CHAPTER I

INTRODUCTION

1.1 Significance of the study

In commercial agricultural crop production, pesticides are necessary to mitigate the impact of pests, diseases, and weeds, which can significantly reduce crop yields. Without effective management strategies, these factors may lead to extensive crop losses, resulting in decreased agricultural productivity and disruptions in the food supply chain. Therefore, the use of pesticides remains a fundamental aspect of agricultural practices.

Carbaryl, or 1-naphthyl methylcarbamate, is a carbamate insecticide. It is used to control various pests, including aphids, fire ants, and spiders, on fruits, vegetables, nuts, and other crops (Thai Agriculture Standard, TAS 9002-2016). Carbaryl contains both polar (carbamate group) and nonpolar (naphthalene ring) regions, as shown in Figure 1.1 This results in its low solubility in water, 40 mg/L at 30 °C. It is also chemically stable with a slow decomposition rate and a half-life of 1600 days in an aqueous solution of pH 5. These properties lead to carbaryl persistence in the environment and crops after harvesting, raising health concerns (Lee et al., 2018).

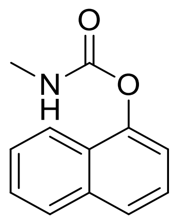

Figure 1.1 A structure of carbaryl.

Human exposure to carbaryl primarily occurs through contaminated agricultural products, with food being the dominant intake route. This pesticide can cause adverse health effects such as headaches, memory loss, muscle weakness, and anorexia due to its inhibition of acetylcholinesterase, a key enzyme that regulates neurotransmission (Yan et al., 2013; Zheng et al., 2011). Although trace levels of carbaryl have been detected in drinking water, significant contamination is uncommon. The World Health Organization (WHO) establishes a safety limit of 0.09 ppm, and general exposure through drinking water remains low except in cases of accidental over-spraying or contamination of surface water (Kanyika-Mbewe et al., 2020; WHO, 2008). Given its widespread use in agriculture, monitoring carbaryl residues in food is critical to ensuring consumer safety. The Thai Agriculture Standard (TAS 9002-2016) regulates maximum residue limits (MRLs) for carbaryl in specific fruits and vegetables. Some examples are shown in Table 1.1. Studies have reported carbaryl residues in vegetables and fruits (Fan et al., 2015). Therefore, it is important to monitor carbaryl regularly in agricultural produce to minimize exposure risks.

Table 1.1 The maximum residue limits of carbaryl in crops regulated by the National Bureau of Agricultural Commodity and Food Standards Ministry of Agriculture and Cooperatives, Thailand.

Agricultural Commodities	**Maximum Residue Limits (MRL), (mg/kg)**
lead tree leaves, cacao beans	0.02
grapes, chili	0.5
rambutan, rice, watermelon, coconut, mangosteen, Thai eggplant	1
peanut	2
mango	3
sweet peppers	5
apple	15
longan	20
durian	30

Carbaryl detection is crucial in environmental and food safety monitoring, requiring reliable analytical methods. Traditional techniques such as gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) are widely used for accurate quantification (Chen et al., 2022). However, these chromatographic methods involve complex sample preparation, require expensive equipment, and can be time-consuming. To address these limitations, researchers have developed alternative detection techniques that are faster and more cost-effective. Among these, spectrometric methods have gained attention due to their efficiency and ability to provide reliable results.

In addition to exploring alternative techniques, researchers often focus on detecting carbaryl's hydrolysis product, 1-naphthol, rather than the parent compound itself. This is because 1-naphthol is more stable and easier to analyze in aqueous environments, with a water solubility of 866 mg/L at 25 °C. Additionally, it exhibits higher sensitivity in spectrophotometric and fluorometric detection methods (Massey et al., 1995), allowing for more accurate measurements.

Since 1-naphthol is the primary hydrolysis product of carbaryl, its formation is a crucial step in detection methods that rely on absorbance or fluorescence measurements. The hydrolysis process occurs in alkaline solutions, where hydroxide ions (OH^-) break the carbamate bond in carbaryl, leading to 1-naphthol formation. Studies have demonstrated that bases such as sodium hydroxide (NaOH) (Xu et al., 2025), potassium hydroxide (KOH) (Jiao et al., 2022), and tetrabutylammonium hydroxide (TBAOH) (Lee et al., 2018) can facilitate this reaction. Among these, NaOH is the preferred reagent due to its high efficiency and widespread availability.

To minimize chemical waste in laboratory analyses, this study explores an alternative approach using mesoporous materials for carbaryl detection. Instead of relying on conventional strong bases such as NaOH, this method utilizes the basicity of Mobil Composition of Matter No. 41 (MCM-41), containing cetyltrimethylammonium bromide (CTAB). The basicity of MCM-41 originates from its siloxy anion (SiO^-) groups, which interact electrostatically with the positively charged head of CTAB molecules. These siloxy anions act as basic sites for the hydrolysis of carbaryl, promoting the formation of 1-naphthol without the need for excess chemical reagents. The hydrolysis product, 1-naphthol, can then be detected fluorometrically, emitting at approximately 470 nm upon excitation at 365 nm.

1.2 Research objectives

This study aims to develop an effective method for detecting carbaryl using MCM-41 containing CTAB (MCM-41-CTAB). To achieve this, the research focuses on investigating key factors that influence the interaction between MCM-41-CTAB and carbaryl, ensuring optimal conditions for detection. Finally, the developed method will be applied to analyze carbaryl residues in vegetable and fruit samples, providing a practical approach for monitoring pesticide contamination in agricultural produce.

1.3 References

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