPS) were procured from Dojindo Chemicals, Japan, and KCl, HCl, NaOH were from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Millipore Elix Advant 3 was used throughout this work.

2.2. Preparation and characterization of Schiff base DSDH ligand

The preparation of Schiff base ligand of N,N′di(3-carboxysalicylidene)-3,4diamino-5-hydroxypyrazole (DSDH) is reported elsewhere [42a] and structure is shown in Scheme 1. The DSDH was



Scheme 1. The synthetic route of N,N′di(3-carboxysalicylidene)-3,4diamino-5-hydroxypyrazole (DSDH) Schiff based organic ligand.