Electroanalytical and naked eye determination of Cu^{2+} ion in various environmental samples using 5-amino-1,3,4-thiadiazole-2-thiol based Schiff bases

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ABSTRACT

Novel polydentate Schiff bases 4-(5-mercapto-1,3,4-thiadiazol-2-ylimino)pentan-2-one (S_1) and (2-(indol-3-yl)vinyl)-1,3,4-thiadiazole-2-thiol (S_2) were synthesized and explored as Cu^{2+} selective polymeric membrane electrodes (PME) using different plasticizers and anionic excluders. The potentiometric data revealed that the PME having the membrane composition (S_2: NaTPB: TBP: PVC as 4: 2: 58: 36 (w/w; mg)) is shown to have good results. Thus the coated graphite electrode (CGE) with the same composition as the best PME was also fabricated and investigated as Cu^{2+} selective electrode. It was found that CGE showed better response characteristics than PME with respect to low detection limit (1.2×10^{-8} mol L^{-1}), near Nernstian slope (29.8 ± 0.4 mV decade^{-1} of activity), wide working concentration range (6.4×10^{-8}–1.0×10^{-1} mol L^{-1}), long shelf life (90 days) and fast response time (9 s). The CGE was used successfully as an indicator electrode for the potentiometric determination of Cu^{2+} ion against EDTA and also used to quantify Cu^{2+} ion in soil, water, medicinal plants, vegetables and edible oil samples. The Schiff base S_2 is used as chemosensor for the selective determination of Cu^{2+} ion.

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1. Introduction

Copper is a nutritionally essential element required for all living species such as humans, animals and plants. It is a normal component in all body tissues and fluids, because it is a co-factor of various enzymes [1] and it also has extensive industrial application. Copper has been used effectively for many years to control algae and fish parasites in freshwater and marine systems. All these reasons are the cause for the presence of copper in the environment. Although copper is an essential metal, higher amount of copper in the environment gives bitter taste to water and causes severe effects to living species. It is recommended to have a daily intake of 2 mg, for higher doses (15 mg day^{-1}) cause severe problems to humans. In mammals including humans, low level chronic exposure to copper has been studied and it is clear that it alters both neurological and endocrine control systems, and produces subtle biochemical and cellular changes in diverse body systems [2]. It mainly affects aquatic life; its adverse effects on respiratory and ion regulatory functions are so dramatic that toxicity is explained by direct damage to specific target organs (e.g. the gills) in the fish [3,4].

Such a great problem occurring with copper in the environment leads for its monitoring. There are a number of sophisticated techniques

such as spectrophotometry [5,6], electrothermal atomic absorption spectrometry (ET-AAS) [7,8], adsorptive stripping voltammetry [9,10], flame atomic absorption spectroscopy (FAAS) [11,12], inductively coupled plasma-optical emission spectrometry (ICP-OES) [13,14] and inductively coupled plasma-mass spectrometry (ICP-MS) [15,16] that have been used for the determination of copper. However, these methods are time consuming, involve sample manipulation, relatively expensive and require large infrastructure backup. Selective analytical methodologies, which are easily operated and involve harmless reagents, and are considered cost effective equipment, have therefore been proposed as an alternative to standard methods. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as selectivity, sensitivity, good precision, simplicity and low cost. A literature survey revealed that the sensors developed for Cu^{2+} ion make use of Schiff bases [17–19], crown ethers [20,21], macrocycles [22], porphyrins [23] and variety of other ligands [24–27] as sensor materials. Some of these are suffering with high detection limit, low working concentration, low pH range and low selectivity. Thus in the search of recovery of such performance characteristics of ion selective electrodes, we prepared the Schiff bases of different kinds containing 1,3,4-thiadiazole-2-thiol moiety. By depending on the electrochemical behavior of the Schiff bases (4-(5-mercapto-1,3,4-thiadiazol-2-ylimino)pentan-2-one (S_1) and (2-(indol-3-yl)vinyl)-1,3,4-thiadiazole-2-thiol (S_2)) polymeric membrane electrode (PME) and coated graphite electrode (CGE) were

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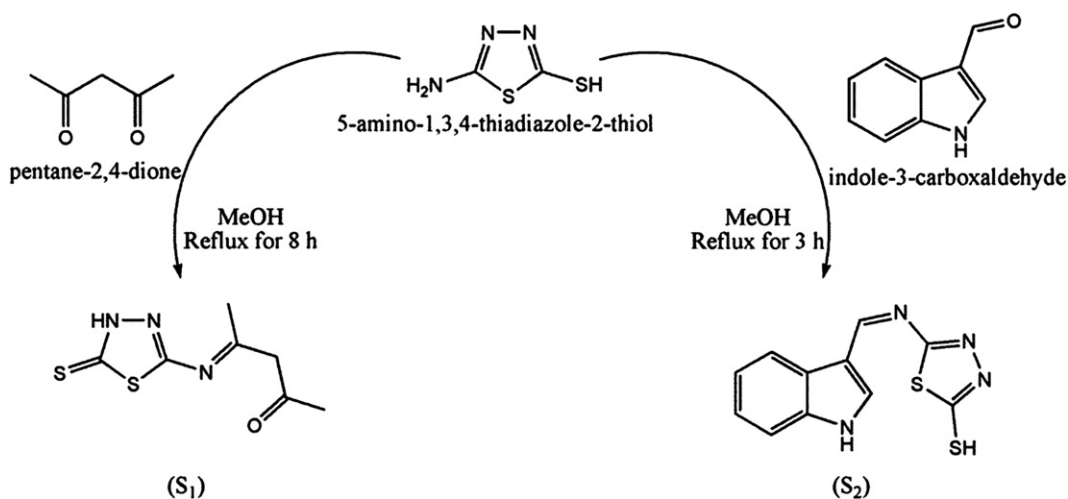
Scheme 1. Synthesis of Schiff bases 4-(5-mercapto-1,3,4-thiadiazol-2-ylimino)pentan-2-one (S₁) and (2-(indol-3-yl)vinyl)-1,3,4-thiadiazole-2-thiol (S₂).

constructed for the selective determination of Cu^{2+} ion. The Schiff bases were also utilized for the determination of Cu^{2+} ion by the naked eye (colorimetric study).

2. Experimental

2.1. Reagents

Reagent grade sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), tetrahydrofuran (THF), high molecular weight polyvinylchloride (PVC) from Merck; potassium tetrakis p-(chlorophenyl)borate (KTpClPB) from Fluka; o-nitrophenyloctyl ether (o-NPOE), oleic acid (OA), dibutylsebacate (DBS), 5-amino-1,3,4-thiadiazole-2-thiol and Indole-3-carboxaldehyde from Aldrich; tri-n-butylphosphate (TBP) from S.D. Fine-Chem, Mumbai; Acetyl acetone and all the nitrate and chloride salts of cations used were of analytical grade (LOBA Chemie) and used without further purification. Millipore water was used for the preparation of metal salt solutions of different concentrations by diluting stock solution of 0.1 mol L^{-1}.

2.2. Synthesis

Two new Schiff bases 4-(5-mercapto-1,3,4-thiadiazol-2-ylimino) pentan-2-one (S₁) and (2-(indol-3-yl)vinyl)-1,3,4-thiadiazole-2-thiol (S₂) were synthesized using 5-amino-1,3,4-thiadiazole-2-thiol (Scheme 1).

2.2.1. Synthesis of 4-(5-mercapto-1,3,4-thiadiazol-2-ylimino)pentan-2-one (S₁)

To the solution of 5-amino-1,3,4-thiadiazole-2-thiol (0.01 mol, 1.332 g) in 20 mL of methanol, pentane-2,4-dione (0.01 mol, 1.0012 g) in 10 mL methanol was added with continuous stirring and stirring was continued for 1 h. The resultant mixture was refluxed for 8 h at 60 °C. The color of solution changed from colorless to yellow. The compound was separated by column chromatography using DCM and recrystallized by MeOH.

Yield: 79%. Anal. Calc. for $C_7H_9N_3S_2O$: C, 39.05; H, 4.21; N, 19.52; S, 29.79; O, 7.43, Found: C, 38.37; H, 4.41; N, 18.92; S, 29.39; O, 8.91. UV–Vis (MeOH, nm) 369.12 (C = N). IR (KBr, cm^{-1}) 3437 (N–H, broad), 1670 (C = O, Str), 1606 (C = N, Str), ^{1}H NMR (CDCl₃, 500 MHz): δ 2.17 (s, 2H), 2.65 (s, 3H), 2.84 (s, 3H), 7.17 (s, 1H).

2.2.2. Synthesis of (2-(indol-3-yl)vinyl)-1,3,4-thiadiazole-2-thiol (S₂)

1.332 g (0.01 mol) of 5-amino-1,3,4-thiadiazole-2-thiol was dissolved in 15 mL of methanol, to this 1.45 g (0.01 mol) of Indole-3-carboxaldehyde in 15 mL methanol was added by continuous stirring. The resulting solution was refluxed for 3 h, a yellow colored solution was formed. The Schiff base was separated with column chromatography
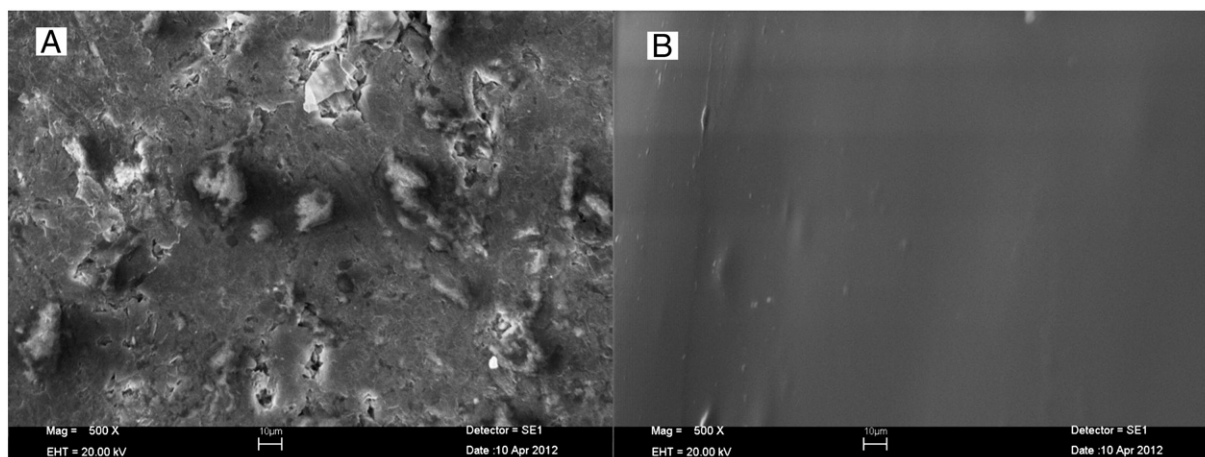
Fig. 1. SEM images of uncoated graphite electrode [A] and coated graphite electrode based on S₂ of electrode no. 16 [B].