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Interference-free detection of trace copper in the presence of EDTA and other metals using two complementary chelating polymers

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ABSTRACT

The presence of copper in water and wastewater is receiving close scrutiny because it is more toxic to fish and aquatic life than to humans. The use of copper, especially in the microelectronics industry, has grown significantly during the last two decades and is often present in the treated wastewater along with EDTA (ethylene diamine tetra acetate) and other strong ligands. Rapid detection of copper in such bodies of water is a scientifically challenging problem. Here, we present a novel sorption technique that senses copper by forming a distinctive turquoise-blue color at concentrations as low as 25 μg/L. Most importantly, the detection technique is free of interference from EDTA or other metals. Two chelating polymers with complementary sorption properties form the heart of the process. While one chelating polymer with only nitrogen donor atoms selectively sorb copper at a very acidic pH (~1.5) in the presence of EDTA and competing metals (e.g. Zn, Ni, Pb), the other with imminodiacetate functionality shows distinctive blue color upon copper sorption. The sensing technique performed very well with tap water, river water and treated wastewater spiked with a trace amount of copper from the background of EDTA and other competing metals.

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1. Introduction

Copper has unique regulatory standards because it is more toxic to aquatic life and fish than to humans. Being an essential micronutrient, the maximum contaminant level (MCL) of copper in drinking water is 1.3 mg/L, according to the Safe Drinking Water Act (SDWA) of the United States Environmental Protection Agency (USEPA) [1]. In contrast, the copper limit in wastewater is several folds lower than drinking water because of its higher toxicity to many aquatic living species. Laboratory studies of 96 h LC_{50} for fishes are reported to be as low as 50 μg/L for some juveniles [2,3].

Recently, with the rapid development of copper interconnect technology, use of copper has increased multifold in semiconductor industries because of its lower electrical resistance and greater corrosion resistance [4–6]. The electroplating techniques, by which copper is applied onto microchips and chemical-polishing units of plated material, generate waste containing copper and chelating agent [6,7]. EDTA, the most widely used chelating agent, enhances the solubility domain of copper over a wide range of pH by forming a stable metal–chelate complex and facilitates homogeneous deposition of metals in the electroplating processes [7,8]. The presence of copper in industrial wastewaters is now a global problem, due to the manufacturing facilities of the microelectronics industry moving their operations to many developing countries during the past two decades [9–11]. The presence of copper in drinking water due to corrosion in copper pipes caused by water quality has also been a matter of concern. Consequently, both USEPA and the American Water Works Association (AWWA) are seeking operationally simple and inexpensive copper detection techniques to inform and alert consumers of potential copper contamination well in advance [12,13].

In laboratories advanced analytical instruments such as atomic absorption spectrophotometer (AAS) or instruments using inductively coupled plasma (ICP) spectroscopy can precisely detect trace copper (or other heavy metals) in water. However, for operationally simple field-level sensing of different heavy metals, to date, nearly all scientific approaches involve use of enzymes with specific interactions resulting in chemical-electrical signals, use of specific organic molecules as chromophores, and fluorescence techniques aided by metal specific ligands [14–20]. In spite of abundant research data, such sensors are often quite delicate with high degrees of sophistication, thus limiting their commercialization and large-scale usage with real-life samples in the public domain. Additionally, such techniques for metal sensing fail to perform in the presence of strong chelating compound such as EDTA which forms strong complex with a variety of metals. Very recently, an easy-to-apply robust technique has been reported that can detect toxic metals through pH changes only [21]. However, the technique is not copper-specific; the presence of iron and other toxic met-

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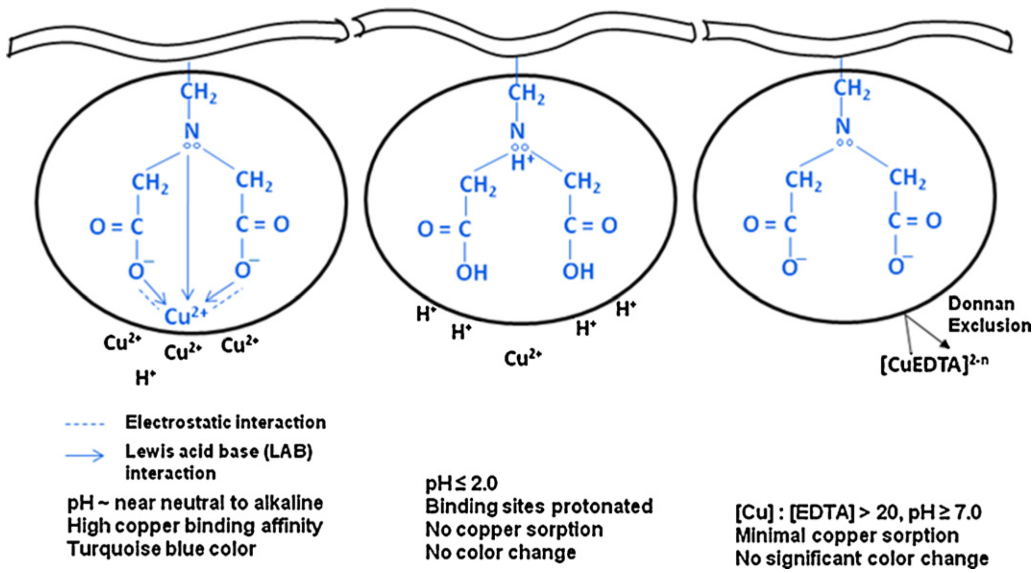


Fig. 1. Schematic illustration of interactions between copper and IDA functionality, at near neutral to alkaline pH, at pH ≤ 2.0 and in the presence of EDTA around neutral pH.

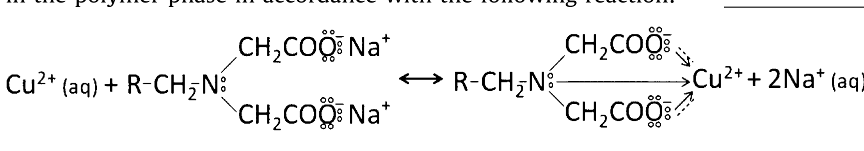
als interfere with copper detection. Although sorption chemistry has been widely applied for the removal of various toxic metals, including copper from water [22–25], a sorption-based technique has seldom been studied as a stand-alone approach for detecting copper or other dissolved solutes.

1.1. Challenges and conceptualized scientific approach

Copper is a borderline soft metal cation. Its coordination properties are influenced by the incomplete 3d orbital in the electronic configuration shown below:

Cu^{2+} : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$

Due to its incomplete d-orbital, Cu^{2+} is a Lewis acid that forms inner-sphere complexes with Lewis base or a ligand (electron pair donor). For a chelating ion-exchange resin with an iminodiacetate (IDA) functional group, it has long been known that copper exhibits very high sorption affinity. Its sorption is accompanied by a sharp, turquoise-blue color formed by a Cu–IDA complex in the polymer phase in accordance with the following reaction:



where '- - -' denotes electrostatic interaction and (→) denotes Lewis acid–base (LAB) interaction between the donor and acceptor atoms.

Such color change is observed even for a trace concentration of copper (less than 100 μg/L) in the presence of other electrolytes in the aqueous phase. However, in the presence of a relatively high concentration of EDTA in the aqueous phase, with an EDTA:Cu molar ratio of greater than 20, the IDA chelating exchanger fails to form any visible blue color. With two nitrogen and four oxygen donor atoms, EDTA is a much stronger complexing agent than IDA (with one nitrogen and two oxygen donor atoms). Hence, copper sorption onto the IDA chelating exchanger at neutral to alkaline pH is practically absent, due to the formation of strong Cu–EDTA complexes for a relatively high aqueous-phase EDTA concentration. At very acidic pH (<2.0), complexation of Cu(II) with EDTA diminishes and Cu(II) exists predominantly as a free divalent cation or Cu^{2+}, as demonstrated in Supplementary Information (SI-1) through computations using available stability constant data in the literature. Nevertheless, formidable competition from H^+ disallows any significant sorption of Cu(II) onto the IDA chelating exchanger. Thus, seemingly easy-to-apply colorimetric detection of trace dissolved copper through sorption onto the IDA chelating exchanger fails altogether when EDTA or other strong ligands are present in sample water along with copper. Foregoing scenarios are illustrated in Fig. 1. Furthermore, ferric ion and other dissolved toxic metals (e.g., Ni^{2+}, Pb^{2+}, Zn^{2+}) when present in the water sample of interest also interfere by competing with copper sorption, thus adversely affecting the efficacy of the technique.

Previous studies demonstrated that among all transition metal cations, copper is unique due to its extraordinarily high sorption affinity toward chelating polymer containing only nitrogen donor atoms under very acidic conditions [26,27]. While Cu(II) is a moderately soft Lewis acid, tertiary or secondary amines are soft Lewis bases. Commercially available Dowex M4195 or DOW 3N (Dow Chemical Co., Midland, MI) is a macroporous resin with a polystyrene matrix and a bispicolylamine functional group containing three nitrogen donor atoms. Table 1 provides salient properties of DOW 3N. At pH ≤ 2.0, Cu(II) is sorbed onto DOW 3N in preference to hydrogen ions and other transition metal cations. Furthermore, copper-loaded DOW 3N is amenable to efficient regeneration with a dilute ammonia solution [26–28]. However, unlike IDA-chelating exchanger, DOW 3N fails to produce sharp turquoise-blue color upon copper sorption.

The proposed scientific approach takes advantage of the complementary properties of these two chelating exchangers in the

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