CHAPTER 1

INTRODUCTION

1.1 Principles, Theory, Rationale and/or Hypotheses

The presence of pesticide in water, soil, and air has raised problems for the protection of the environment. Pesticides are sprayed on the field to cause the damage of pest and insects. Only a part of pesticide applied effects in field, the remains can be attached to the soil or adsorbed by dust particles or which can migrate into the ground or water is distributed for surface runoff. Certain can reach to the air and diffuse to the long distances. This loss means the amount of pesticide requires higher amount to be applied and become the cause environmental problems. An important way to achieve this aim is design of modification which material could take into account for adsorption of pesticide residue with a minimum of cost. Therefore, the study of pesticide-clay interaction with environmental aspects is valuable for coming studies.

Clays and clay minerals are reasonable materials, which are high adsorption properties and simple to modified, due to the high specific surface areas associated with their small particle size. After the surface of clay is simply modified with organic and inorganic cations, they can be used as adsorbent for many hazardous pesticides to eliminate these pollutants from water and soil. Some pesticides are cationic and could be absorbed by clay minerals via ion exchange process.

Bentonite clay belongs to a group of clay minerals formed. The adsorption properties of clay minerals can be modified by replacing the organic interlayer cations with selected quaternary cation compound [1].

Berberine (5,6-dihydro-9,10-dimethoxybenzo[g]-1,3 benzodioxolo[5,6-a] quinolizinium), $(C_{20}H_{18}NO_4)^+$ is a quaternary alkaloid compound, derived from the roots and bark *Coscinium fenestratum*. Due to its strong yellow color then, it also used in the natural dying process of dye wool, leather and wood. Recently, berberine is also used as quaternary cations compound for an enhanced the properties of mineral clay for applications adsorption of anthocyanin [2, 3] and preparation for formulation of metolachlor [4]. An important way to achieve this aim is to design the organoclay under the modification of commercial bentonite clay with *C. fenestratum* extract, which provides the minimize cost, and maximum yield to adsorb pesticides.

In the last decade, the natural clay minerals such as bentonite clay are widely used in catalysis [5-7], adsorbents [8-11], electrode [12], an antibacterial material [13, 14], etc. But, nowadays, surface modification of clay minerals has become increasingly important for improving the practical application.

For the protection of environment, the present of pesticides raised in water, soil and air are problems. There are several possibilities to reduce the pesticide issues out by mineral clay as bentonite clay. The clay has been modified by ion exchange with organic cations when used as adsorbent for pesticide, bentonite clay can be directly transferred to Na-bentonite clay form, and showed the higher adsorption capacity for metolachlor and did not diffuse significantly to greater depths. The modification by using thermal as calcinations method at 350-450°C for 12 hr was strongly decreased the specific surface area. The adsorption was enhanced, the metolachlor molecules very likely interact with aluminum ions or oligomeric hydroxoaluminum cations enriched on the edges of the silicate layers [4]. Inorganic-organic bentonite clay were prepared by co-adsorption of Cetyl- trimethylammonium (CTMA) ions on bentonite clay intercalated by poly(hydroxo aluminum) or poly(hydroxo iron) cations [15]. The enhancement may be attributed not only to the Van Der Waals interaction between 2,4-dichlrophenoxyacetic acid (2,4-D) and the organic cations, but also to the strong bonding of 2,4-D on the inorganic cations, which was confirmed by desorption studies, X-ray diffractometer (XRD) measurements and Fourier Transform Infrared Spectroscopy (FTIR) analysis [16].

Berberine is isoquinoline alkaloid, and known to possess a wide variety of pharmacological activities, including, anti-diarrheal [17-19], anti-diabetes [18, 20], toxicity activity [21], inhibited the digestion in intestine [22], anti-proliferative [23], etc. Berberine come to play in role of the modification of clay, the adsorption of cationic alkaloid berberine by montmorillonite was investigated [24]. An adsorption isotherm of berberine and desorption isotherms of exchangeable Na^{+}, and Ca^{2+} was determined by chemical analysis of the non-adsorbed berberine and released cations in supernatants and examined by X-ray diffraction, and after gradual heating up, the basal spacing after thermal treatment was increased [25], thus proving that the adsorbed berberine was located in the interlayer space. These contain organophilic adsorption and it is suggest that due to the thermal treatment berberine was related to the Tetrahedral sheet – Octahedral sheet – Tetrahedral sheet (TOT) layer, with anhydrous Cl^- between the berberine cation [26].

After that, this berberine was used in the preparation of berberine-montmorillonite to detect in several water wells in agricultural and even urban areas. The adsorption of metholachlor on berberine-montmorillonite was found to be more than 30%. The hydrophobicity of the organoclay was demonstrated when berberine were 75% or higher, and has been proved also by Pollution Control Department (PCD) measurements [4].

Study the influence of preliminary adsorption of berberine on anthocyanins by bentonite clay, the cation exchange adsorption mechanism was found to be replaced by hydrophobic sorption of anthocyanins after clay modification with berberine. And the enthalpy of adsorption along the initial isotherm part changed from endothermic to exothermic [2, 3].

Rytwo *et al.,* (2011) reported that the interaction between organic modifiers and raw material clay were aimed to produce of low-cost organoclay [26]. The study reported the intercalation between berberine, a monovalent organic cation and three commercial bentonite clay and Turkish zeolite. The Turkish zeolite exhibited adsorption at values 5-10% of the Cation Exchange Capacity (CEC). Adsorption of the organo-cation on Egyptian bentonite clay, Volclay KWK and Pure-Flo B80 was above the CEC of the bentonite clay, by Electron microscopy and X-ray diffraction results showed expansion of the basal spacing of smectite. Such low-cost bentonite clay might be suitable for environmental applications.

1.2 Research Objectives

1.2.1 To modify the organobentonite clay adsorption by alkaloid crude extract of *C. fenestratum* by providing carbamate pesticide as a model

1.2.2 To investigate the adsorption property of modified organobentonite clay with carbamate pesticides (carbaryl, methomyl and methiocarb)

1.3 Usefulness of the Research (Theoretical and/or Applied)

1.3.1 The low-cost modified organobentonite clay will be obtained and used as the alternative adsorbent to reduce the residue of pesticides in environment such as water, wastewater and soil.

1.3.2 The modified organobentonite clay can be used for large scale in the future study for model pesticide adsorbent in agricultural production.

1.4 Research location

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