CHAPTER II
LITERATURE REVIEW

2.1 Carbaryl detection

Carbaryl is widely used in agriculture, and its residues may remain in food products, posing risks if consumed above permissible limits. Monitoring carbaryl is crucial due to its potential effects on human health and the environment.

Carbaryl is typically determined using chromatographic methods, such as gas chromatography-mass spectrometry and high-performance liquid chromatography (Chen et al., 2022) with either UV/ vis absorbance or fluorescence detection (Massey et al., 1995). Despite offering robust trace analysis characterized by exceptional sensitivity and high reproducibility, these methods have some limitations. Sophisticated equipment is required, and sample preparation and purification are laborious and time-consuming. Alternative methods have also been reported, such as electrochemical methods (Kunpatee et al., 2023; Lv et al., 2023; Silva J. d. O. S. et al., 2024) and colorimetric methods (Amatatongchai et al., 2023; Raja et al., 2023). Extensive research has been devoted to developing methods for carbaryl analysis that are simple, fast, sensitive, selective, accurate, and user-friendly. Spectrometric methods are among those that serve such requirements. Some reported spectrometric methods for carbaryl determination are shown in Table 2.1.

In this study, a fluorometric method for determining carbaryl was developed based on the reaction of carbaryl with Mobil Composition of Matter No. 41 (MCM-41) containing cetyltrimethylammonium bromide (CTAB) to produce 1-naphthol. 1-Naphthol yielded a fluorescence signal at 470 nm upon excitation at 365 nm, which could be used for carbaryl determination.

Table 2.1 Some reported spectrometric methods for carbaryl determination.

Probe	Method	LOD ($\mu g\ mL^{-1}$)	Samples	Ref.
$H_{39}GFP\text{-}Cu^{2+}$	Fluorometric	7.03×10^{-6}	Apple, tomato & cucumber	(Lei et al., 2015)
CdSe–ZnS-MIP	Fluorometric	2.9×10^{-2}	Rice & Chinese cabbage	(Zhang et al., 2015)
SiQDs–AChE–ChOx	Photoluminescence	7.25×10^{-6}	Tomatoes & cucumbers	(Yi et al., 2013)
CQDs-AChE& ChOx	Photoluminescence	5.39×10^{-6}	Apples	(Li et al., 2016)
Cys-AuNPs	UV-vis	7.5	Chili	(Rujiralai et al., 2020)

2.2 Hydrolysis of carbaryl

The detection of carbaryl using spectroscopic techniques revealed that carbaryl absorbs light in the UVB range and emits light in the UVA range, producing a low signal unsuitable for quantification. Therefore, it is necessary to convert carbaryl into other substances that absorb or emit light with a sufficiently strong signal for accurate quantification.

Carbaryl can undergo a hydrolysis reaction in an NaOH solution (Shahdost-Fard et al., 2021), according to Figure 2.1, to form 1-naphthol, which can be used as an indicator for the detection and quantification of carbaryl based on absorbance or fluorescence measurement, as 1-naphthol exhibits blue fluorescence. However, a limitation of using NaOH in solution form is its inability to be separated and recovered after the reaction, resulting in waste generation and increased costs for reagent replacement. Additionally, the basic nature of NaOH may lead to undesired side reactions with other compounds in the sample, potentially interfering with fluorescence measurements. In summary, while NaOH has been traditionally used for

the hydrolysis of carbaryl in fluorescence detection methods, its limitations have prompted the exploration of alternative solid-phase reagents like MCM-41. These alternatives offer benefits in terms of reusability, specificity, and safety, making them attractive options for developing more efficient and sustainable analytical methods. In this research, MCM-41-CTAB will be investigated for its ability to hydrolyze carbaryl to produce 1-naphthol.

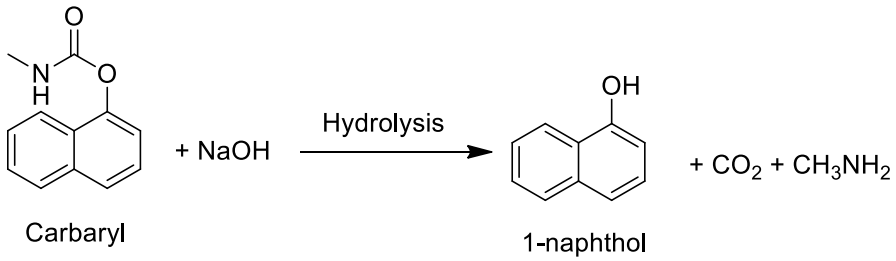

Figure 2.1 Reaction of carbaryl in NaOH solution (Lee et al., 2018).

2.3 Mobil Composition of Matter No. 41 (MCM-41)

According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be classified into three types based on pore size, including microporous (pore size <2 nm), mesoporous (2-50 nm), and macroporous (>50 nm) materials (Chaudhary et al., 2017). MCM-41 is a mesoporous silica material used in various applications, including catalysis, chemical separation, adsorption, drug delivery, and sensors (Costa et al., 2020), due to its high surface area, tunable pore sizes ranging from 2.5 to 6 nm (Gil García et al., 2017), and significant thermal and chemical stability. Additionally, it has the ability to incorporate various metal oxides into its framework and can be easily functionalized with organic or inorganic molecules.

Mesoporous silica materials can be synthesized through various methods, with the choice of method often depending on the desired structure, pore size, and application. For MCM-41, a typical synthesis method is a sol-gel process using tetraethoxysilane (TEOS) as a silica precursor and cetyltrimethylammonium bromide as a surfactant that acts as a template to create the mesoporous structure. CTAB creates spherical micelles and TEOS is used to form the mesoporous structure in MCM-41. CTAB forms spherical micelles, with the hydrophobic tails of the surfactant

molecules oriented inward and the hydrophilic heads pointing outward, in the aqueous phase, as shown in Figure 2.2. TEOS undergoes hydrolysis and condensation to form silica. The silica molecules are attracted to the hydrophilic heads of the CTAB surfactant molecules and get deposited on the surface of the micelles, leading to the formation of a mesoporous silica structure around the micelles. The silica precursor polycondenses around the micelles, forming a hexagonal arrayed structure (Hoffmann et al., 2006).

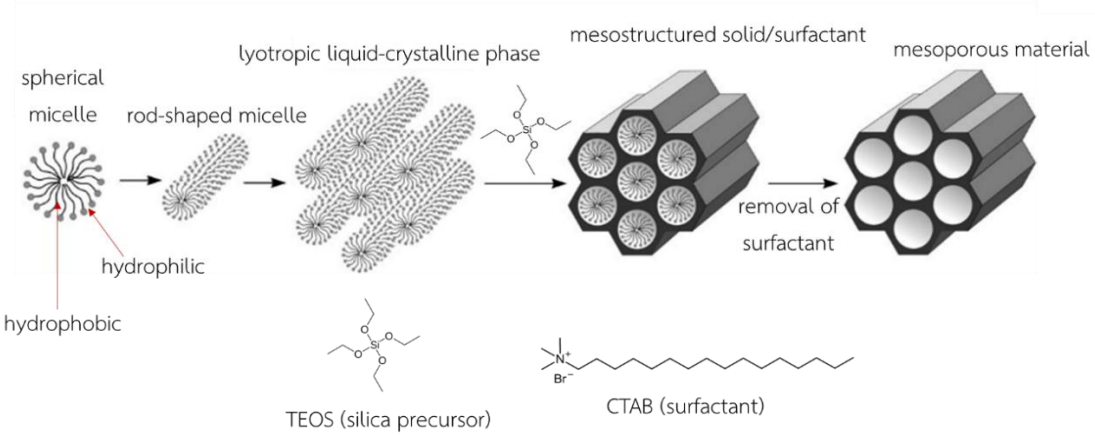

Figure 2.2 Formation of mesoporous materials (Hoffmann et al., 2006).

This study used the as-synthesized MCM-41, which still contains the surfactant within the pores, as an alternative solid-phase reagent to convert carbaryl to 1-naphthol. The basicity of MCM-41 arises from the presence of siloxy anion (SiO^-) groups, which electrostatically interacted with the positive head of the CTAB molecules. These negatively charged siloxy groups contribute to MCM-41's basicity by acting as Lewis bases, as shown in Figure 2.3. (Zapelini I. W. et al., 2018). The siloxy anions could be useful for a hydrolysis reaction of carbaryl to produce 1-naphthol, which can be monitored fluorometrically.

Figure 2.3 An illustration of the MCM-41 structure's basic siloxy site with charge compensation provided by CTA^+ or CTAB (Zapelini I. W. et al., 2018).

The basicity of MCM-41 containing CTAB has been widely utilized in various studies due to its rapid and simple synthesis, regular pore structure, uniform pore diameter, and high surface area. The as-synthesized MCM-41, with the surfactant present inside the pores, exhibits basic catalytic activity. A study conducted by Kubota et al. (2006) showed that the material exhibited exceptional performance as a basic catalyst in the Knoevenagel condensation reaction at room temperature. No activity was observed when calcined MCM-41 was used in the reaction. Characterization of the as-synthesized MCM-41 by ^{29}Si MAS NMR and O 1s XPS techniques verified that the active sites responsible for the catalysis were the basic siloxy anion, SiO^-. Because the mesopores were occluded, a reaction involving the as-synthesized MCM-41 occurred at the entrance of the pores (Martins et al., 2007). There has been no report on using MCM-41-CTAB for carbaryl detection. Therefore, in this work, MCM-41 was employed for carbaryl analysis.

MCM-41 possesses several properties that make it highly effective for adsorption applications. Its large surface area provides numerous sites for adsorption, making it ideal for capturing molecules from gases or liquids. The narrow pore size distribution allows for selective adsorption of molecules of specific sizes, improving its efficiency in separating or capturing target molecules. The pore size can be adjusted during synthesis, enabling optimization for various applications such as gas storage, pollutant removal, or selective separation. Additionally, MCM-41 has a relatively large

pore volume, which enhances its ability to adsorb significant amounts of low-molecular-weight compounds or gases. With high thermal stability (up to 800°C) and chemical stability (Kim et al., 1995), MCM-41 is well-suited for adsorbing molecules in harsh environments without degradation. The well-organized mesoporous structure also provides high accessibility for molecules interacting with the surface, making MCM-41 effective for adsorbing both small and large molecules. Beyond these advantages, MCM-41's strong adsorption capabilities make it particularly useful in analytical applications. By capturing foreign species that could interfere with fluorescence measurements, it helps improve the accuracy of fluorescence-based carbaryl detection.