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Solid phase extraction–preconcentration and high performance liquid chromatographic determination of 2-mercapto-(benzothiazole, benzoxazole and benzimidazole) using copper oxide nanoparticles

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ABSTRACT

This study introduces a novel method of solid phase extraction (SPE), preconcentration and HPLC determination of 2-mercaptobenzimidazole (2MBI), 2-mercaptobenzoxazole (2MBO) and 2-mercaptobenzothiazole (2MBT) from an aqueous solution by a SPE cartridge loaded with copper oxide nanoparticles. Results demonstrated that copper oxide nanoparticles are quite efficient for extraction and preconcentration of trace amounts of these mercaptans at room temperature. The study also investigated the effects of parameters such as pH, buffer and its volume, electrolyte concentration, flow rate of the test solution, composition and volume of the desorbing solvent, accepted tolerable volume, amount of adsorbent, reusability of cartridges and evidence of some co-existing species on extraction and determination of the above mentioned mercaptans. The method showed good linearity for determination of these mercaptans in the range of 0.01–10 μg mL^{-1} with regression coefficients better than 0.9969. The limits of detection (LODs) evaluations were 0.0021, 0.0027 and 0.0019 μg mL^{-1} for 2MBT, 2MBO and 2MBI, respectively. The relative standard deviations (RSDs) for 0.2 μg mL^{-1} and 5 μg mL^{-1} of the measured mercaptans were below 3.04% and 4.23%, respectively. Ramin Power Plant (3000 MW, Ahvaz, Iran) cooling water containing some 2MBT (as corrosion inhibitor) was used as the real sample. Recovery tests with spiked levels of 2MBT, 2MBI and 2MBO were carried out and satisfied results were obtained.

1. Introduction

Discharge of untreated or inadequately treated industrial wastewater in the environment may cause serious disease and major health problems in many developing countries. Water polluted with toxic compounds incurs devastating impacts on all living creatures and may negatively affect water resources used for drinking, household consumption, recreation, fishing, transportation, agriculture and commerce. Therefore, wastewater requires effective treatment to remove at least the most toxic and hazardous pollutants in order to improve and purify water. The process will also make the water suitable for reuse or reproduce it as discharge and send it back to the environment. Maintaining overall acceptable water quality requires appropriate methods of water treatment.

Chemicals including 2-mercaptobenzothiazole (2MBT), 2-mercaptobenzoxazole (2MBO) and 2-mercaptobenzimidazole (2MBI) (Fig. 1) are in a class of high production volume chemicals that are employed in many different industrial processes. These compounds are used as corrosion inhibitor agent [1–3], antifungal drug in medical applications [4], coating agent of metallic surfaces [5] and predominately, as vulcanization accelerator in rubber industry [6–8]. Use of these chemical compounds is widespread and they are well known toxic and poorly biodegradable pollutants. Such chemicals are frequently released to the environment and could be found in effluent of wastewater treatment plants and surface waters. They are the most important volatile organic compounds contributing to the unpleasant stench in wastewater treatment plants [9,10].

Annual release of 2MBT into the environment has been estimated to be 1 million lb, according to the United States Environmental Protection Agency (US EPA) [11]. Toxicity and allergenicity of these chemicals, when released to the environment, is a cause for concern and needs effective management [11–15]. Some reports state that the use of 2MBT, 2MBO and 2MBI may induce tumors, cause allergic reactions and be toxic to aquatic organisms. Additionally, it has been demonstrated that 2MBT can inhibit the degradation of easily degradable organics; hence wastewater nitrification was inhibited at far lower concentrations of 2MBT [1]. High eco-toxic properties of 2MBT, 2MBO and 2MBI and their toxic threat to ecosystems and human health is the main concern for chemists to monitor the concentration of these compounds in water samples. Several methods have been cited in the literatures which are commonly used to analyze 2MBT, 2MBO and/or 2MBI and thiols in environmental samples. Among these are spectrophotometric and electrochemical methods used for analysis

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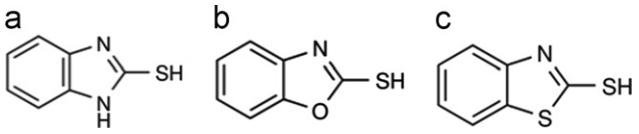

Fig. 1. Chemical structure of (a) 2MBI, (b) 2MBO and (c) 2MBT.

of mercaptans [16–20]. Methods for simultaneous determination of aromatic thiols [21–25] and aliphatic thiols [26,27] are mainly based on different chromatographic techniques [21–27]. However, to the best of our knowledge there have not been any reports hitherto on simultaneous solid-phase extraction and high performance liquid chromatography (HPLC) for determination of trace amounts of 2MBT, 2MBO and 2MBI in water solution samples.

We report herein for the first time, a new procedure for solid phase extraction that introduces highly efficient preconcentration of toxic sulfur containing compounds such as 2MBT, 2MBO and 2MBI from water samples by passing a contaminated water solution through a cartridge containing CuO nanoparticles (CONs). The proposed method demonstrated high potential ability of CuO nanoparticles to separate these hazardous compounds even at very low concentrations with a high level of efficiency on the one hand and monitoring the preconcentrated 2MBT, 2MBO and 2MBI by HPLC method after desorption by an efficient desorbing solvent on the other hand.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade. Acetone (99.5% w/w), acetonitrile (HPLC grade), water (HPLC grade), 2MBI, 2MBT and 2MBO, phosphoric acid (85% m/m), methanol (99.9% m/m), ammonia solution (25% m/m) and acetic acid (99.9% m/m) were purchased from Merck (Darmstadt, Germany) and were used without further purification. Copper oxide nanoparticles (purity 99+%, specific surface area $>80\,m^2\,g^{-1}$, average particle size <50 nm) were obtained from Neutrino (Tehran, Iran). A 2000 μg mL^{-1} mixture of CONs was prepared by an addition of 100 mL water to 0.200 g of nanoparticles. This mixture was prepared just prior to use. Stock solutions (1000 μg mL^{-1}) of 2MBI, 2MBT and 2MBO were prepared by dissolving 0.1 g of each mercaptan into 10 mL of acetone, which was then diluted to the mark with water in 100 mL volumetric flask. Other concentrations were prepared by successive dilution of stock solutions with water. Acetic acid solution (0.25% v/v) was prepared by dissolving 0.5 mL of concentrated acetic acid into 100 mL water, which was then diluted to the mark in 200 mL volumetric flask. The buffer solution was prepared by adjusting the pH of a phosphoric acid solution (0.1 M) to 6.5 using NaOH solution (0.1 M).

2.2. Apparatus

Chromatographic measurements were carried out using a Knauer (Germany) HPLC system consisting of a K-1001 pump and a k-2501 UV detector. Cellulose acetate filter (SCA grade, 0.2 μm, 25 mm, CHMLAB. Barcelona, Spain) was applied as the cartridge bed. A one stage vacuum pump (RS-4, REFCO, Switzerland) was used to control the flow rate of solutions and a pH-meter (827 pH lab, Metrohm®, Herisau, Switzerland) was also used to control the solution pH.

2.3. Chromatographic analysis procedure

A Eurosphere (C18, 250 mm × 4.6 mm) column with a mixture of acetic acid (0.25% V/V), acetonitrile and water at the ratio of 10:30:60, respectively, was used throughout as the mobile phase with a 20 μL injection loop. The temperature of the column oven was adjusted to a constant temperature (40 °C). Flow rate was increased linearly for the first 5 min after injection, from 1 mL min^{-1} up to 1.3 mL min^{-1} and then remained constant for up to 10 min. Under these conditions, retention times for 2MBI, 2MBO and 2MBT chromatographic peaks were 3.5, 6.7 and 9.2 min, respectively. Detection wavelength was set to 300 nm in the first 8 min of each chromatogram for the analysis of 2MBI and 2MBO and then was switched to 320 nm for determination of 2MBT.

2.4. General procedure

The CONs mixture (2000 μg mL^{-1}) was shaken vigorously and 7 mL of the mixture (equivalent to 14 mg CONs) was immediately transferred to a cartridge using a 10 mL syringe and passed through it leaving nanoparticles employing a positive pressure on the piston of the syringe to produce the copper oxide nanoparticles loaded cartridge (CONLC). Preconcentration was carried out using a 10 mL solution of 2MBI, 2MBT and 2MBO (each 1.5 μg mL^{-1}) transferred to the previously prepared CONLC using a syringe and then letting to pass through the cartridge by applying a positive pressure on the piston of the syringe or by a vacuum pump providing a flow rate of 0.5 mL min^{-1}. Any adsorbed mercaptans deposited on the nanoparticles were desorbed by washing the cartridge twice with 0.5 mL methanol. The washings were combined and 20 μL of the methanolic solution was injected to HPLC. Fig. 2 shows chromatograms of solution mixture of 2MBI, 2MBO and 2MBT (8 μg mL^{-1} for each) in initial solution, remained mercaptans in the initial solution after removal by the CONs, and preconcentrated 2MBI, 2MBO and 2MBT after desorption by two 0.5 mL methanol as desorbing solvent.

Optimization of parameters affecting the preconcentration process was carried out using peak areas for each mercaptan obtained from corresponding chromatograms of the solutions.

3. Results and discussion

3.1. Mechanism of adsorption

The chemical reactions that occur between copper and thiols are well-known, and so are the reactions between copper oxide, CuO, and thiols as well as some proposed mechanisms which can be found in the literature [21]. It is well known that mercaptans

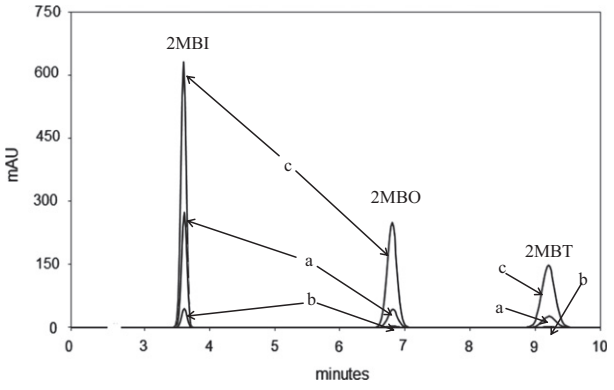

Fig. 2. Typical chromatograms of solution mixture of 2MBI, 2MBO and 2MBT (8 μg mL^{-1} for each): (a) initial solution, (b) remained mercaptans in the initial solution after removal by the CONs, and (c) preconcentrated 2MBI, 2MBO and 2MBT after desorption by two successive 0.5 mL of methanol. [Conditions: initial volume of test solution: 10 mL; adsorbent: 14 mg CONs loaded on SPE cartridge; flow rate: 0.5 mL min^{-1}].