



# Selective and sensitive fluorimetric determination of carbendazim in apple and orange after preconcentration with magnetite-molecularly imprinted polymer

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## ABSTRACT

In this study, magnetite-molecularly imprinted polymer has been used for the first time as selective adsorbent before the fluorimetric determination of carbendazim. Adsorption capacity of the magnetite-molecularly imprinted polymer was found to be  $2.31 \pm 0.63 \text{ mg g}^{-1}$  ( $n = 3$ ). Limit of detection (LOD) and limit of quantification (LOQ) of the method were found to be 2.3 and  $7.8 \mu\text{g L}^{-1}$ , respectively. Calibration graph was linear in the range of  $10\text{--}1000 \mu\text{g L}^{-1}$ . Rapidity is an important advantage of the method where re-binding and recovery processes of carbendazim can be completed within an hour. The same imprinted polymer can be used for the determination of carbendazim without any capacity loss repeatedly for at least ten times. Proposed method has been successfully applied to determine carbendazim residues in apple and orange, where the recoveries of the spiked samples were found to be in the range of 95.7–103%. Characterization of the adsorbent and the effects of some potential interferences were also evaluated. With the reasonably high capacity and reusability of the adsorbent, dynamic calibration range, rapidity, simplicity, cost-effectiveness and with suitable LOD and LOQ, the proposed method is an ideal method for the determination of carbendazim.

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## 1. Introduction

Carbendazim (methyl-2-benzimidazole carbamate) is a systemic benzimidazole fungicide which has been widely used to control various kinds of diseases in agricultural processes. Carbendazim can also be used as a worm controlling agent in golf courses and tennis courts [1]. It is also a metabolite of two other fungicides; benomyl and thiophanate methyl [2]. In the environment, benomyl and thiophanate methyl can be degraded into carbendazim rapidly [3]. However, the usage of benomyl is now restricted in many countries all over the world [4]. Carbendazim is relatively more stable than both benomyl and thiophanate methyl in the environment. Its longer half-life time depends on the type and conditions of the environmental medium [5]. Trace levels of carbendazim give serious damages to endocrine system and show mutagenic and teratogenic effects on animals [6]. Panades et al. indicate that carbendazim is embryotoxic and phytotoxic and it also shows negative effects on the male mammalian reproductive system [7]. Therefore, quantitative determination of trace levels of carbendazim is very important.

High-performance liquid chromatography (HPLC) [8–10], liquid chromatography–mass spectrometry (LC-MS) [11], fluorescence

spectrometry [12–14], excitation-emission matrix fluorescence spectrometry [15], spectrophotometry [16], surface enhanced Raman scattering spectroscopy [17,18] and electrochemical methods [19,20] are widely used for the determination of carbendazim. Most of these methods are time-consuming, expensive and consume large amounts of solvents. Thus, developing a method which is simple, cost-effective and rapid for the determination of carbendazim is being more useful.

In recent years, fluorescence spectrometry has become one of the most popular measurement techniques due to its high sensitivity, good selectivity, rapidness and low cost [21]. A series of fluorescent sensors and probes have been developed by several authors for the detection of different metal ions and organic compounds [22–26]. Over the last decade, molecularly imprinted polymers (MIPs) have been used as adsorbents for the separation and sensitive and selective determination of organic compounds. MIPs are macro-molecular compounds that have special binding sites to bind a target molecule in a matrix. They have some important properties such as high thermal and chemical stability, high selectivity and reusability which make them attractive adsorbents [27]. Therefore, these polymers have been used widely in the determination of carbendazim [28,29].

In recent years, preparation of MIPs on the surface of a supporting substrate, especially on magnetic particles, has been executed [30]. The magnetic molecularly imprinted polymers (MMIPs) can be easily separated from the solution using a permanent magnet without

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applying any centrifugation or using filtration system and this brings effective and rapid separation [31,32]. MMIPs also have some important advantages over MIPs such as improved binding capacity, economical separation, improved kinetics and favorable selectivity [33]. MMIPs have therefore been widely used for the separation and selective determination of pesticides [34–37]. However, according to our knowledge, use of MMIPs as adsorbent for the fluorimetric determination of carbendazim has not been reported. In this paper, MMIPs have been used as adsorbent for the preconcentration of carbendazim for the first time and with the fluorimetric detection, sensitive and selective method for the preconcentration and detection of carbendazim has been developed. Using MMIPs as adsorbent in the preconcentration of carbendazim, rapid and easy separation of adsorbent from the solution can be proceeded with the aid of magnetic properties of the adsorbent, when compared to MIPs. MMIPs can also be used repeatedly for quantitative determination of carbendazim without any efficiency loss since the loss of adsorbent during separation is negligible.

This study presents, MMIP-based low-cost, simple, rapid, selective and sensitive fluorimetric method for the determination of carbendazim. MMIP acts as a selective-adsorbent and was used to separate carbendazim from the matrix. Accurate and sensitive determination of trace carbendazim could be achieved with the aid of the native fluorescence of the analyte. Native fluorescence of the pesticide depends on the fluorophore, benzimidazole ring, which displays large Stokes shifts and high fluorescence quantum yields [38]. This analytical procedure has been applied to determine carbendazim residues in apple and orange. Since the re-binding studies can be carried out in water, the proposed method can also be used for the preconcentration of carbendazim in real water samples. The optimization of the experimental conditions, analytical performance of the method and its application to real samples are presented in the following sections.

## 2. Materials and Methods

### 2.1. Reagents

Carbendazim (97%) was purchased from Sigma Aldrich (USA). Methacrylic acid, ethylene glycol dimethacrylate (97%), chloroform, ethanol, methanol, acetonitrile, dichloromethane, 2,2'-azobis(isobutyronitrile), tetrahydrofuran,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and NaOH were purchased from Merck (USA). *N,N*-dimethylformamide was purchased from Carlo Erba (Italy). Thifensulfuronmethyl, chlorothalonil and tebuconazole were purchased from TCI (USA). 1-Naphthol and tetramethylthiuram disulfide were purchased from Alfa Aesar (USA).

Stock standard solutions ( $50 \text{ mg L}^{-1}$ ) of carbendazim were prepared by dissolving pesticide in 5 mL methanol and diluting it with distilled water to the final volume. Working standard solutions were prepared by diluting the stock standard solutions daily. All solutions were stored at 4 °C.

### 2.2. Apparatus

Shimadzu RF-5301 PC model spectrofluorometer (Kyoto, Japan) was used for the determination of carbendazim. pH measurements were performed using a calibrated Mettler Toledo pH meter (Schwerzenbach, Switzerland). All weight measurements were performed using Precisa XB220A balance (Dietikon, Switzerland). Fourier transform infrared spectra were recorded on a Perkin-Elmer FTIR One B spectrometer (USA). The morphologies of magnetite and magnetite-molecularly imprinted polymers were analyzed by scanning electron microscopy (SEM) (JEOL, Tokyo, Japan). Magnetic measurements were carried out using a vibrating sample magnetometer (Cryogenic Limited PPMS) in Middle East Technology University Central Laboratory.

### 2.3. Synthesis of Magnetite Particles

The magnetite was synthesized by the coprecipitation method as stated in the literature [39,40]. 0.01 mol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.02 mol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 100 mL of distilled water in a polypropylene bottle and the mixture was stirred and degassed with  $\text{N}_2$  gas while the temperature was increased to 80–90 °C in water bath. 50 mL of  $2 \text{ mol L}^{-1}$  NaOH solution was added to the solution. Instantly, black precipitates were observed in the polypropylene bottle. After 2 h, the magnetite precipitates were isolated from the solvent by a permanent magnet and washed several times with distilled water. Magnetite particles were dried under  $\text{N}_2$  gas.

### 2.4. Preparation of Magnetite-molecularly Imprinted Polymers (MMIPs)

1.0 mmol carbendazim was dissolved in 15 mL *N,N*-dimethylformamide under gentle heating. 4.0 mmol methacrylic acid was added and this mixture was stirred for 45 min. This mixture was named as preassembly solution (solution #1). In an other beaker, 1.0 g magnetite was mixed with 3.0 mL oleic acid and stirred for 10 min (solution #2).

20 mmol ethylene glycol dimethacrylate and the solution #1 were added to solution #2 and this new mixture was named as mixture A.

1.8 g of polyvinylalcohol which is used as disperser was dissolved in 60 mL distilled water under gentle heating while the solution was purged with nitrogen gas in order to obtain a saturated polyvinyl alcohol solution.

Mixture A and saturated polyvinyl alcohol solution were mixed in a two-necked-flat-bottomed-flask and then 0.1 g 2,2'-azobis(isobutyronitrile) was added to the mixture. The polymerization reaction was carried out at 55 °C under nitrogen atmosphere for 5 h.

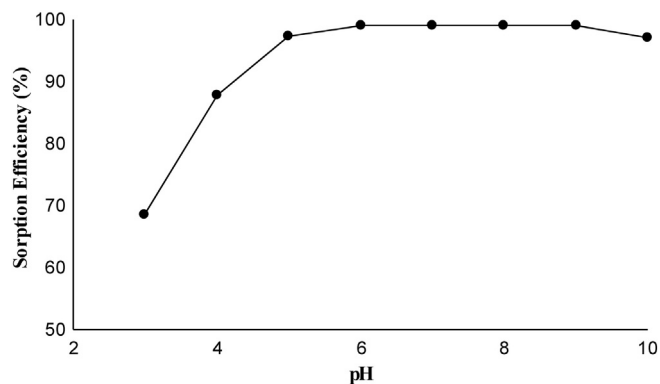
After polymerization, magnetite molecularly imprinted polymers (MMIPs) were separated using a permanent magnet and washed with methanol: acetic acid (9:1, v/v) and methanol, successively. The MMIPs were dried at 60 °C.

For the extraction of carbendazim, the prepared MMIPs (0.5 g) were washed with methanol: acetic acid (9:1) in an orbital shaker until it could not be detected by fluorimetry. The magnetite non-imprinted polymers (MNIPs) were prepared using the same procedure except that the template molecule (carbendazim) was not used during the process. All polymers were dried at 60 °C before use in the re-binding studies.

Synthesized polymers have been used as adsorbent for the preconcentration of carbendazim for the first time in the literature.

### 2.5. Re-binding and Recovery Procedures of Carbendazim

For the re-binding studies of carbendazim, 100 mg of polymer was added to a 50-mL falcon tube containing 15 mL  $0.2 \text{ mg L}^{-1}$  carbendazim



**Fig. 1.** Effect of initial pH on re-binding of carbendazim (amount of polymer: 100 mg, sample volume: 15 mL, initial carbendazim concentration:  $0.2 \text{ mg L}^{-1}$ , contact time: 60 min).

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