ADSORPTION STUDY OF PESTICIDES FROM AQUEOUS SOLUTION USING UNMODIFIED AND MODIFIED ZEOLITE Y

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การศึกษาการดูดซับสารกำจัดศัตรูพืชโดยใช้ซีโอไลต์ Y และซีโอไลต์ Y ดัดแปร

นางสาวยุวธิดา ปักโคทานัง

วิทยานิพนธ์เล่มนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

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งานวิจัยนี้มุ่งเน้นการศึกษาความสามารถในการดูดซับสารกำจัดศัตรูพืชจากสารละลาย โดยการศึกษาเปรียบเทียบระหว่างซีโอไลต์ HY (HYZ) ที่มีอัตราส่วนโดยโมลของ SiO_2/Al_2O_3 ต่างกันคือ10 (HY10) 100 (HY100) และ 500 (HY500) การปรับปรุงคุณสมบัติในการดูดซับสารกำจัดศัตรูพืชของ HY10 และ HY100 ทำโดยการเปลี่ยนชนิดของเคาน์เตอร์ไอออนในซีโอไลต์จากไฮโดรเจนไอออน (H^+) เป็นโซเดียมไอออน (Na^+) และการดัดแปรด้วยสารลดแรงตึงผิวเฮกซะเดซิลไตรเมทิลแอมโมเนียมคลอไรด์ (HDTMA) และโซเดียมโดเดซิลซัลเฟต (SDS) ซึ่งลักษณะเฉพาะของซีโอไลต์ Y และซีโอไลต์ Y ที่ถูกดัดแปรได้ทำการตรวจสอบด้วยหลากหลายเทคนิคเช่น FTIR TG/DTG NH_3–TPD XRD WD–XRF CHN/S BET และ การหาขนาดอนุภาค (particle size) ในส่วนของการศึกษาเปรียบเทียบความสามารถในการดูดซับอาทราซีน ไดยูรอน กรด 2,4–ดี พาราควอต และ ของ HY10 HY100 และHY500 พบว่าอัตราส่วนโดยโมลของ Si/Al ส่งผลต่อความสามารถในการดูดซับของซีโอไลต์ HY โดยความสามารถในการกำจัดพาราควอตของตัวดูดซับเรียงตามลำดับคือ HY10 > HY100 > HY500 ซึ่งตรงข้ามกับผลของการดูดซับกรด 2,4–ดี อาทราซีน และ ไดยูรอนที่มีลำดับความสามารถในการดูดซับเป็น HY500 > HY100 > HY10 แต่อย่างไรก็ตาม HY100 นั้นยังสามารถดูดซับพาราควอตได้อีกด้วย และมีความสามารถสูงที่สุดในการดูดซับสารกำจัดศัตรูพืชหลายชนิดพร้อม ๆ กัน ค่าการดูดซับ พาราควอตจะเพิ่มขึ้นเมื่อเพิ่ม pH ของสารละลาย ในทางตรงกันข้ามกลับส่งผลต่อการลดลงของค่าการดูดซับกรด 2,4–ดี อย่างไรก็ตามการเพิ่ม pH ของสารละลายจะส่งผลต่อการลดความสามารถในการกำจัดอาทราซีนและไดยูรอนเฉพาะ HY10 เท่านั้น ในส่วนของการดัดแปรซีโอไลต์โดยการเปลี่ยนชนิดของเคาร์เตอร์ไอออนด้วย Na^+ เพื่อนำมาใช้ในการดูดซับสารกำจัดศัตรูพืชแปดชนิดซึ่งได้แก่กรด2,4–ดี อาทราซีน ลินูรอน พาราควอต เบนทาโซน คาร์โบฟูแรน ไซยานาซิน และไดเฟนโซควอต ผลปรากฏชัดเจนว่าซีโอไลต์ที่มีเคาน์เตอร์ไอออนเป็น H^+ สามารถดูดซับ 2,4–ดี ได้มากกว่าซีโอไลต์ที่มีเคาร์เตอร์ไอออนเป็น Na^+ ส่วนในกรณีของการดัดแปร ZY10 และ ZY100 ด้วยสารลดแรงตึงผิวทั้งสองชนิดพบว่าความสามารถในการดูดซับสารกำจัดศัตรูพืชจะขึ้นอยู่กับลักษณะการจัดเรียงตัวของสารลดแรงตึงผิวบนพื้นผิวของซีโอไลต์ โดยการเพิ่มความเข้มข้นของสาร HDTMA สามารถเพิ่มค่าการดูดซับของ ZY10 ได้แต่กลับส่งผลในการลดค่าการดูดซับของ ZY100 ในส่วนของการใช้ SDS

ในการดัดแปรซีโอไลต์ พบว่า SDS สามารถเข้าจับได้กับพื้นผิวของ ZY100 เท่านั้น โดยความสามารถในการกำจัดพาราควอต และ 2,4–ดี ของ ZY100 ที่ถูกดัดแปรด้วย SDS จะขึ้นอยู่กับปริมาณน้ำในโครงสร้างของซีโอไลต์ และยังพบว่าการเพิ่มค่า pH ของสารละลายจะส่งผลต่อการเพิ่มความสามารถของ HZY100 และ SZY100ในการดูดซับ 2,4–ดี ได้เพิ่มขึ้นแต่ส่งผลให้ความสามารถในการดูดซับพาราควอตลดลง สำหรับกระบวนการดูดซับสารกำจัดศัตรูพืชของตัวดูดซับส่วนใหญ่จะเป็นไปตามจลนพลศาสตร์แบบอันดับสองเทียม และมีไอโซเทอร์มของการดูดซับแบบแลงเมียร์

สาขาวิชาเคมี ลายมือชื่อนักศึกษา ____________
ปีการศึกษา 2560 ลายมือชื่ออาจารย์ที่ปรึกษา ____________

YUWATIDA PUKCOTHANUNG : ADSORPTION STUDY OF PESTICIDES FROM AQUEOUS SOLUTION USING UNMODIFIED AND MODIFIED ZEOLITE Y. THESIS ADVISOR : ASST. PROF. KUNWADEE RANGSRI WATANANON, Ph.D. 122 PP.

ZEOLITE Y, Si/Al RATIO, MODIFICATION, HDTMA, SDS, ADSORPTION

The main of this work focuses on the study of adsorption ability of pesticides from aqueous solution comparing between HY zeolite with the different Si/Al mole ratios as 10 (HY10), 100 (HY100) and 500 (HY500) and the improvement of the adsorption properties of HY10 and HY100 by changing the countercation of zeolite from H^+ to Na^+ and modifying with hexadecyltrimetylammonium (HDTMA) chloride and sodium dodecyl sulfate (SDS). The characteristics of unmodified and modified zeolite were investigated by several techniques such as FTIR, TG/DTG, NH_3-TPD, XRD, WD-XRF, CHN/S, BET and particle size analysis. The study of the adsorption ability comparing between HY10, HY100 and HY500 to adsorb atrazine, diuron, 2,4-dichlorophenoxyacetic acid (2,4-D) and paraquat ion (PQ^{2+}) reveals that Si/Al ratio affects to the adsorption ability of HY zeolite. For the removal of PQ^{2+}, the ability of the adsorbents lines in the order of HY10 > H100 > HY500. In contrast, the adsorption capacity of the adsorbents to adsorb 2,4-D, atrazine and diuron is in the order of HY500 > HY100 > HY10. However, HY100 can also adsorb few amounts of PQ^{2+} and has the highest ability in the simultaneous adsorption of various pesticides. The adsorption value of PQ^{2+} increases with increasing pH of the solution, but it decreases in the case of 2,4-D. However, with increasing pH it causes a decrease in the adsorption capacity of HY10 only, in the removal of atrazine and diuron. In the part of the modified zeolite with Na^+, eight species of pesticides such as 2,4-D, atrazine, Linuron, PQ^{2+}, bentazon, carbofuran, cyanazin and difenzoquat methylsulfate (DQ^+) were used as adsorbates. It is obvious that in the adsorption of 2,4-D by ZY10 and ZY100 in H-form (HYZ) and Na-form (NaYZ) exhibits the adsorption value of HYZ higher than that of NaYZ. In the case of the modification with surfactants, the adsorption capacity of ZY10 and ZY100 depends on the surfactants loading level on the zeolite surface. An increase in HDTMA concentration is able to increase the adsorption capacity of ZY10, but it decreases the adsorption of ZY100. The modification of the zeolite with SDS was achieved only in the case of ZY100. The increment of the adsorption capacity of SDS-modified ZY100 for removing PQ^{2+} or 2,4-D depends on the water content in the zeolite. An increase in pH of the solution of 2,4-D has an effect on a decrease in the adsorption ability of HZY100 and SZY100, which is in contrast to the PQ^{2+} adsorption. The adsorption process of these pesticides on the adsorbents is mostly fitted well with pseudo-second order of kinetics model and Langmuir isotherm model.

School of Chemistry Student's Signature __________

Academic Year 2017 Advisor's Signature __________

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LIST OF ABBREVIATIONS

ATR	Attenuated Total Reflection
BET	Brunauer–Emmett–Teller
DTG	Differential Thermogravimetric
HPLC	High Performance Liquid Chromatography
TGA	Thermogravimetric Analysis
TPD	Temperature Programmed Desorption
S_{BET}	Specific Surface Area
S_{ext}	External Surface Area
S_{micro}	Micropore Surface Aarea
XRD	X-ray Diffraction
WD-XRF	Wavelength Driffraction-X-ray Fluorescence
CMC	Critical Micelle Concentration
D_a	Average Pore Diameter
V_t	Total Pore Volume
HYZ	Zeolite Y in H-form
NaYZ	Zeolite Y in Na-form
ZY	Zeolite Y (both in H- and Na-form)
ZY10	Zeolite Y10 (both in H- and Na-form)
ZY100	Zeolite Y100 (both in H- and Na-form)
HDTMA	Hexadecyltrimethyammonium

LIST OF ABBREVIATIONS (Continued)

HHY	HDTMA-modified zeolite Y in H-form
HNaY	HDTMA-modified zeolite Y in Na-form
HZY	HDTMA-modified zeolite Y (both in H- and Na-form)
SDS	Sodium Dodecyl Sulfate
SHY	SDS-modified zeolite Y in H-form
SNaY	SDS-modified zeolite Y in Na-form
SZY	SDS-modified zeolite Y (both in H- and Na-form)
MZY	Modified zeolite Y with both HDTMA and SDS

CHAPTER I

INTRODUCTION

Nowadays, several toxic pesticides are banned but some pesticides are used worldwide because of the increasing demand on production of food. In 1950, the world population was reported as 2.5 billion and it has been predicted that the population will rise to 9.3 billion in 2050 and 10.1 billion in 2100 (Foo and Hameed, 2010; Nations, 2011). It is possible that food may be insufficient for the growing population. In order to increase the sufficient source of food, pesticides have become the most important substances in crop production and animal husbandry. Furthermore, due to the climate change, a lower pesticide residue on crops results in an increase in the prevalence of pests, diseases and weeds. Thus, in the future, farmers may have to spray more often during the growing season (Delcour, Spanoghe, and Uyttendaele, 2014). The presence of pesticides in natural and drinking water is a serious problem in the environment and human health.

Pesticides comprise a diverse group or mixture of chemical substances, biological agents, antimicrobials, disinfectants or devices which are intentionally applied for selective administration and attenuation against any pests (Foo and Hameed, 2010). The group of the "older" organochlorine pesticides includes compounds such as DDT, endrin, dieldrin, aldrin and lindane (γ-HCH). Many were phased out of legal use in the 1970s to 1980s in North America. The "older" organochlorines are well known for their toxicity, and most are classified as probable human carcinogens by the United StatesEnvironmental Protection Agency (USPEA), based on the results of animal studies (Warren, Allan, Carter, House, and Parker, 2003). For this reason, new insecticides have been developed to be more effective, even in small quantities, more target specific, and less persistent in the environment. Today, more than 500 different formulations of pesticides are being applied in the environment, and almost all come from agricultural activities. It is estimated that four million tons of pesticides are applied to crops annually worldwide for pest control. However, less than 1% of the total applied pesticides accesses to the target pests, it so may be concluded that pesticides are used overused. Under these conditions, the negative impacts of the use of pesticides to human health and the environment have attracted more and more attention (Gavrilescu, 2005). Thus, the main sources of pesticides contamination are agricultural runoffs. However, these pollutants are also release from wastewaters generated at pesticide manufacturing plants (Farré, Doménech, and Peral, 2006; Jamil, Gad-Allah, Ibrahim, and Saleh, 2011; Leite, dos Reis, Robaina, Pacheco, and Cassella, 2013; Rao and Chu, 2010; Salman, Njoku, and Hameed, 2011). Due to the harmful influence of pesticides on human health, animals and environment, thus, it has the imposition of stringent legislation on the purity of drinking water have been imposed in many countries. For example, the European directive Nr. 98/83/CE for drinking water allows 0.1 μg L^{-1} for a single pesticide and 0.5 μg L^{-1} for the total amount of the pesticides (Bouras, Bollinger, Baudu, and Khalaf, 2007; Chingombe, Saha, and Wakeman, 2006). The EC drinking water directive (80/778/EC) stipulates the requirement that no single pesticide should exceed 0.1 mg L^{-1} and total pesticides should not exceed five-fold of this level in drinking water from the tap (Pavlovic, González, Rodríguez-Rivas, Ulibarri, and

Barriga, 2013). However, as a result of the wide application of pesticides, they have frequently been detected in surface and drinking waters at levels exceeding the permissible limits. Therefore, it is necessary to limit the agrochemical substances discharged into the environment as much as possible, and also to act on removing them completely.

Thailand is one agricultural country that exported various kinds of agricultural products, such as rice vegetables, tropical fruits, industrial processed food and, etc., to many countries around the world. To prevent crop losses, pesticides are then used to control insect and increase agricultural product. Most of pesticides used in Thailand are imported only, and the imported pesticides in 2010, about 33% fall into the WHO hazard categories. Several information suggests that pesticides may be related to various diseases, including cancers, as well as having neurological, mental and reproductive. The hazard pesticides such as dichlorophenoxyacetic acid (2,4-D), atrazine, paraquat and linuron. Atrazine is recognized as an endocrine disruptor for mammals and aquatic life. The toxicity of paraquat for humans is manifested in different organs, including livers, brain, kidneys, heart, adrenal glands and muscles. Linuron has been reported to inhibit the activity of 5α-reductase, which is one of the key enzymes of human androgen metabolism. The last one, 2,4-D exposure causes serious eye and skin irritation, nausea, weakness, fatigue and in some cases neurotoxic effects including inflammation of nerve endings.

The wide range of pesticides in use makes research extremely difficult for producing method for the removal of pesticides that applies universally. Various methods have been used for the removal of these substances including Fenton process (Navarro, Fenoll, Vela, Ruiz, and Navarro, 2011), biological treatment (González et al., 2012), advanced oxidation treatment (Badawy, Ghaly, and Gad-Allah, 2006), membrane technologies (Plakas and Karabelas, 2012), ion exchange treatment (Humbert, Gallard, Suty, and Croué, 2008), chemical coagulation (Alexander, Hai, and Al-aboud, 2012) and adsorption (Chaara et al., 2012; Leite et al., 2013; Salvestrini, Sagliano, Iovino, Capasso, and Colella, 2010). Among these possible techniques for water treatments, the adsorption process by solid adsorbents is one method that has been used widely for removing organic agrochemical because it is an effective and simple method for water environment treatment. Adsorption has been found to be superior to other techniques in terms of initial cost and land required, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, and reduced production of secondary harmful substances (Li, Dong, Wu, Peng, and Kong, 2011).

Zeolite is one popular adsorbent which has been used in the field of cleaning environment, due to their structural, ion exchange and sorption properties. Zeolites have been investigated because of their peculiar performance: i) high selectivity; ii) high specific capacity; iii) reliable release performances (to be exploited within regenerative methodologies) and iv) excellent resistance to chemical, biological, mechanical and thermal stress (Perego, Bagatin, Tagliabue, and Vignola, 2013).

The term *zeolite* refers to a large number of natural and synthetic minerals that have certain characteristics in common. Zeolites are hydrated aluminosilicates belonging to the family of the tectosilicates. Zeolites composed of corner-sharing AlO_4 and SiO_4 tetrahedra linked into three-dimensional frameworks. The partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge that is compensated by exchangeable cation (e.g. Na^+, K^+, Ca^{2+} or Mg^{2+}). Owing to their porous structures, high specific surface areas and high cation exchange capacities, zeolites are useful materials in a wide range of applications. The negative surface charge in zeolite structure has a good affinity toward inorganic cations. In contrast, it is difficult to adsorb anionic and non-ionic species. However, the cation-exchange properties of zeolites can be exploited to modify their outer surfaces so that other classes of compounds (anionic and non-polar organic) can also be adsorbed, resulting in having more possibility for their use in environmental remediation (Vidal et al., 2012). Several reports have been shown that zeolites can be modified by quaternary ammonium compounds which have a hydrophilic and positively charged head group and a hydrophobic tail.

1.1 Research objectives

1.1.1 To study the adsorption ability of pesticides using various forms of zeolite Y such as Si/Al ratio, countercations and surfactant modifications.

1.1.2 To characterize the physicochemical properties of unmodified and modified zeolites Y.

1.1.3 To investigate the adsorption isotherms and equilibrium parameters of pesticides adsorbed by unmodified and modified zeolites Y.

1.1.4 To evaluate the possibility of the multifunctional ability of modified zeolites Y to adsorb pesticides in quaternary mixture solution.

1.2 Scope and limitations of the study

1.2.1 The source of zeolites; zeolite as commercial adsorbents obtained from Tosoh Co. Ltd. with three different SiO_2/Al_2O_3 mole ratios of 10, 100 and 500.

1.2.2 The nine pesticides are selected based on their physicochemical properties and behaviors in water and soil, such as paraquat dichloride and difenzoquat methyl sulphate, atrazine and cyanazin, 2,4-D and bentazon, diuron, linuron and bentazon which are cationic, basic, acidic and non-ionic pesticide, respectively, which are PESTANAL® analytical standard grade.

1.2.3 The four pesticides as commercial grade are most used in agricultural area of Thailand such as paraquat, atrazine, diuron and 2,4-D.

1.2.4 The unmodified and selected-modified zeolites will be characterized by XRD, WD-XRF, FT-IR spectroscopy, TG/DTG technique, BET analysis, NH_3-TPD, CHN/S analyzer and particle size analyzer.

CHAPTER II

LITERATURE REVIEW

2.1 Importance of pesticides for the human life

Water scarcity and pollution rank equal to climate change as the most intricate environmental turmoil for the 21st century. Over the past several decades, the exponential population and social civilization growth change affluent and resource use, and continuing progress of the industrial and technologies has been accompanied by the sharp globalization and vast generation of agrochemical wastes, which create the most intransigent paradox abroad the nations. Simultaneously, the departure of the pesticide practice, notably in the form of herbicides, insecticides, fungicides, algaecides, antimicrobials, avicides, miticides, molluscides, nematicides, rodenticides, bactericides, defoliants, pesticides and virucides, has prevailed to be a growing branch that protests against the invasive species.

In general, pesticide is defined as a diverse group or mixture of chemical substances, biological agents, antimicrobials, disinfectants or devices which are intentionally applied for selective administration and attenuation against any pests including insects, plant pathogens, weeds, mollusks, birds, mammals, fish, nematodes, and microbes that compete for the production, processing, storage, transport, or marketing of food, agricultural commodes, destroy property, or widespread of diseases (Foo and Hameed, 2010). Pesticides can be classified in many different ways: according to the target pest, the chemical structure of the compound used, or the degree or type of health hazard involved that are shown in Figure 2.1.

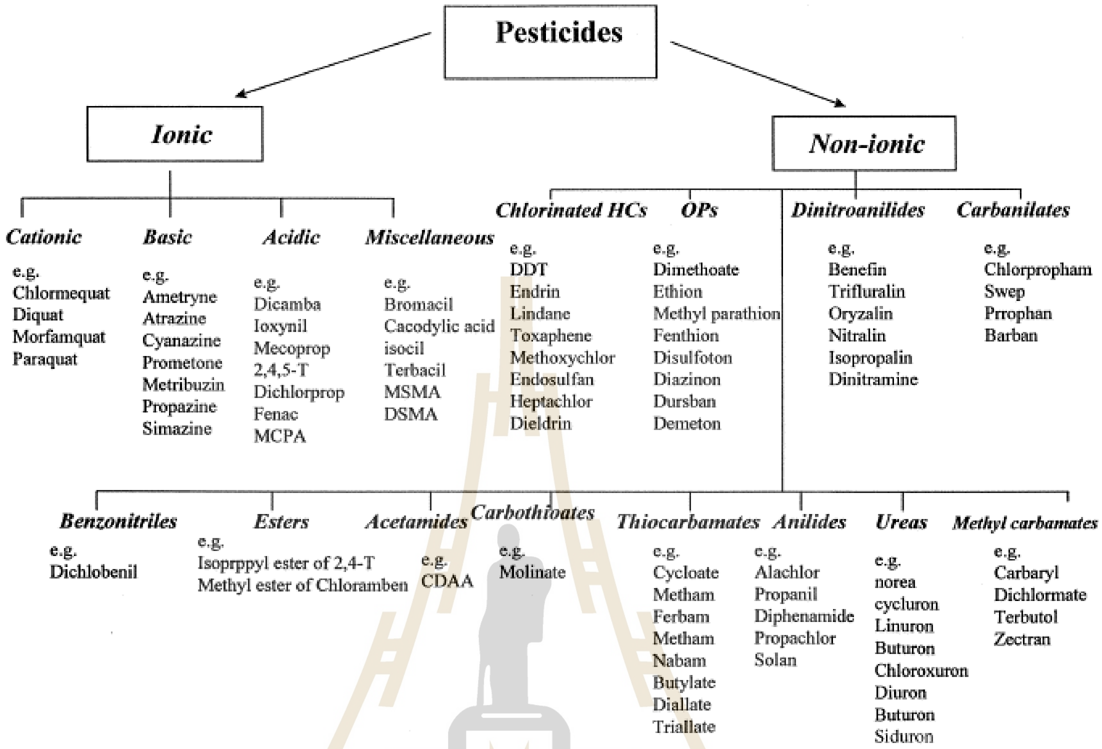


Figure 2.1 The classification of pesticides on the basis of the significant physicochemical properties and behavior in water and soil (Gevao, Semple, and Jones, 2000).

We intend to use unmodified and modified zeolite Y for removal of four classes of pesticides which are cationic-, basic-, acidic- and non-ionic pesticides. Each pesticide has the difference in the characteristics which are shown in Table 2.1 and Table 2.2.

Table 2.1 The information on the IUPAC name and chemical structure of pesticides.

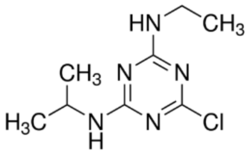
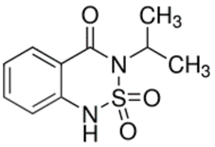
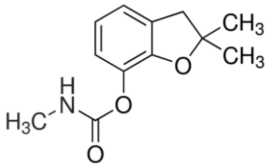
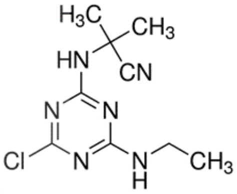
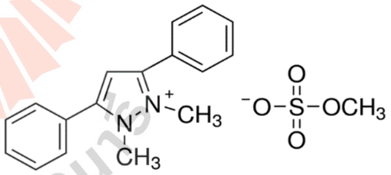
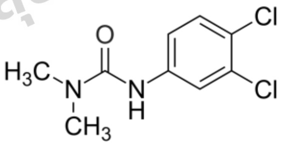
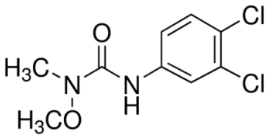
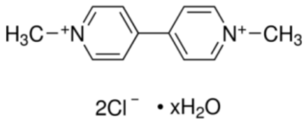
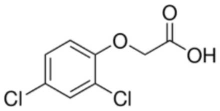
Pesticides	**IUPAC name**	**Chemical structure**
Atrazine	2-chloro-4-ethylamino-6-isopropylamine-5-triazine	
Bentazon	3-isopropyl-1H-2,1,3-benzo thiadiazin-4(3H)-one 2,2-dioxide	
Carbofuran	2,3-dihydro-2,2-dimethyl-7-benzofuranol *N*-methylcarbamate	
Cyanazin	2-[[4-chloro-6-(ethylamino) -1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile	
Difenzoquat	1,2-dimethyl-3,5-diphenylpyrazolium methyl sulfate	
Diuron	3-(3,4-dichlorophenyl) -1,1-dimethylurea	
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	
Paraquat	1,1´-dimethyl-4,4-bipyridinium dichloride	
2,4-D	2,4-dichlorophenoxy acetic acid	

Table 2.2 Characteristics of the studied pesticides.

Pesticides	**Molecular weight (g mol^{-1})**	**pK$_a$**	**Log K$_{ow}$**	**Solubility at 25°C (mg L^{-1})**
Atrazine	215.68	1.68	2.5	30
Bentazone	240.28	3.3	2.8	500
Carbofuran	221.25	11.90	2.32	351
Cyanazine	240.69	0.87	2.2	170
Difenzoquat	360.43	7.0	-0.6	7.6 x 10^5
Diuron	233.09	13.55	2.68	42
Linuron	249.09	12.1	3.0	81
Paraquat	257.16	6.6	-4.5	6.2 x 10^5
2,4-D	221.04	3.55	2.8	900

Cyanazin is a triazine herbicide approved for use in the EU and many other countries. It is moderately soluble in water and many organic solvents and it is relatively volatile. It is not persistent in soil systems but can often be persistent in water. It is moderately toxic to mammals and may have serious adverse health effects if ingested as it is a neurotoxin, a suspected endocrine disrupter and a development orreproduction toxin. Bentazon is an herbicide that is highly soluble in water, volatile and, as it is mobile, may present a risk of leaching to groundwater. It is not likelyto be persistent in soil systems but may be persistent in water under certain conditions. It is moderately toxic to humans and a recognized skin and eye irritant. Bentazon is also moderately toxic to birds, fish, aquatic invertebrates and earthworms. Carbofuran is an insecticide and nematicide. It is moderately soluble in water, is relatively volatile and, based on its chemical properties, has a high potential for leaching to groundwater. It is not persistent in soil but may persist in water under some conditions. Carbofuran has a high mammalian toxicity and a low potential for bioaccumulation. It is an endocrine disruptor and a probable reproduction or development intoxicant. It is highly toxic to birds and honeybees whilst having a moderate to high toxicity to most aquatic organisms. It is moderately toxic to earthworms. 2,4-D is a selective, systemic herbicide used for the control of broad-leaved weeds. It is highly soluble in water, volatile and has a low potential to leach to groundwater based on its chemical properties. It is non-persistent in soil but may persist in aquatic systems under certain conditions. It is moderately toxic to mammals but should not bioaccumulate. It may have negative effects on reproduction, development and is considered to be a neurotoxin and an irritant. It is moderately toxic to birds and most aquatic species as well as honeybees and earthworms. Diuron is a pre-emergence herbicide that has a low aqueous solubility, a low volatility and may, under certain conditions, leach to groundwater. It may be moderately persistent in soil systems and may also persist in water. It is moderately toxic to mammals and is classified as an irritant. It is moderately toxic to birds, earthworms, most aquatic species but is slightly more toxic to algae. It has a low toxicity to honeybees. Atrazine is an herbicide has selective, systemic action with residual and foliar activity. It has a low aqueous solubility, it is volatile and, based on its physicochemical properties there is some concern that it could leach to groundwater. It is generally not persistent in the field nor in aquatic systems. It is moderately toxic to mammals, is not expected to bioaccumulate and is a skin, eye and respiratory system irritant. Atrazine is moderately toxic to most aquatic life, earthworms and honeybees but presents less of a risk to birds (The PPDB: A to Z List of Pesticide Active Ingredients, 2007)

Based on the information above, it is a challenge to select some new solid materials as adsorbent for removal these pesticides, which have differences in their properties, contaminating in aqueous solution. Numerous researches attempt to develop a new proper adsorbent as mentioned in the following reports.

2.2 Zeolite and adsorption processes

The application of adsorption as a means of separating mixtures into two or more streams, each enriched in a valuable component which is to be recovered, it has been developed. Early example includes the adsorption process for recovery of aromatic hydrocarbons which was introduced in the early 1950s and variety of processes, first introduced in the early 1960s, for the separation of linear paraffins from branched and cyclic isomers. During the 1970s there has been a significant increase in both the range and scale of such processes. However, for an adsorption process to be developed on a commercial scale the availability of a suitable adsorbent in tonnage quantities at economic cost is required. This has stimulated fundamental research in adsorption and led to the development of adsorbents. The earlier adsorption processes used either activated carbon or silica gel adsorbents but the potential of adsorbent as a separation process was greatly enhanced by the development of molecular sieve adsorbents, especially the synthetic zeolite, which first became available on a commercial scale in late 1950s (Ruthven, 1984).

The term “zeolite” was initially used to designate a family of natural minerals that presented particular properties on the exchange of cations and the reversible desorption of water. Today, zeolite includes a great number of natural and synthetic minerals with common structural characteristics. The natural ones are formed in a variety of geological sites and from precursors, such as volcanic ash, clay, biogenic silica and different forms of quartz. Among more than 40 natural and 200 synthetic zeolites, the most common are mordenite, clinoptilolite, chabazite, erionite and phillipsite (Valdés, Pérez-Cordoves, and Díaz-García, 2006). Zeolites can be divided in those having low Si/Al molar ratio (from 1 to 5 mol/mol) and those of high Si/Al molar ratio (from 5 to ∞ mol/mol). The most of naturally occurring zeolites are hydrophilic zeolite which have low Si/Al molar ratio (Perego, Bagatin, Tagliabue, and Vignola, 2013). However, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes. Moreover, synthetic zeolites are also very attractive because they offer several possibilities in term of pore size, Si/Al ratio and they can be easily tailored (Chaouati, Soualah, and Chater, 2013; Ríos R, Oviedo V, Henao M, and Macías L, 2012).

Zeolites are crystalline aluminosilicates of alkali and alkaline earth group, in particular, sodium, potassium, magnesium, calcium, strontium, and barium. The molecular structures of zeolites are characterized by the unique ways in which their tetrahedral components are linked to each other to create open microporous frameworks. The void volume of some zeolites can be as high as 50% of the total crystal structure. They contain repeating elements of structure which are known as secondary building units. Zeolite is common to simplify the tetrahedral linkages to lines which represent the oxygen atom. The tetrahedra make rings of oxygen atoms, and the resulting restrictions to the channels and cavities making up the interior void of structure (Figure 2.2). These restrictions are of molecular dimensions. They are responsible for the ability of zeolite to act as molecules sieves and perform selective sorption of molecules on the basis of their size to achieve useful separations. Similarly, cation-sieving can occur in certain structures (Dyer, 2001).

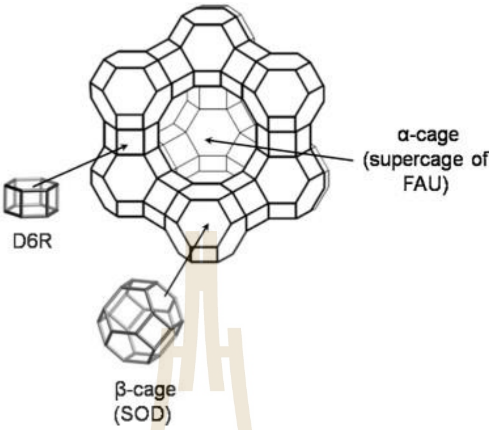


Figure 2.2 Framework structure of NaY zeolite (FAU), showing its characteristic cages and channels (Ríos R et al., 2012).

Zeolites are porous crystalline aluminosilicates. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Since the micropore structure is determined by the crystal lattice, it is precisely uniform with no distribution of pore size. It is this feature which distinguishes the zeolite from the traditional microporous adsorbents. In considering zeolite frameworks, it is convenient to regard the structures as built up from assemblages of secondary building units, which are themselves polyhedral made up of several SiO_4 and AlO_4 tetrahedra. The secondary building units and some of the commonly occurring polyhedral are shown schematically in Figure 2.3.

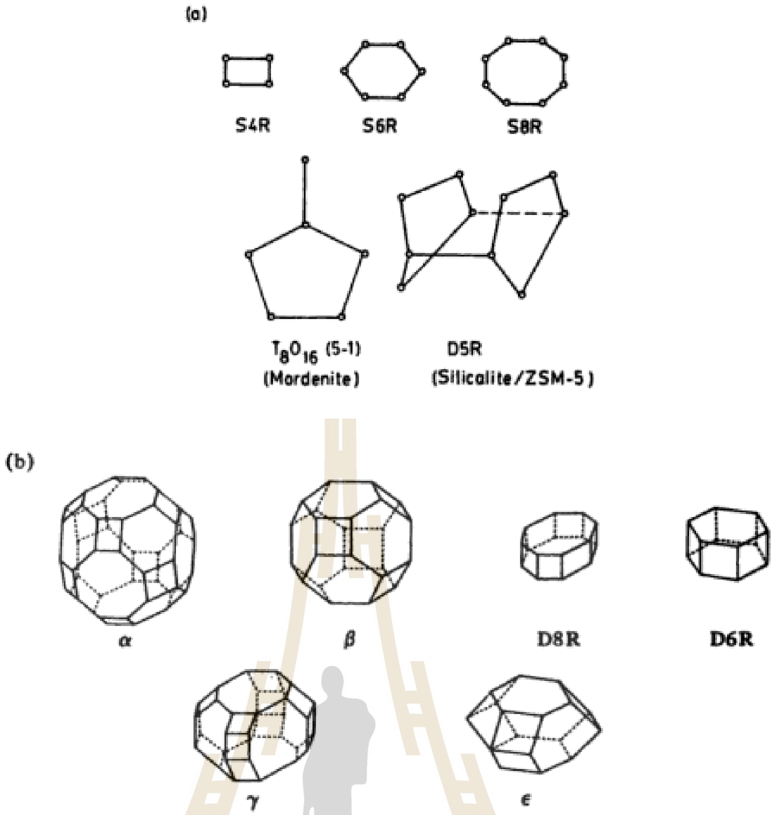


Figure 2.3 (a) Secondary building units and (b) commonly occurring polyhedral units in zeolite framework structures (Ruthven, 1984).

The Si/Al ratio in a zeolite is never less than 1.0 but there is no upper limit and pure silica analogs of some of the zeolite structures have been prepared. The adsorptive properties show a systematic transition from the aluminum rich sieves, which have very high affinities for water and other polar molecules, to the microporous silicas such as silicalite which are essentially hydrophobic and adsorb *n*-paraffins in preference to water. The transition from hydrophilic to hydrophobic normally occurs at a Si/Al ratio of between 8 and 10. By appropriate choice of framework structure, Si/Al ratio and cationic form, adsorbent with widely different adsorptive properties may be prepared (Ruthven, 1984).

Faujasite (International Zeolite Association structure type FAU) crystallizes in the cubic space group Fd3m, with a lattice constant ranging from about 24.2–25.1 Å, depending on the framework aluminium concentration, cations, and state of hydration. There are 192 tetrahedral sites per unit cell. FAU zeolite is formed from 24-tetrahedra cuboctahedral units (sodalite cages), joined through hexagonal prisms (also known as double 6-rings). The pore structure is characterized by super-cages approximately 12Å in diameter, which are linked through windows about 8Å in diameter composed of rings of 12 linked tetrahedral (12-rings) (Figure 2.4) (Kaduk and Faber, 1995).

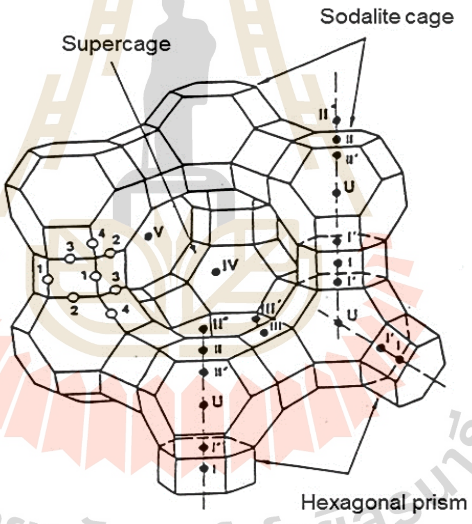


Figure 2.4 The schematic diagram of the faujasite structure, illustrating the standard nomenclature for the framework atoms and the extraframework Na^+ sites (Kaduk and Faber, 1995).

Kaduk and Faber (1995) described several extra framework sites commonly populated in cation-exchanged faujasites (Figure 2.4). Five sites will be found to be occupied in this zeolite:

I at the center of the double 6-rings

I´ in the sodalite cage, adjacent to a hexagonal ring shared by the sodalite cage and a double 6-ring

II in the supercage, adjacent to an unshared hexagonal face of a sodalite cage

II´ in the sodalite cage, adjacent to an unshared hexagonal face

V near the center of the 12-ring apertures between supercages

Faujasite zeolites are commonly separated into two classes: zeolite X having an Si/Al ratio between 1 and 1.5 and zeolite Y having an Si/Al ratio above 1.5 (Frising and Leflaive, 2008). The framework of zeolite Y is based on sodalite cage that is joined by oxygen-bridges between the hexagonal faces. Eight sodalite cages are linked leaving a large central cavity or supercage, with a diameter of 12 Å. The supercages share a 12-membered ring with an open diameter of 7.4 Å (Neves, Botelho, Machado, and Rebelo, 2006). Zeolite Y is of utmost importance in heterogeneous catalysis and is generally synthesized in the Na-form. Most of the catalysis of interests is acid catalysis, which requires replacing the Na-cation by protons, converting the sieve into the H-form. H-faujasited can be done by indirect method. An ammonium exchange is carried out, followed by a calcination to decompose the NH_4^+ cations into ammonia and protons (Kaduk and Faber, 1995). In addition, due to zeolite Y has large channels and high surface area; it has high adsorption capacity as well as their ion exchange properties.

In discussing the fundamentals of adsorption, it is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces, and chemisorption which involves, essentially, the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. The general features which distinguish physical adsorption chemisorption are as follows (Ruthven, 1984)

Physical Adsorption	Chemisorption
- Low heat adsorption (< 2 or 3 times latent heat of evaporation).	- High heat of adsorption (> 2 or 3 times latent heat of evaporation.)
- Non specific.	- Highly specific.
- Monolayer or multilayer.	- Monolayer only.
- No dissociation of adsorbed species.	- May involve dissociation.
- Only significant at relatively low temperatures.	- Possible over a wide range of temperature.
- Rapid, non-activeted, reversible.	- Activated, may be slow and irreversible.
- No electron transfer although polarization of sorbate may occur.	- Electron transfer leading to bond formation between sorbate and surface.

2.3 Modification of zeolite

The adsorption characteristics of zeolites are dependent upon the detailed chemical and structure of the adsorbent. The Si/Al ratio, cation type, number and location are particularly influential in adsorption. These properties can be changed by several chemical treatments to improve separation efficiency of original zeolites. Thus, in order to increase their ability to absorb various pesticides. Many processes were used to change properties of zeolite, for example, metal ions treatment, acid/base treatment and surfactant modification by ion exchange.

Ibrahim and Jbara (2009) studied the conversion of natural zeolite tuff from Jordan (containing about 44% faujasite) to various forms by chemical activation with $CaCl_2$, KCl, $MgCl_2$ or NaCl to produce Ca-F, K-F, Mg-F and Na-F forms for removal paraquat from synthetic wastewater. The experiments were performed by socking about 50 g zeolite at 80 °C with 200 ml of 0.5 M of each solution. This research showed that in the non-thermal condition the trend of paraquat removal is Na-F > K-F > F > Mg-F > Ca-F. However, thermal activation of faujasite forms at 200 °C showed the paraquat removal in order of K-F > F > Na-F > Mg-F > Ca-F. Thus, these results indicate that Na- or K-loading of the original sample give more paraquat removal.

Salvestrini et al. (2010) studied the efficiency of two different acid-activated zeolite-rich tuffs for atrazine removal from water. Neapolitan yellow tuff as chabazite-rich (NYT, containing 37% phillipsite and 17% chabazite) and clinoptilolite tuff from Turkey (T-CPL, 79% clinoptillolite) were activated with HCl in the concentration range 0.01–6.00 M and kept under continuous stirring for 1, 4 and 8 days. The experiments of adsorption were performed by batch experiments and acid-activated or untreated tuff was reacted for 10 days with an atrazine solution at concentration range 1.25–25 mg L^{-1} with mass ratio 1:100. It was found that the atrazine adsorption capacity increased with an increase in concentration of HCl. T-CPL tuff activated with 0.5 M H^+ exhibited the highest adsorption capacity of the maximum value of 1000 mg kg^{-1}. A similar behavior was observed for NYT activated with 0.1 M H^+ giving the adsorption maximum of 250 mg kg^{-1}. Similarly, Sannino et al. (2012) reported on using zeolite Y in H-form and its regeneration by thermal treatment to remove simazine from waters by cyclic process. In this research Na-form of zeolite Y was changed into H-form under the condition of 0.1 M NH_4NO_3 aqueous solution at solid/liquid ratio = 1/100 for 2 h at ambient temperature. Subsequently, the zeolite was calcined at 550 °C for 3 h. The amount of simazine adsorbed on the HY zeolite calculated at initial concentration of simazine 20 μmol dm^{-3} was 14,758.4 μmol kg^{-1}. Due to the negative charge on the framework of zeolite, it is facilitated to change surface properties. One of the modification methods widely employed is using organic surfactants. Surfactants have a hydrophilic and positively charged head group and a hydrophobic tail. A general model of adsorption of ionic surfactants on a solid surface is the formation of a monolayer or “hemimicelle” at the solid-aqueous interface via strong coulombic or ionic interaction at surfactant concentration equal or less than below its critical micelle concentration (CMC). If the surfactant concentration in solution exceeds the CMC, the hydrophobic tails of the surfactant molecules associated to form a bilayer or “admicelle” as shown in Figure 2.5 (Wang and Peng, 2010).

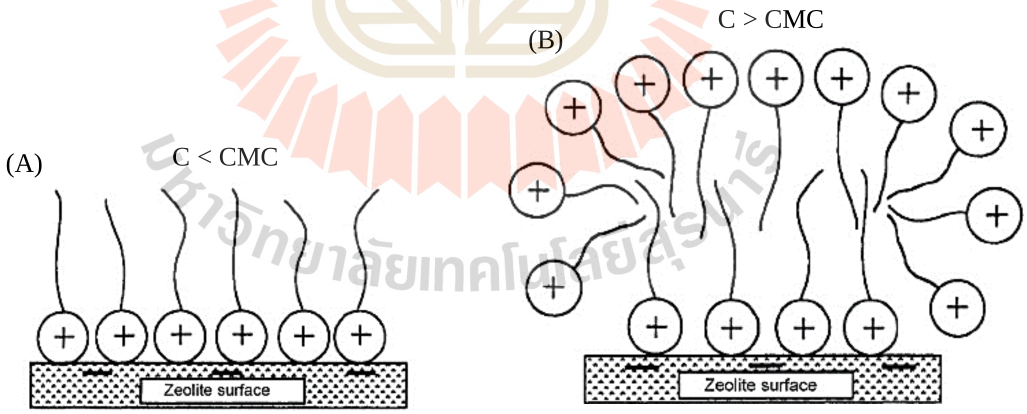


Figure 2.5 Hemimicelle (A) and admicelle (B) formation by cationic surfactants on zeolite surface.

Extensive researches also take advantages of the modified zeolites with surfactant to absorb agricultural substance such in the following examples;

Lemic et al. (2006) investigated the efficiency of zeolite that was modified by stearyldimethylbenzylammoniumchloride (SDBAC) for removal of atrazine, lindane and diazinone from water. Zeolites with different particle sizes (Z I, Z II and Z III with 0–0.4 mm, 0.4–0.8 mm and 0.8–3.0 mm, respectively) were modified by SDBAC solutions of five initial concentrations: 25, 50, 75, 100 and 150 mmol dm^{-3}. The organo-zeolite (OZ II) with a monolayer covered surface was the most effective for the adsorption of pesticides. The adsorption capacities, calculated by fitting the experimental data to the Langmuir-Freundlich equation, were 2.0 μmol g^{-1}, 4.4 μmol g^{-1}, and 3.4 μmol g^{-1} for atrazine, diazinone and lindane, respectively.

Zhang et al. (2006) demonstrated the feasibility of storage and controlled release of paraquat from surface-modified zeolite Y. Paraquat was ion-exchanged into the zeolite pores followed by surface modification under mild conditions by reaction with 1,1,3,3–tetramethyldisilazane (TMDS). The loading of paraquat into zeolite was determined by ion-exchange with 1.0 M Na$^+$ that was estimated to be 0.75 mmol g^{-1}. The total amount of paraquat released was dependent on the concentration of Na$^+$ in solution. In the absence of surface modification, equilibration occurred within 20 min, whereas with surface modification, the equilibration time was extended to 7 days. The result suggests that TMDS-modified zeolite is an effective material for slow-release of paraquat.

Nur et al. (2005) verified the simultaneous adsorption of zeolite NaY was covered with *n*–octadecyltrichloro–silane (OTS) for adsorption of a mixture of paraquat and dye. Modification of zeolite was divided into two types. The first type was modified with alkylsilyl groups on the external surface partially but the other type was fully covered. The modified zeolite was prepared by using the NaY powder containing water (0.25, 0.50, 0.75 and 1.0 g per gram of NaY) and was immersed in 5 mL toluene containing 500 μmol of OTS. The suspension was shaken for 5 min at room temperature. It was found that OTS is attached on the external surface, leaving the internal pore accessible to adsorbate molecules. These results indicated that NaY zeolite modified with alkylsilane is particularly capable of simultaneous adsorption of paraquat and blue dye, in which paraquat was selectively adsorbed into the internal pore of the zeolite whereas the dye attached on the external surface.

Bakhtiary et al. (2013a) demonstrated adsorption-desorption behavior of 2,4-D on bentonite and zeolite which were modified with N–cetylpyridinium (NCP). The organo-minerals were prepared by treating the minerals with an ethanol:water (1:1) solution containing NCP^+ equal to either 100% or 200% of the CEC of the bentonite and zeolite. In the part of NCP-modified zeolite, it was found that at initial concentration of NCP^+ (200% of cation exchange capacity, CEC) the adsorption capacity of 2,4-D was increased up to 58.89±2.27 mmol kg^{-1} whereas unmodified zeolite was not investigated. Similarly, bentonite that was modified by NCP^+ at 200% of CEC increased the adsorption capacity from 6.5±1.2 mmol kg^{-1} to 171.1±2.27 mmol kg^{-1} when compared with unmodified bentonite. Moreover, the adsorbed 2,4-D on the adsorbents showed gradual release pattern with time, that makes these NCP-modified minerals suitable candidate for slow release formulation of 2,4-D.

2.4 Modification of other adsorbents for adsorption of agrochemical pollutant from water and wastewater

Clay minerals are abundant and cheap resources. Natural clays are good sorbents of ionic and polar compounds, but not for hydrophobic organic compounds. Clays contain a net negative charge due to isomorphic substitution in the aluminosilicate layers neutralized by inorganic cations, which are strongly hydrated and provide the clay surface a hydrophilic character. The intercalation of a cationic surfactant between the clay layers changes the surface properties from highly hydrophilic to increasingly hydrophobic, and it increases the basal spacing of the layer, which yield an exposure of new sorption sites of clays. According to Azejjel et al. (2009), swelling clay and non-swelling clay were used as sorbents to remove ionizable herbicides (terbutryn, dichamba and paraquat) in aqueous medium. Sorption was studied on natural and modified clays with three quaternary alkyl ammonium cations of different long-chains, such as octadecyltrimethylammonium (ODTMA), octatrimethylammonium (OTMA) and tetramethylammonium (TMA). Natural clays were treated with warm deionized aqueous solutions containing an amount of alkyl ammonium cation equivalent to 1.25- or 0.5-times (ODTMA-Br), 2-times (OTMA-Br) and 3-times (TMA-Br) the CEC of the clays. These results were founded that the ability to retain terbutryn and dicamba may be improved by saturating the clays with long-chain alkyl ammonium organic cations such as ODTMA, whereas the ability to retain paraquat can be improved with small-chain organic cation as TMA-modified clay. In addition, the sorption of herbicides was higher by swelling clay than non-swelling clay. Similarly, Sanchez-Martin et al. (2006) studied the adsorption of the hydrophobic pesticides penconazole, linuron, alchlor, atrazine and metalaxyl using a series of clay minerals (montmorillonite, illite, muscovite, sepiolite and palygorskite) modified with the cationic surfactant octadecyltrimetylammonium bromide (ODTMA). In this research, organo clays were prepared by treating natural clays with a solution of ODTMA-bromide in warm deionised water containing an amount of organic cation equivalent to 1.25 times the CEC of clay mineral. It was found that the efficiency of ODTMA-montmorillonite was 100-fold greater than that of natural montmorillonite in the adsorption of penconazole and metalaxyl, while the efficiency of the other modified clay minerals was low. Non-expandible layered and fibrous clay minerals may also be of interest as adsorbents derived from their density charge. These minerals, when modified with ODTMA and used in appropriate amounts, their adsorption capacity higher than that of montmorillonite, or when present in soils with high clay contents, even in the absence of montmorillonite, may be good adsorbents for hydrophobic pesticides. There are also some reports that the fibrous clay modified with cationic surfactant can improve the adsorption capacity for removing organic contaminant from aqueous media. For instance, Bakhtiary et al. (2013b) reported the using sepiolite nanofibers modified with N-cetylpyridinium (NCP) for removal 2,4-D from synthetic aqueous media. In this paper, two methods were used to modify Na-sepiolite. For the first method Na-sepiolite was treated with 100 ml of 50% ethanol, and the concentration of NCP^+ equal to 100% and 200% of the clay CEC (NCP_{100}-Sep and NCP_{200}-Sep) were used. In the other one, Na-sepiolite and 100 ml of 24 mmol L^{-1} NCP solution in 0.01 M NaCl were used to target maximum NCP adsorption at 240 mmol kg^{-1} (NCP_{max}-Sep). The studied showed that the batch adsorption was closely fit to the Langmuir and Fruendlich models. The maximum adsorption capacities of NCP_{200}-Sep and NCP_{max}-Sep for 2,4-D adsorption, estimated from the Langmuir q_{max} values, were

10.04 and 34.46 mmol kg^{-1}, respectively. These results suggested that the amount of surfactant loading on the clay surfaces is the key factor affecting adsorption of 2,4-D by NCP-modified sepiolites.

Bouras et al. (2007) demonstrated the effect of adsorbing diuron by using surfactant-modified pillared clays. These surfactant-modified pillared clays (SMPC) were prepared by intercalation of polycations of aluminium (III), iron (III) or titanium (IV) into the interlamellar space of montmorillonite, followed by co-adsorption of cetyltrimethylammonium bromide. For studying adsorption isotherm, 100 ml of herbicide solution at a fixed concentration 250 μg L^{-1} were placed in contact with various weighed masses ($5 < m < 80$ mg) of surfactant-modified pillared clays. These results showed that the adsorption increases at pH 6 with diuron residual concentration. High retention was obtained in the following order; Ti- > Fe- > Al-pillared clay surfactant matrix, and SMPC showed high diuron adsorption more than pillared clay. Similar phenomena were observed for degradation products of diuron adsorption on the same SMPC. The maximum uptake was obtained in acidic medium (pH 3) with an increase in adsorption mainly with CTA-Ti$_x$H$_y$-mont morillonite. In addition, a comparative study of the adsorption of diuron and its metabolites on each SMPC adsorbent showed the high adsorption capacity of diuron in comparison with its degradation products in the following order diuron > DCPMU > DCPU > DCA.

Rodríguez-Cruz et al. (2007) studied the effect of a clayey soil modified *in situ* and *ex situ* with the cationic surfactant octadecyltrimethylammonium bromide (ODTMA), on the retention of linuron, atrazine and metalaxyl. Leaching experiments were carried out in column packed with 100 g of natural soil (< 2 mm). The columns packed with soil A (clayey soil) and soil B (sandy soil) were saturated with water and allowed to drain for 24 h so that humidity conditions were equivalent to field capacity. The columns of soil A were modified with ODTMA, by loading an aqueous solution containing 6.4 meq of ODTMA (*in situ*). The amount of ODTMA used was calculated to saturate the cation exchange capacity (CEC) of 25 g of soil by 1.25 times. The columns packed with soil B, were modified with a barrier (10 g of soil a saturated with ODTMA) intercalated in the upper part of the column (*ex situ*). Then, each column was loaded with 1 mL of a solution of 1000 μg mL^{-1} linuron, atrazine or metalaxyl in methanol on the top part of the columns. The columns were then washed by continuously applying 500 mL of water. It was found that a clayey soil modified *in situ* with the surfactant ODTMA and the use of such a soil modified *ex situ* as a barrier in a sandy soil gave rise to a complete immobilization of linuron and a major decrease in the leaching kinetics of atrazine and metalaxyl.

Tsai et al. (2005) investigated on the successful implementation of a spent and treated diatomaceous earth for removing herbicide paraquat from aqueous solution. Treated diatomaceous earth was prepared by treating spent diatomaceous earth form the beer brewery with sodium hydroxide 2.5 M and boiling at 100 °C for 2 h. This adsorbent was used for adsorption of paraquat at initial concentration 15-200 mg L^{-1}, pH 11.0 and 25 °C. It was founded that the treated diatomaceous earth was more favorable for paraquat adsorption than the untreated spent diatomaceous earth (17.54 and 3.46 mg g^{-1} for treated- and spent diatomaceous earth, respectively).

Chingombe et al. (2006) reported the adsorption capacity for removal atrazine compared between a conventional activated carbon (F400), an annealed carbon (F400AN) and an aminated carbon ($F400NH_2$). The F400 was obtained from a coal based commercial granular activated carbon, and F400AN was obtained by annealing

F400. An aminated sample F400NH$_2$ was produce from the furnace treated carbon F400AN. Batch adsorption experiments were performed at a temperature of 298±1 K, initial atrazine concentrations between 2 and 140 μg L^{-1}, adjusted to pH 5.0. About 5 mg of each adsorbent was mixed with 10 mL of atrazine solution, and the mixture was shaken for 7 days. The adsorption performance of the samples for herbicide atrazine seems to follow the sequence F400AN (40.32 μmol g^{-1}) > F400 (39.37 μmol g^{-1}) > F400NH$_2$ (34.60 μmol g^{-1}).

Brigante and Schulz (2011) investigated on the effects of pH, ionic strength and temperature for adsorption of paraquat (PQ^{2+}), using mesoporous silica modified with titania as adsorbents. The results showed the adsorption of PQ^{2+} was very low on the bare silica surface, but important on the composed TiO$_2$-SiO$_2$ adsorbent. The result showed that adsorption of PQ^{2+} on silica was very low on the contrary to the adsorption on TiO$_2$-modified SiO$_2$. The amount of PQ^{2+} adsorbed in the equilibrium was 13.68 mg g^{-1}. The adsorption capacity was increased with increasing pH and decreased significantly at low pH. The adsorption of PQ^{2+} also depends on the ionic strength, however, the effects of temperature is not significantly affected.

Han et al. (2010) used modified silica gel as a selective adsorbent to remove 2,4-D and 2,4-dichlorophenol (2,4-DCP) from water. The activated silica gel was performed by mixing silica gel with 33% methanesulfonic acid and refluxed under stirring for 8 h. The 2,4-D-imprinted amino-functionalized silica gel sorbent was prepared by using 2,4-D dissolved in ethanol, and mixing with APTES. Afterwards the mixture was added with TEOS. Then the obtained solid was extracted with ethanol and HCl to remove 2,4-D. In the case of non-impriented functionalized silica gel sorbent was prepared using an identical procedure, but without an addition of

2,4-D. The measurement adsorption capacity was done by mixing 20 mg of 2,4-D imprinted or non-imprinted sorbents with 10 mL of various concentrations of 2,4-D solutions in optimum pH. The Adsorption and competitive recognition studies were performed with the mixture solution of 2,4-D and 2,4-DCP at the 200 mg L^{-1}. It was found that the loading capacity and selectivity for 2,4-D of the imprinted sorbent is obviously larger than that of the non-imprinted sorbent. For the competitive recognition studies, the binding capacity of 2,4-D and 2,4-DPC were 30.4 and 2.4 mg g^{-1} for imprinted sorbent, and 8.5 and 4.5 mg g^{-1} for non-imprinted adsorbent.

Furthermore, a few reported revealed about using modified-layer double hydroxide (LDH) as adsorbents for adsorption of pesticides. For instance, Chaara et al. (2012) studied on linuron adsorption by using organohydrotalcites. The hydrotalcite-like compounds with $[Mg_3Al(OH)_8][CH_3(CH_2)_{10}CH_2SO_4]$ nH_2O (HT-DDS) and $[Mg_2Al(OH)_8]_2[OOC\text{-}(CH_2)_8\text{-}COO]$ nH_2O (HT-SEB) chemical formula were used as pesticide adsorbents. Adsorption-desorption experiments were conducted using solid/solution ratio 0.025 g/20 mL of an aqueous solution of pesticide. These results showed that the higher amount of linuron adsorbed on HT-SEB (0.170 mmol g^{-1}) than those adsorbed on HT-DDS (0.110 mmol g^{-1}). The research of Pavlovic et al. (2013) was carried out to elucidate the synthesis of caprylate intercalated layer double hydroxide (LDH-Cap) and its capacity to adsorb pesticides linuron, 2,4-DB and metamitron from water. The LDH-Cap was obtained by an anion exchange method by suspending 1 g of LDH-Cl in 500 mL of 0.014 M sodium caprylate solution under N_2 stream at 75 °C at pH 8.0. The adsorption experiments were carried out by adding samples of 0.03 g of adsorbent LDH-Cap in 30 mL of the pesticide solution. The maximum amount of pesticide removed from the solution per gram of adsorbent was 260 μmol g^{-1} for metamitron, 72 μmol g^{-1} for linuron and 102 μmol g^{-1} for 2,4-DB. Moreover, this study of the adsorption of these pesticides on inorganic LDH-Cl suggested that the organophilic LDH modification improved the uptake of linuron and metamitron, whereas the adsorption of 2,4-DB was almost the same.

2.5 Utilization of SDS-modified adsorbents for removal of organic substrances

From the data above, most of researches used cationic surfactant to change surface properties of solid adsorbents for removal of organic pollutants from aqueous environment. However, few researches have been reported on using anionic surfactant modified adsorbents for enhancing adsorption ability to reduce organic substance from aqueous system.

Leite et al. (2013) reported about the adsorption of the herbicide paraquat by the polymeric resins Amberlite XAD-2 and XAD-4, in a medium containing sodium dodecylsulfate (SDS). This experiment was performed on keeping the concentration of paraquat constant (5.0 mg L^{-1}), and varying the concentration of SDS between 0 and 200 mg L^{-1} with the mass of resin 200 mg. The results showed that the use of Amberlite XAD-2 and XAD-4 resins appeared as a simple alternative for the removal of paraquat present in aqueous solution due to the affinity observed between the ion-associate formed between the dodecylsulfate anion and the cationic pesticide. The Amberlite XAD-4 resin presented a slightly higher efficiency than Amberlite XAD-2. It was founded the higher efficiency of retention of paraquat when the concentration of SDS was higher than 50 mg L^{-1}, which represented a molar concentration of about 10 times higher than the concentration of pesticide and the change of pH had no significant effect on the retention capacity.

Shariati et al. (2011) demonstrated the efficiency of Fe_3O_4 magnetic nanoparticles (NP) modified with sodium dodecyl sulfate (SDS) for removal of safranin O dye from aqueous solutions. The experiment was performed by adding 1.0 mL of Fe_3O_4 NP suspension (containing 10 mg of Fe_3O_4 NPs) into the dye solution. After that, pH of the solution was adjusted to the desired value and then SDS (concentrations lower than CMC) was added into the dye solutions (0.5 mL of 5 mg mL^{-1} solution). The SDS-coated Fe_3O_4 NPs is able to absorb cationic dye up to 769.23 mg g^{-1}, while Fe_3O_4 NPs cannot remove it. Because the negative groups of SDS can interact with the surface of NPs to form double layer on the surface of particles, resulting the negative charge increases. Thus, the cationic dye can be adsorbed to the surface of SDS-coated Fe_3O_4 NPs via electrostatic interactions.

Jin et al. (2008) studied adsorption of cationic methylene blue (MB) and anionic orange II (OII) onto unmodified and surfactant-modified zeolites using a batch method. Cationic surfactants including cetylpyridinium bromide hexadacyl (CPB) and hexadecylammonium bromide (HDTMA) were used for OII, while similarly sodium dodecyl benzenesulfonate (SDBS)- and sodium dodecyl sulfate (SDS)-modified zeolites were used for MB. These results suggested that 2% CPB- and 2% HDTMA-modified zeolites were the best adsorbents for OII. Similarly, 2% SDBS- and 3% SDS-modified zeolites had higher adsorption capacities for MB. From this information, it indicates that anionic surfactant can be used to modify zeolite in order to change their surface properties.

Moral et al. (2006) reported on the extraction/preconcentration of benzimidazolic fungicides (BFs) such as carbendazim (CB), thiabendazole (TB) and fuberidazole (FB) from river and underground waters by using SDS-coated-γ-alumina. The influence of SDS-coated alumina on the percentage of BFs adsolubilized was investigated in the batch mode by adding 250 μL of a solution containing 200 mg L^{-1} CB, 30 mg L^{-1} TB and 1 mg L^{-1} FB to 25 mL aqueous SDS-γ-alumina (0.5 g) mixtures at pH 2.0. The results were founded that BFs were not retained on γ-alumina in the case of absence of SDS, while the retention of BFs on hemimicelles of SDS-coated-γ-alumina, which have a hydrophobic surface, was clearly dependent on analyte polarity (e.g. log $K_{o/w}$ were 1.5, 2.5 and 2.7 for CB, TB and FB, respectively) and it increased as the amount of hemimicelles did. The formation of minute amounts of admicelles was essential to achieve complete adsolubilization of BFs. Electrostatic interactions between the admicelle surface and analytes, which bear opposite charge, were responsible for BFs increased retention.

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CHAPTER III

INFLUENCE OF Si/Al RATIO ON THE ADSORPTION CAPACITY OF HY ZEOLITE FOR REMOVAL OF PESTICIDES FROM AQUEOUS SOLUTION

3.1 Abstract

A study of adsorption capacity of HY zeolite with the mole ratio of Si/Al varying as 10, 100 and 500 was performed by batch adsorption for removal of atrazine, diuron, 2,4-D and PQ^{2+} with analytical standard grade and commercial grade. The result showed that HY10 can adsorb PQ^{2+} better than the other pesticides, on the other hand HY500 shows conversely result. HY500 exhibits the best adsorption of atrazine, diuron and 2,4-D, while HY100 shows less adsorption efficiency in removal of these pesticides but increasingly in removal of PQ^{2+} when compared to HY500. In addition, the result of the pesticides adsorptions from commercial grade was found to be similar profiles to analytical standard grade except the case of 2,4-D for which the adsorption value is inverse to Si/Al mole ratio. The effects of the pH were also investigated and it was found that an increase in the initial pH of solution increase the adsorption of PQ^{2+}, but the adsorption of 2,4-D was decreased and approached to zero when pH was over 6.0. The adsorption isotherms of four pesticides on high silica zeolites (HY100 and HY500) follows Langmuir model whereas HY10 fits to Langmuir or Fruendlich model depending on the type of pesticides.

3.2 Introduction

Zeolites are class of crystalline microporous aluminosilicates with more than 200 different framework structures and multiple functionalities (Wei, Yang, Scott, Aguey-Zinsou, and Zhang, 2018). The three-dimensional crystalline zeolite structures are formed by corner sharing SiO_4^{4-} and AlO_4^{5-} tetrahedra. Owing to the difference in valencies between Si and Al, each framework Al creates a negative charge in the lattice that requires the presence of a charge balancing cation to ensure the electroneutrality of the solid. The ionic nature of the bond between these counter cations and the zeolite framework allows the exchange of a cation by other cations without altering the crystalline structure of the solid with their negatively charged porous framework and the small and mobile cations existing in the pores, zeolite is typically ion exchange. An as high as possible cationic exchange capacity, hence, the highest possible aluminum content in the framework (Deka, 1998; Weitkamp, 2000), but high Al contents make zeolite having little affinity toward organic pollutants. However, most pesticides are more or less hydrophobic, various adsorbents were used to decontaminated them from water or wastewater.

In this work HY zeolites have been used to evaluate the capability in removal of pesticides with different classes. HY zeolites with different mole ratios of Si/Al such as 10, 100 and 500 are denoted as HY10, HY100 and HY500 (Table 3.1), respectively, were used as adsorbents for removal of 2,4-D, atrazine, diuron and PQ^{2+}. The Si/Al ratio is an important characteristic of zeolite. An increase in Si/Al ratio results in an increase of the thermal stability, acid strength and hydrophobicity. The adsorption of pesticides was conducted with various pesticide concentrations, pHs and temperatures. Moreover, the simultaneous adsorption of four pesticides on these adsorbents was also studied.

Table 3.1 Physicochemical properties of high silica zeolite adsorbents from Tosoh corporation.

Physicochemical properties	HY10	HY100	HY500
SiO_2/Al_2O_3 mole ratio	10	100	500
Specific surface area ($m^2\ g^{-1}$)	650	600	630
Mean Particle size (nm)	5-7	2-3	5-7
Na_2O (wt%)	0.1	0.1	0.05
NH_3-TPD (mmol/g)	1.1	-	< 0.1
Code of product	350 HUA	385 HUA	390 HUA

3.3 Experiment

3.3.1 Materials

Zeolite 350HUA, 385HUA and 390HUA denoted as HY10, HY100 and HY500, respectively, were obtained from Tosoh corporation. The PESTANAL® analytical standard grade as paraquat dichloride hydrate (98% purity), 2,4-D (99.9% purity), atrazine (99.5% purity) and diuron (99.6% purity) were obtained from Sigma. The commercial grade pesticides such as paraquat dichloride (ingredient as 27.6% w/v) derived from US Technical company Limited, 2,4-D (ingredient as 84% w/v) obtained from Pato Chemical Industry Public company Limited, atrazine (ingredient as 80% w/w) as Twin Bells brand and diuron (ingredient as 80% w/w) obtained from Zenthai company limited. A stock of PQ^{2+} solution was prepared by calculating the mass of PQ^{2+} from paraquat dichloride.

3.3.2 Characterization of physical and chemical properties of zeolite HY with difference in Si/Al mole ratio

The zeolites HY were characterized by the techniques usually employed in porous materials, such as XRD, FT-IR spectroscopy, thermogravimetric-differential thermal analysis (TG/DTG) and TPD.

X-ray diffractometry patterns (XRD) of all zeolite samples were acquired using a Bruker D8 advance X-ray diffractometer and using Cu Kα radiation (40 kV, 40 mA). Mid infrared spectroscopy measurements were performed on a Bruker Tensor 27 FTIR spectrometer with an attenuated total reflection (ATR) accessory. Spectra were recorded from 4000 to 350 cm^{-1}. All samples were degassed under vacuum at 100 °C overnight. TG/DTG curves were obtained by placing samples in an alumina pan and heating in air from 35 to 900 °C at a constant rate of 10 °C min^{-1}, using a thermogravimetric analyzer (TGA-DSC, METTLER). Zeolite HY/NaY (50 mg) acidity was determined using NH_3 temperature-program desorption (TPD) (BEL Japan, model BELCAT-B). For acidity analysis, the samples were pretreated under He at 500 °C for 2 h and then exposed to a flow of NH_3/He at 100 °C for 30 min. Weakly adsorbed NH_3 was removed by flushing with He at 100 °C for 30 min. The NH_3 TPD profile was obtained from 100-1000 °C at a heating rate of 10 °C/min. Desorbed NH_3 was detected using a thermal conductivity detector (TCD).

3.3.3 Effect of Si/Al mol ratio

Si/Al mol ratio affects to the adsorption property. The batch adsorption was performed by using three zeolites with different trend of negative charge and different classes of pesticides both in analytical grade and commercial grade. The mixture was shaken overnight at ambient temperature. The solution of pesticides was prepared with proper concentration of 25–150 ppm for PQ^{2+}, 100–500 ppm for 2,4-D and 5–30 ppm for diuron and atrazine in the ratio of 10 mg : 10 mL for PQ^{2+} and 2,4-D and 10 mg : 200 mL for diuron and atrazine. The residual atrazine, diuron, paraquat and 2,4-D concentrations were finally determined by UV-Vis spectroscopy at the wavelength of the maximum adsorption of 222, 246, 254 and 283 nm, respectively. The pesticides adsorption capacity and the removal efficiency for each adsorbent at present time were calculated with equation (1) and (2), respectively.

$$q_t = \frac{(C_o\text{-}C_t)V}{m} \qquad \text{.....................(1)}$$

$$\text{Removal efficiency (\%)} = \frac{C_o\text{- }C_t}{C_o} \times 100 \qquad \text{.....................(2)}$$

Where C_o and C_t are the concentrations of adsorbates in aqueous solution at initial time and at time t, respectively (mg L^{-1}); V is the volume of adsorbate solution (L); m is the mass of adsorbent (g); q_t is the amounts of pesticide adsorbed at time t (mg g^{-1}).

3.3.4 Effect of the pH

The effect of pH on the adsorption of each pesticide on zeolites HY was investigated in the pH range of 2.0 to 12.0. Pesticide solutions were prepared by dissolving a suitable amount of pesticides in distilled water. The pH of the solution was adjusted by adding with 0.1 or 0.01 mol L^{-1} of HCl or NaOH solutions before performing the adsorption experiment. The adsorbent was contacted with pesticide solution at solid/liquid ratio = 10 mg : 10 mL. The mixture was placed on a water shaker bath at 30 °C until it reached equilibrium, and then it was filtered. The filtrate was analyzed for residual pesticide concentration. Duplicate test was performed in all cases.

3.3.5 Adsorption isotherms

The adsorption isotherms were conducted by mixing adsorbent with aqueous solutions of pesticide at different concentrations at a specified optimal pH. Then, the mixtures were shaken continuously on a shaker bath for 24 h.

The adsorption equilibrium was evaluated with the adsorption model of Langmuir and Freundlich. The simplest model for adsorption events corresponds to the Langmuir isotherm which is used to describe adsorption by homogenous surface given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} K_L} \qquad \text{.....................(3)}$$

where C_e is the solute concentration at equilibrium (mg L^{-1}) and q_e is the amount of pesticide that is adsorbed at equilibrium time (mg g^{-1}); A q_{max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the affinity constant or Langmuir constant (L mg^{-1}). The plot of C_e/q_e versus C_e is linear; its slope is $1/q_{max}$ and the intersection with the C_e/q_e axis is $1/q_{max}K_L$.

Another simple equation for representing adsorption data is the Freundlich isotherm used to describe adsorption by heterogeneous surface as well as multilayer sorption and is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \quad \text{or} \quad \log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{.....................(4)}$$

where q_e is the amount of pesticide adsorbed per unit mass of adsorbent (mg g^{-1}); K_f is an indicative constant of the adsorption capacity of the adsorbent (L mg^{-1}); and n is an empirical constant called the Freundlich coefficient.

3.3.6 Adsorption study of quaternary mixture solution of pesticides

The adsorbent was added to the quaternary mixture solution (using at concentration 75 ppm/each pesticide). Pesticides in commercial grade were prepared as stock solution in absolute ethanol at concentration 1000 ppm, except paraquat dissolved in water. The suspensions were shaken at ambient temperature, for 24 h at 130 rpm, and then filtered using a 0.45 µm membrane. The concentrations of each pesticide were determined by HPLC (Agilent infinitely better 1200 infinity series) with diode array detector and UV detector. The ZORBAX Eclipse ODS C18 column (250 mm×4.6 mm, particle size 5µm) was equipped with HPLC system and the UV detector wavelength was set at 225, 257 and 283 nm. Acetonitrile (A) and water pesticide (0.5% phosphoric acid) (B) used as mobile phases. The gradient program of HPLC was as follows: 0–3 min 100% B, 3–13 min 90% A and 10% B, 13–20 min 100%(A) and 20–25 min 100%(A). The flow rate was set as 1.0 mL min^{-1}.

3.4 Results and Discussion

3.4.1 Solid adsorbents characterization

The surface properties of all HYZ were investigated using FTIR-ATR, XRD, NH_3-TPD, TG/DTG.

3.4.1.1 Thermogravimetric analysis

The thermal behavior of HY was evaluated using thermogravimetric analysis. Figure 3.1 shows TG and DTG thermograms for HY10, HY100 and HY500. A single DTG peak of these adsorbents occurs around 50 °C, resulting from loss of water molecules adsorbed on these adsorbents. The thermogram of HY10 shows a larger peak than that of the others indicating that HY10 contains the highest amount of water suggesting that HY10 possesses the highest hydrophilic property, while HY500 has the lowest hydrophilicity (Table 3.2).

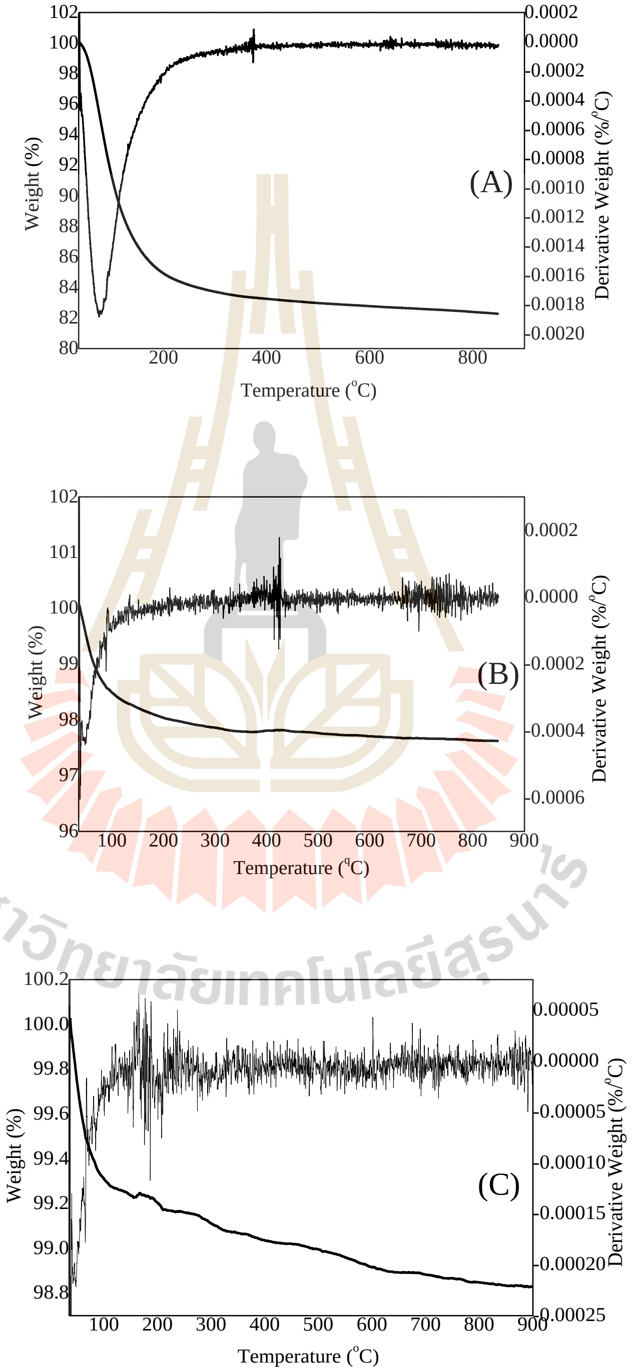

Figure 3.1 TG/DTG thermograms of (A) HY10, (B) HY100 and (C) HY500.

Table 3.2 The percent composition of water of adsorbents.

Adsorbents	Water contain (%)	
	35 - 150 °C	150 – 400 °C
HY10	13.28	3.47
HY100	1.78	0.41
HY500	0.76	0.21

3.4.1.2 Temperature-program desorption (TPD)

The strength and density of acid sites were investigated by NH_3-TPD. The NH_3-TPD curves were divided in to three peaks to compare density of acid site. The NH_3-TPD profile of HY10 displayed a low temperature desorption peak with a maximum around 200 and 380 °C arising from NH_3 adsorbed on surface sites of weak and strong Brønsted acid site, respectively, and a broad band in the range around 500–1000 °C as Lewis acid site. These peaks of HY10 are sharp and has higher density value than the other. Comparing the TPD profile of HY100 and HY500, it was found that acidic sites were decreased with increasing Si/Al ratios (Figure 3.2).

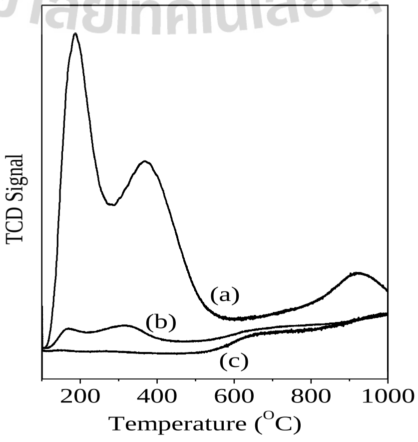

Figure 3.2 Normalized NH_3-TPD profiles of (a) HY10, (b) HY100 and (c) HY500.

The density values of acid sites are shown in Table 3.3, low silica zeolite contains higher amount of acid sites than high silica zeolite.

Table 3.3 Densities of acid site.

adsorbents	acid site density (mmol/g)		
	Peak 1	Peak 2	Peak 3
HY10	0.717	0.900	0.625
HY100	0.040	0.101	0.336
HY500	0.006	0.007	0.335

3.4.1.3 FTIR and XRD

FTIR-ATR spectra were used to investigate the surface characteristics of HYZ. The spectra of HYZ samples in the OH stretching region (1600–3700 cm^{-1}) (Hassan and Hameed, 2011) are shown in Figure 3.3. The spectra of HY10 (Figure 3.3B) show a broad band with a center at around 3500 cm^{-1} and a sharp band at 1600 cm^{-1} attributed to OH stretching vibration and OH blending vibration, respectively, of zeolitic water. These bands of HY10 are notable compared to the others, indicating that HY10 has higher hydrophilic properties than the others. For the band at 350–1300 cm^{-1} (see Figure 3.3C) are associated with Si–O–Si and Si–O vibrations which are the characteristic of zeolite Y. These peaks of HY100 and HY500 are sharper than that of HY10 because they have a large quantity of Si in their framework. In addition, the XRD pattern of each zeolite in Figure 3.4 shows all HY zeolites in crystalline phase and reveals a typical zeolite Y type structure. However, the intensity of the major peak at the position (111) plane increases with an increase in Si/Al ratios. A decrease of Al in the framework supports an increase in the crystallinity of HY zeolite.

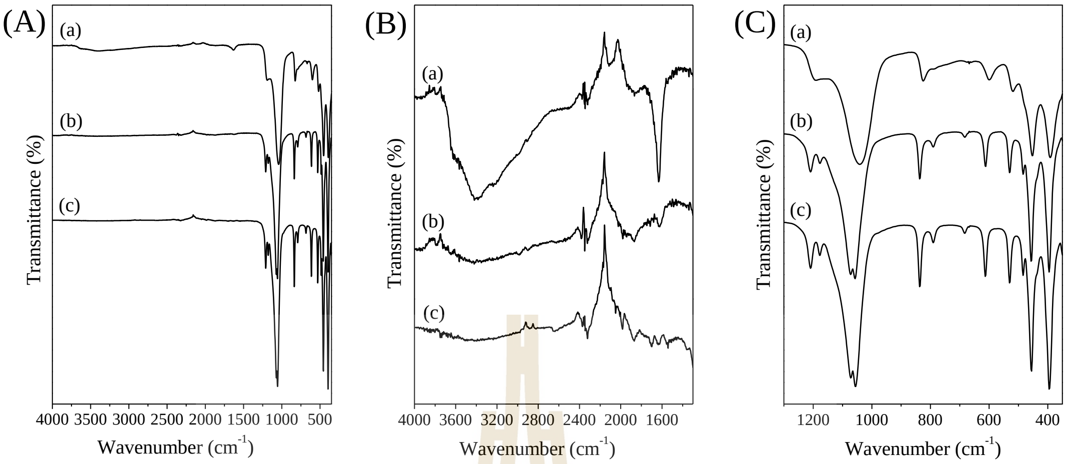

Figure 3.3 ATR-FTIR spectra of HYZ with different Si/Al ratios (A) in the region of 4000–350 cm^{-1}, (B) in the region of 4000–1300 cm^{-1} and (C) in the region of 1300–350 cm^{-1}. (a) HY10, (b) HY100 and (c) HY500.

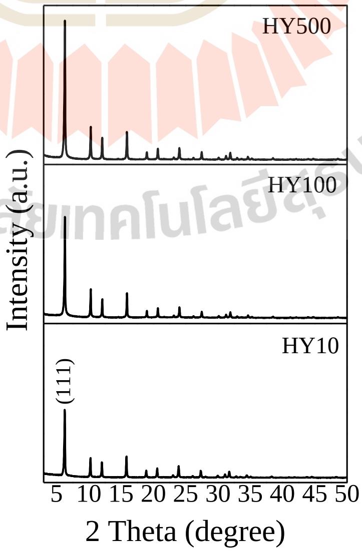

Figure 3.4 XRD patterns of HY zeolites.

3.4.2 Results of adsorption study

3.4.2.1 Effect of Si/Al mole ratio on the adsorption capacity

The mole ratios of Si/Al affect the ability of zeolite to adsorb various pesticides. The adsorption results as shown in Figure 3.5 illustrate the influence of Si/Al ratios on the adsorption capacity of HY zeolite. When considering the used pesticides in analytical grade (see Figure 3.5A, C, E and G), it indicates that HY10 is capable to adsorb PQ^{2+} better than the other pesticides, while HY100 and HY500 are active to remove 2,4-D, atrazine and diuron more than PQ^{2+}. Comparing between HY100 and HY500, it was found that HY500 overcome HY100 in the adsorption of 2,4-D, atrazine and diuron, but PQ^{2+} can be adsorbed by HY100 better than that by HY500. When considering the properties of each adsorbent, HY10 has Brønsted acid sites more than the others (see Table 3.2). Therefore, PQ^{2+} can attach to these active sites by ion exchange. In the case of HY100 and HY500, they have an attractive interaction with 2,4-D, atrazine and diuron due to their high hydrophobicity according to high Si content in their framework resulting in the surface favorable to adsorb non-polar molecules. However, the existence of 2,4-D in the solution can be in both neutral and anionic forms, consequently negatively charged 2,4-D is able to form H-bond on HY10. Moreover, the pesticides with commercial grade (see Figure 3.5B, D, F and H) were also used in the study for comparison to the pesticides with analytical grade. The result was found that the trend of the adsorption capacity of the pesticides with commercial grade by each adsorbent is similar to the adsorption result of pesticides with analytical grade, except in the case of 2,4-D adsorption result. The adsorption capacity of 2,4-D with analytical grade is in the order of HY500 > HY100 > HY10, which is contrast to commercial grade of 2,4-D (HY10 > HY100 > HY500) may be due to other in gradients

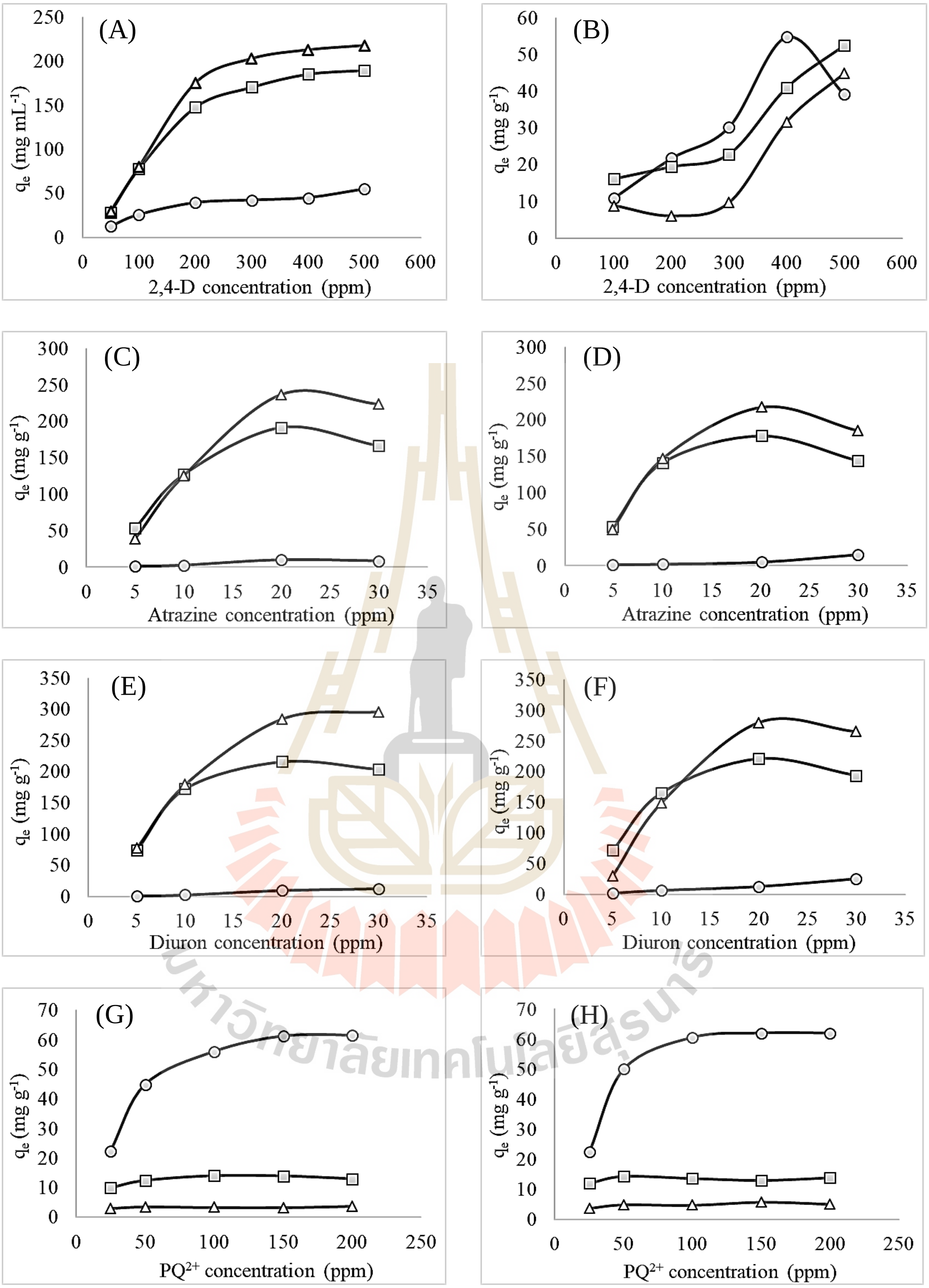

Figure 3.5 Effect of Si/Al mol ratio on the adsorption of (A, C, E and G) 2,4-D, atrazine, diuron and PQ^{2+} as AR grade and (B, D, F and H) 2,4-D, atrazine, diuron and PQ^{2+} as commercial grade. (-○- HY10 -□- HY100 -△- Y500)

resulting change the properties of 2,4-D or support the surface of zeolite with high Al can interact with this pesticide.

3.4.2.2 Effect of initial pH

The adsorption capacity of adsorbents varies with changing initial pH of solution. The changes in pH of the solution affect the speciation of adsorbent species, the adsorbent surface charge, and the degree of pesticide ionization (Moradi, 2014; Nejati, Davary, and Saati, 2013). Generally, when the zeolite presents in acid medium the framework of zeolite able to decompose, but the acid tolerance of HY zeolite depends on the Si/Al ratio; higher Si/Al ratio (up over 10) increase their acid resistance (Hassan and Hameed, 2011; Nezamzadeh-Ejhieh and Badri, 2011).

The condition of the experiment was varied by adjusting pH ranging from 2.0–12.0 resulting in the change of surface properties of zeolite and ionization of pesticide molecules. Generally, the H^+ and OH^- are the potential determining ions. The mineral oxide surfaces like silica surfaces acquire a charge in contact with water and potential determining ions shown by the following equations (Paria and Khilar, 2004);

$$\mathrm{SiOH} + \mathrm{H}^+ \rightarrow \mathrm{SiOH_2}^+ \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$\mathrm{SiOH} + \mathrm{OH}^- \rightarrow \mathrm{SiO}^- + \mathrm{H_2O} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Thus, zeolite surface exists in typically positive charged at low pH and the charge decreases and eventually becomes negative as pH increases. Considering the case of ionic pesticides, with this reason, all the adsorbents display the adsorption capacity of PQ^{2+} increased with an increase in pH of the solution as shown in Figure 3.6B. The adsorption value of hydrophobic zeolites increases drastically at high pH because possibly their SiOH group on the surface changing to SiO^- that prefer to adsorb PQ^{2+}.

In contrast to the case of 2,4-D adsorption (Figure 3.6A), 2,4-D has a p*K*a of 3.55; it can exist in both neutral and anionic form. At pH 3–6 anionic forms appear as around 22% – 99.5% in aqueous solution (Ding, Lu, Deng, and Zhang, 2012). Thus, at high pH 2,4-D exists almost in anionic form, consequently it can't attach to the surface of each zeolite.

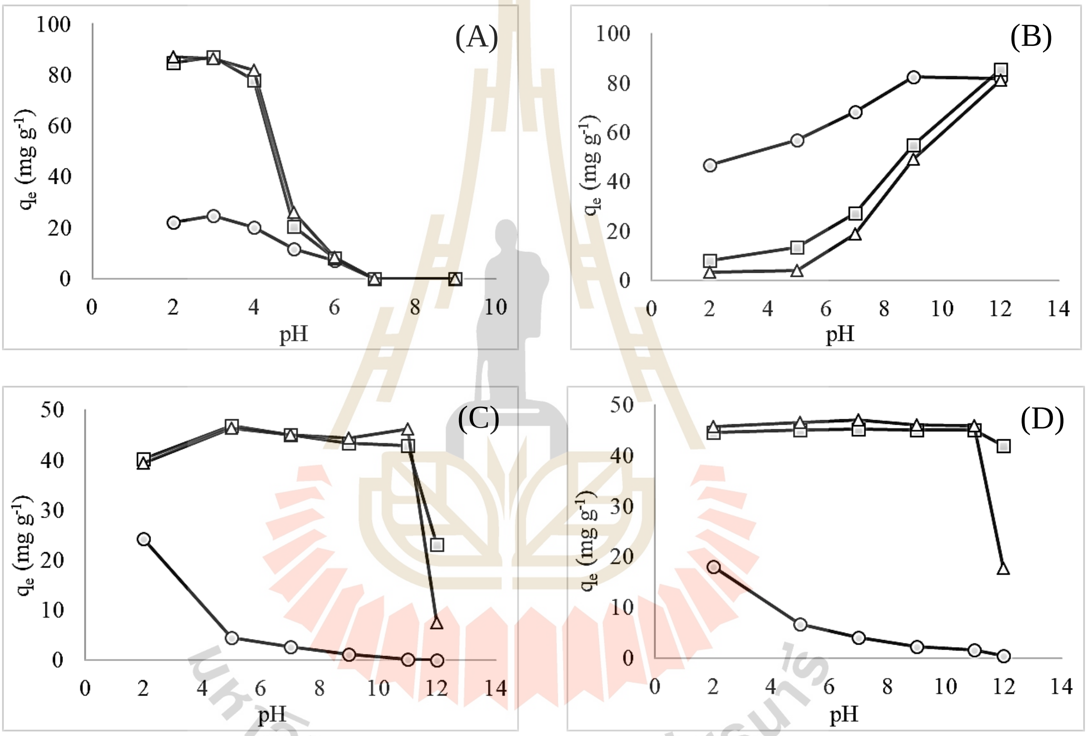

Figure 3.6 Effect of pH to adsorption capacity for removal of (A) 2,4-D, (B) PQ^{2+}, (C) atrazine and (D) diuron. (-○- HY10 -□- HY100 -△- Y500).

The adsorption profiles of HY10 are similar trendy for atrazine and diuron adsorption (Figure 3.6C and D). The adsorption amount of the pesticides in HY10 decrease with increasing pH level. At near the pH numerically equal to pK_a of atrazine (pK_a= 1.68), a half of atrazine exists in the cationic form while the other half stays in the non-ionic form,(Yue et al., 2017). For diuron, it reported that diuron exists a half of neutral form and a half of cationic form at pH around 4 (Fontecha-Cámara, López-Ramón, Álvarez-Merino, and Moreno-Castilla, 2007) According to the data, the high adsorption capacity of HY10 at low pH may be the cationic form of atrazine and diuron can adsorb by ion exchange with Brønsted acid site and ion exchangeable cation of HY10. When pH increased the adsorption value decreases because the cationic form of the pesticide is reduced. The adsorption profiles of high silica zeolite (HY100 and HY500) are different from HY10. A change in initial pH of the solution is negligible effect on the adsorption process, except at pH 12. It suggests that the interaction between both pesticides with HY100 and HY500 is mainly hydrophobic interaction.

3.4.2.3 The study of adsorption isotherms

The adsorbed amounts of atrazine, diuron, PQ^{2+} and 2,4-D onto the various hydrophobic zeolites versus the equilibrium pesticide concentrations are shown in Figure 3.7–3.10. The initial and equilibrium adsorbate concentrations are important parameters which can affect the adsorption process considerably. Generally, an increase in concentration of adsorbates leads to an increase in the quantity uptake. For the considering the R^2 value of isotherm adsorption models of 2,4-D (Figure 3.7 and Table 3.4), it was found that R^2 values confirm the adsorption equilibrium data fitted well with the Langmuir model.

Based on the Langmuir adsorption model the predicted maximum monolayer (q_m) of 2,4-D adsorbed on HY500 higher than that on HY100 and HY10. It indicates that high silica zeolite is outstanding for adsorption of 2,4-D in both forms of anionic and neutral form.

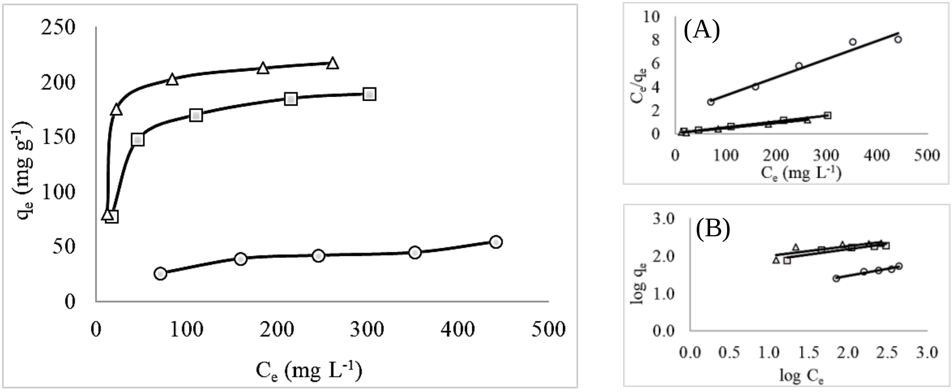

Figure 3.7 Adsorption isotherms of 2,4-D and plot of (A) Langmuir isotherm, (B) Freundlich isotherm. (-○- HY10 -□- HY100 -△- Y500).

Table 3.4 Langmuir and Freundlich isotherm modeling of 2,4-D adsorbed by HY10, HY100 and HY500.

Adsorbents	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F*	1/*n*	R^2
HY10	64.52	0.0088	0.9643	5.54	0.3702	0.9500
HY100	204.08	0.0443	0.9991	39.91	0.2905	0.8507
HY500	232.56	0.0701	0.9970	56.39	0.2616	0.6823

* Unit of K_F is (mg g^{-1})(L mg^{-1})$^{1/n}$

In the case of atrazine adsorption, it is quite similar adsorption isotherm of diuron (see Figure 3.8–3.9 and Table 3.5–3.6), but the adsorption isotherm model is different. Considering the R^2 values of HY10, the Freundlich isotherm was found to be satisfactory for describing the equilibrium relationships. For HY100, it seems that the Langmuir isotherm is adequate for describing the adsorption model of both atrazine and diuron. However, the result of adsorption isotherm of atrazine and diuron on HY500 are different. The diuron adsorption isotherm was fitted to Langmuir isotherm better than Freundlich isotherm, while the adsorption process of atrazine on HY500 showed R^2 value similarly in both Langmuir and Freundlich isotherm.

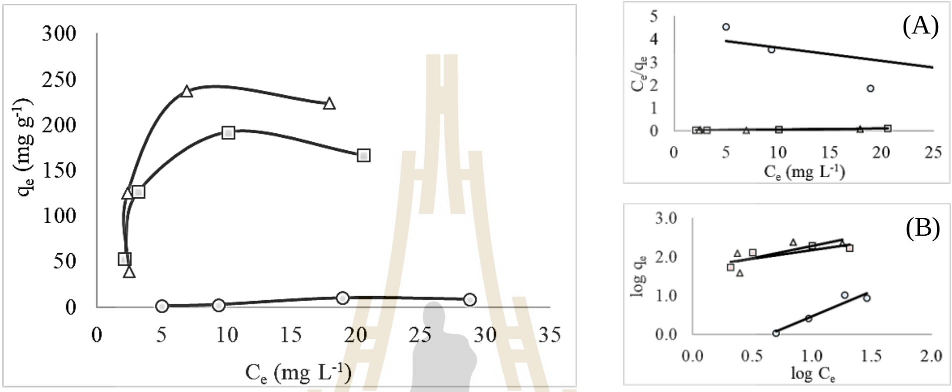

Figure 3.8 Adsorption isotherms of atrazine, and plot of (A) Langmuir isotherm, (B) Freundlich isotherm. (-○- HY10 -□- HY100 -△- Y500).

Table 3.5 Langmuir and Freundlich isotherm modeling of atrazine adsorption by HY10, HY100 and HY500.

Adsorbents	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F*	1/n	R^2
HY10	-	-	-	0.15	1.3074	0.9206
HY100	200.00	0.3226	0.9271	54.43	0.4435	0.6581
HY500	384.62	0.0897	0.4281	44.24	0.6370	0.5312

* Unit of K_F is (mg g^{-1})(L mg^{-1})$^{1/n}$

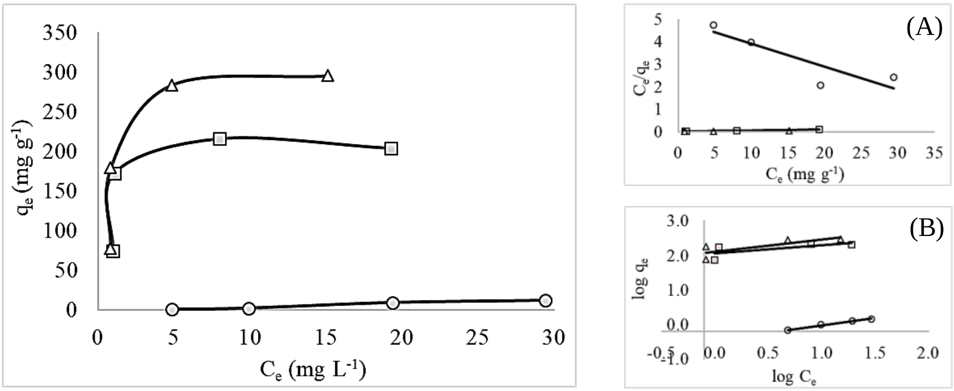

Figure 3.9 Isotherm adsorption of diuron, and plot of (A) Langmuir isotherm, (B) Freundlich isotherm. (–○– HY10 –□– HY100 –△– Y500).

Table 3.6 Langmuir and Freundlich isotherm modeling of diuron adsorption by HY10, HY100, and HY500.

Adsorbents	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	$K_F{}^*$	1/n	R^2
HY10	-	-	-	0.36	0.4223	0.9889
HY100	217.39	1.1795	0.9900	114.02	0.2354	0.4922
HY500	322.58	0.7045	0.9811	131.22	0.3486	0.6363

[*] Unit of K_F is (mg g^{-1})(L mg^{-1})$^{1/n}$

Finally (see Figure 3.10 and Table 3.7), considering the adsorption isotherm for removal of PQ^{2+} from aqueous solution, the R^2 values from Langmuir isotherm of all adsorbents are closed to 1 indicating that the surface of each adsorbent is unique for PQ^{2+} adsorption in monolayer adsorption.

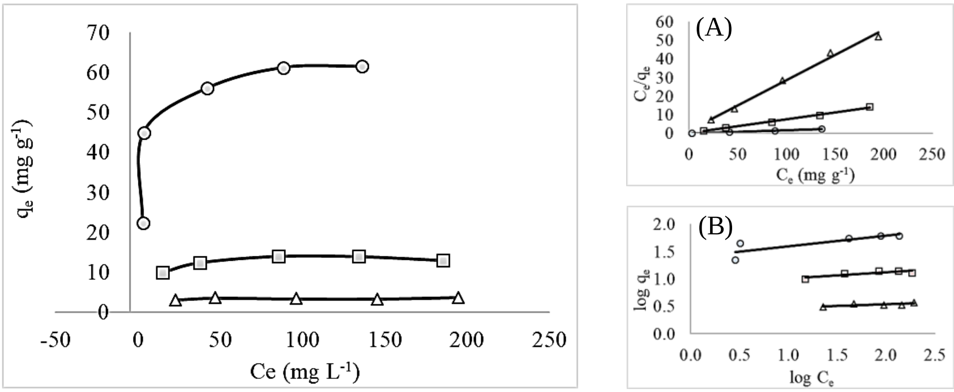

Figure 3.10 Isotherm adsorption of PQ^{2+}, and plot of (A) Langmuir isotherm, (B) Freundlich isotherm. (-○- HY10 -□- HY100 -△- Y500).

Table 3.7 Langmuir and Freundlich isotherm modeling of PQ^{2+} adsorption by HY10, HY100 and HY500.

Adsorbents	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F*	1/*n*	R^2
HY10	63.29	0.2701	0.9991	25.86	0.1899	0.6745
HY100	13.53	0.5291	0.9948	7.82	0.1140	0.7329
HY500	3.7	0.1670	0.9900	2.69	0.0541	0.4419

* Unit of K_F is (mg g^{-1})(L mg^{-1})$^{1/n}$

3.5 Adsorption capacity for simultaneous adsorption of various pesticides in solution

This study concerns with the adsorption of these pesticides simultaneously by HY10, HY100 and HY500 and the results are shown in Table 3.8. The total values of pesticides removed from aqueous solution is the maximum which is of HY100. These total values proved that HY100 is the most suitable for removal various pesticides simultaneously in one time, consequently it can be used as multifunctional adsorbent.

Table 3.8 Adsorption capacity of adsorbents for simultaneous removal of various pesticides in solution.

adsorbents	Adsorption capacity (mg g^{-1})				
	Atrazine	Diuron	2,4-D	PQ^{2+}	Total
HY10	0	4.7	26.5	41.7	72.9
HY100	79.6	78.1	6.8	16.3	180.8
HY500	41.0	72.2	1.8	11.8	126.8
HY10:HY100	5.2	26.3	24.3	29.5	85.3
HY10:HY500	1.2	11.0	20.9	29.5	62.6

3.6 Conclusions

In the study of the pesticides adsorptions, high silica zeolites Y were used as potential adsorbents by varying hydrophobicity of their surfaces. Low silica zeolite Y as HY10 was appropriate to remove cations pesticide such as PQ^{2+}, whereas high silica zelite Y as HY100 and HY500 were suitable to adsorb neutral and anion pesticides. When considered the capability of adsorbent to eliminate pesticides in the individual pesticide solution, it seems that HY500 has the highest capacity for removal 2,4-D, atrazine and diuron, but in the simultaneous removal of these pesticides, HY100 shows the best potentiality to remove the multiple pesticides. The interaction between PQ^{2+} or 2,4-D and the surface of the adsorbents depends on the pH of the solution. However, it does not affect the adsorption capacity of atrazine and diuron in the pH range 4–10. According to the adsorption isotherm model, it seems the adsorptions of several pesticides by HY100 and HY500 found to followed the Langmuir model, while the adsorption of pesticides with HY10 followed Langmuir or Fruendlich model depends on the structure of pesticides.

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CHAPTER IV

ADSORPTION STUDY AND CHARACTERIZATION OF UNMODIFIED AND MODIFIED ZEOLITE Y

4.1 Abstract

The propose of this study is to improve the adsorption capacity of zeolite by changing the cationic type from H^+ to Na^+ and by modifying with cationic surfactant (HDTMA) and anionic surfactant (SDS). The achievement of modified zeolite was investigated with FT-IR, XRD, WD-XRF, CHN/S analyzer, BET, TG/DTG and TPD. The data reveal that HDTMA can attach on both surface of ZY10 and ZY100, but SDS can attach only on the surface of ZY100. The adsorption result was found that the change in cationic type in zeolite framework shows significant effect only on 2,4-D adsorption. Modification of zeolite with HDTMA assists to improve the adsorption capacity of ZY10, but not for ZY100. In the case of SDS modification, it was found that the arrangement of SDS on the surface of zeolite does not affect the reduction or increment of the adsorption capacity, except in the adsorption of 2,4-D and PQ^{2+}. The adsorption capacity of PQ^{2+} is increased with increasing SDS concentration. Conversely, with high HDTMA density results in a decrease in the adsorption capacity. Additionally, it was found that the water content in SDS-modified zeolite plays an important role in the removal of pesticide.

4.2 Introduction

The contamination of surface and ground water by pesticides has become a serious environmental problem due to the extensive application of these agrochemicals in crop farms, orchards, fields and forest lands. This contamination arises from surface runoff, leaching, wind erosion, deposition from aerial applications, industrial discharges and various other sources (Salman, Njoku, and Hameed, 2011). Pesticides were produced in various forms for human purpose such as cationic pesticide. It is easy to remove them from water if focus only one class of pesticides, but it is quite difficult to eliminate simultaneously classes of pesticides by one adsorbent.

The use of natural zeolites in wastewater treatment is in one of the oldest and the most perspective areas of their application. Particularly, zeolites are excellent adsorbents for removal of cationic pollutants, but have disadvantage to adsorb organic pollutants. On the other hand, the permanent negative charges in their crystal structures enable them to be modified by cationic surfactant and that surfactant modified zeolite are able to effectively retain organic pollutants, including non-ionizable hydrophobic organic contaminants, ionizable phenolic compounds as well as organic anions (Xie et al., 2013). Several reports found that cationic surfactant is convenient to adsorb on the negative surface of zeolite Y and these adsorbents are utilized to remove multiple types of contaminants from aqueous solution by varying the quantity of cationic surfactant. At concentrations lower than the critical micelle concentration (CMC) of surfactant, cations are retained by ion exchange, which leads to the formation of a monolayer on the external surface of the zeolite. The retained surfactant provides a hydrophobic surface to the zeolite, thus making it suitable for retaining organic compound (Vidal et al., 2012) such as BTEX (Ranck, Bowman, Weeber, Katz, and Sullivan, 2005). At surfactant concentration greater than CMC, the adsorbed surfactant molecules form a bilayer on the external surface of zeolite cause a reversal charge on the external zeolite surface. This formation provides site where anions can be retained (Anari-Anaraki and Nezamzadeh-Ejhieh, 2015). However, there are a few reports to inform an achievement of modification of zeolite by anionic surfactant for improving the adsorption capacity, for example, sodium dodecyl sulfate (SDS) and sodium dodecyl benzenesulfonate used to enhance zeolite adsorption capacity for removal of organic dyes (Jin, Jiang, Shan, Pei, and Chen, 2008)

The work in this section studied on the efficiency of ZY10 and ZY100 which were modified by cationic surfactant (HDTMA) and anionic surfactant (SDS) for removal of pesticides from aqueous solution by batch adsorption process. The effect of the surfactants loading level was studied and the achievement of modification was confirmed by various techniques such as FT-IR, XRF, XRD, BET, CHN/S and TG/DTG.

4.3 Experiment

4.3.1 Materials

Zeolite 350HUA and 385HUA as a high-silica zeolite as HSZ-300 series was obtained from Tosoh corporation. The analytical standard grade, paraquat dichloride hydrate (99.9% purity), 2,4-D (99.9% purity), atrazine (99.5% purity), linuron (99.7% purity), difenzoquat methyl sulfate (99.9%purity), bentazon (99.9% purity), cayanazin (99.9% purity), carbofuran (99.9% purity), SDS, and hexadecyltrimethylammonium (HDTMA) chloride were obtained from Sigma. A stock of PQ^{2+} solution was prepared by calculating the mass of PQ^{2+} from paraquat dichloride.

4.3.2 Modification of zeolite

4.3.2.1 Changing H-form of zeolite Y10 and zeolite Y100 into Na-form

The commercial H-form of zeolite Y10 and Y100 were converted into Na-form by the following procedure: The zeolite H-form of zeolite Y10 and Y100 was contacted under continuous stirring with 1M NaCl solution (20 mL g^{-1} of zeolite) at ambient temperature for 24 h, then the mixture was centrifuged, decanted, and refreshed with a new NaCl solution. The exchange was repeated 3 times in order to achieve the maximum exchange of Na^+ ions. The zeolite Na-from was washed with DI water several times and dried at 110 °C for 3 h.

4.3.2.2 Preparing organo-zeolite by modification with HDTMA solution

HDTMA-modified zeolite was prepared by using zeolite Y in Na-form and H-form dispersed in deionized-water (ratio of 1 g zeolite/10 mL DI water) around 10–15 min, then a HDTMA solution was added dropwise into the zeolite suspension (ratio of 1g zeolite/50 mL HDTMA solution calculated from total volume) and stirred continuously for 24 h at ambient temperature. The mixture is then filtered by vacuum filtration and washed with DI-water until without Cl^- (detected by $AgNO_3$ solution). Finally, the solid sample was dried at room temperature for 2–3 days. The HDTMA-modified zeolites were denoted in this work as HNaY (HDTMA-modified zeolite Y in Na-form) and HHY (HDTMA-modified zeolite Y in (H-form).

4.3.2.3 Preparing organo-zeolite by modification with SDS solution

Each zeolite was modified with SDS solution. The zeolite was homogenized by stirring in DI water (ratio of 1 g zeolite/10 mL DI water) around 10–15 min. After that it was mixed dropwise with SDS solution (ratio of 1g zeolite/100 mL SDS solution) and stirred continuously for 24 h, at ambient temperature. The excess SDS was removed by washing with DI water and filtering with vacuum filtration for several times. Then the solid was dried at room temperature for 2–3 days. The SDS-modified zeolites were denoted in this work as SNaY (SDS-modified zeolite Y in Na-form) and SHY (SDS-modified zeolite Y in H-form).

4.3.3 Batch adsorption study

4.3.3.1 Effect of surfactant loading

The adsorption efficiency of pesticides depends on the formation of surfactant on the surface of adsorbents. Thus, the first parameter related to the adsorptive evaluation in this study is the effect of the concentration of surfactant loading on the surface of zeolite. The experiment was performed by keeping the desired concentration of pesticides constant (depending on the type of pesticide) and varying the concentration of each surfactant. The modified-zeolites were treated with various concentrations of the surfactant of 0.5, 1, 5, 10 and 20 mM. For this purpose, 10 mg of adsorbent samples were added into 125 mL conical flasks with 10 mL of pesticides aqueous solution. The experiments were carried out at ambient temperature for 24 h on a shaker equipped at 130 rpm. After that the suspensions were centrifuged at 3000 rpm, for 10 min and filtered (using nylon syringe filter) before using in the next step. The residual atrazine, cyanazin, linuron, carbofuran, paraquat (PQ^{2+}), difenzoquat (DQ^{+}), 2,4-D and bentazon concentration were finally determined using a UV-Vis spectrophotometer at the wavelength of the maximum adsorption of 222, 220, 246, 276, 257, 254, 283 and 334 nm, respectively. The pesticides adsorption capacity and the removal efficiency for each adsorbent at present time were calculated with equation (1) and (2), respectively.

$$q_t = \frac{(C_o - C_t)V}{m} \qquad \text{.....................(1)}$$

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \qquad \text{.....................(2)}$$

Where C_o and C_t are the concentrations of adsorbates in aqueous solution at initial time and at time t, respectively (mg L^{-1}); V is the volume of adsorbate solution (L); m is the mass of adsorbent (g); q_t is the amounts of pesticide adsorbed at time t (mg g^{-1}).

4.3.3.2 Optimum contact time and equilibrium time

A batch adsorption experiment was conducted for removal of pesticides at ambient temperature and natural pH of each pesticide solution by contacting adsorbent with pesticide solutions at solid/liquid ratio = 150 mg/150 mL. The mixtures were shaken for 24 h. After that, some aliquots of the supernatants were withdrawn for analysis at different time intervals.

4.3.3.3 Effect of the pH

The effect of pH on the adsorption of each pesticide on unmodified and modified zeolites Y was investigated over the pH range of 2.0 to 12.0 (depending on the type of pesticide). Pesticide solutions were prepared by dissolving a suitable amount of pesticides in distilled water. The pH of the solution was adjusted by adding with 0.1 or 0.01 mol L^{-1} of HCl or NaOH solutions before performing the adsorption experiment. The adsorbent was contacted with pesticide solution at solid/liquid ratio = 10 mg/10 mL. The mixture was placed on a water shaker bath at 30 °C until it reached to equilibrium, and then it was filtered. The filtrate would be analyzed for residual pesticide concentration. Duplicate test was performed in all cases.

4.3.4 Adsorption isotherm study

The adsorption isotherms were conducted by mixing unmodified and modified zeolite Y (10 mg) with aqueous solutions of pesticide (10 mL) at different concentrations at specified optimal pH and optimal temperature. Then, the mixtures were shaken continuously on a shaker bath for 24 h.

The adsorption equilibrium was evaluated with the model of Langmuir and Freundlich. The simplest model for adsorption events corresponds to the Langmuir isotherm which is used to describe adsorption by homogenous surface given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} K_L} \qquad \text{.....................(3)}$$

where C_e is the solute concentration at equilibrium (mg L^{-1}) and q_e is the amount of pesticide that is adsorbed at equilibrium time (mg g^{-1}); A q_{max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the affinity constant or Langmuir constant (L mg^{-1}). The plot of C_e/q_e versus C_e is linear; its slope is $1/q_{max}$ and the intersection with the C_e/q_e axis is $1/q_{max}K_L$.

Another simple equation for representing adsorption data is the Freundlich isotherm used to describe adsorption by heterogeneous surface as well as multilayer sorption and is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \quad \text{or} \quad \log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{.....................(4)}$$

where q_e is the amount of pesticide adsorbed per unit mass of adsorbent (mg g^{-1}); K_f is an indicative constant of the adsorption capacity of the adsorbent (L mg^{-1}); and n is an empirical constant called the Freundlich coefficient.

4.3.5 Study the multifunctional possibility of modified zeolite Y for simultaneous adsorption of various pesticides

Modified zeolites Y were added to the quaternary solution (using appropriate concentration ratio of 2,4-D: atrazine: linuron: paraquat). The suspensions were shaken at ambient temperature, for 24 h at 130 rpm, and then filtered using a 0.45 μm membrane. The concentrations of the pesticides were simultaneously determined by HPLC and the condition was established as in the chapter III.

4.3.6 Characterization of physical and chemical properties of unmodified and modified zeolites Y

The unmodified and modified zeolites Y were characterized by the techniques usually employed in porous materials, such as XRD, XRF, FT-IR spectroscopy, BET analyzer, Particle analysis, TG-DTG, NH_3-TPD and CHN/S analyzer

The XRD patterns of adsorbents were recorded with CuK_{α} filtered radiation and with the Bragg angle 2θ of 3–50 °C to compare crystallinity by comparing the intensity of the modified zeolites Y with those parent zeolites Y which are considered to be 100% crystallinity. The chemical composition of each adsorbent was determined by a PANalytical AXIOS^{mAX} sequential WD-XRF spectrometer. Samples were prepared by spreading dried powder over a surface of sample holders. The C, N, and S contents of modified-zeolite were determined by CHN/S analysis (Leco, CHN 628 series elemental analyzer with sulfur add-on module) by high-temperature combustion. Sample preparations for C and N analysis were prepared by weighing samples accurately on a tin foil liner and inserted into the CHN628 analyzer. Elemental analysis for S was performed by weighing the sample onto a ceramic boat before placing in the CHN 628 analyzer. Mid infrared spectroscopy measurements were performed on a Bruker Tensor 27 FTIR spectrometer and obtained with an attenuated total reflection (ATR) accessory. Spectra were recorded from 4000 to 350 cm^{-1}. This technique is used to analyze mineral surfaces after modification. Particle size analysis of unmodified and modified zeolite were performed by laser scattering method with particle size distribution analyzer instrument (Horiba, LA-950V2). The particle size of the adsorbents was analysis by median value which defines as the value where half of the population resides above this point, and half resides below this point. All samples were dispersed in DDI water and were subject to ultrasonicated for 1 min before analysis. Zeolite specific surface area (S_{BET}), total pore volume (V_t) and average pore diameter (D_a) were analyzed using the Brunauer–Emmett–Teller (BET) method. The external surface area (S_{ext}) and micropore surface area (S_{micro}) were determined using a *t*-plot method. All samples were degassed under vacuum at 100 °C overnight. TG/DTG curves were obtained by placing samples in an alumina pan and heating in air from 35 to 900 °C at a constant rate of 10 °C min^{-1}, using a thermogravimetric analyzer (TGA-DSC, METTLER). TGA is a technique that measures changes in weight in relation to changes in temperature. The measured weight loss curve gives information on changes in sample composition and thermal stability. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. For acidity analysis, samples were pretreated under He at 500 °C for 2 h and then exposed to a flow of NH_3/He at 100 °C for 30 min. Weakly adsorbed NH_3 was removed by flushing with He at 100 °C for 30 min. The NH_3 TPD profile was obtained from 100–1000 °C at a heating rate of 10 °C/min. Desorbed NH_3 was detected using a thermal conductivity detector (TCD).

4.4 Results and Discussions

4.4.1 Characterization of unmodified and modified zeolite Y

The surface properties of adsorbents were investigated using FTIR-ATR, XRD, XRF, CHN/S analysis, TG/DTG, and BET.

4.4.1.1 FTIR spectra

FTIR-ATR spectroscopy was used to investigate the loading of surfactants on to the surface of zeolite H-form and Na-form. Representative spectra of HDTMA, SDS, ZY and MZY in the range of 4000–350 cm^{-1} are shown in Figure 4.1 and 4.2. The spectra of MZY are different from those of ZY. For MZY, the major bands in the region 2800–3000 cm^{-1} arise from symmetric and asymmetric C–H stretching of the alkyl chains of both surfactants, and bands in the range 1400–1500 cm^{-1} result from C–H bending vibrations. These absorption bands indicate successful loading of surfactant on the zeolite surface. These bands were detected only in zeolites modified with HDTMA and SDS. They are slightly shifted to higher wavenumbers, corresponding to a more disordered alignment of surfactant on the zeolite surface, compared to that of the pure surfactants (Bouras, Bollinger, Baudu, and Khalaf, 2007; Lin and Zhan, 2012). Characteristic zeolite absorption bands in the range 460–1220 cm^{-1} were observed for both unmodified and modified zeolites. These bands are associated with Si–O–Si and Si–O vibrations, which are exhibited by all adsorbents (Figure 4.1 and 4.2) and indicate that zeolite structures are stable after modification and that chemical bonding did not occur during the adsorption process. These data are in good agreement with earlier reports by Bakhtiary and Shirvani (2013).

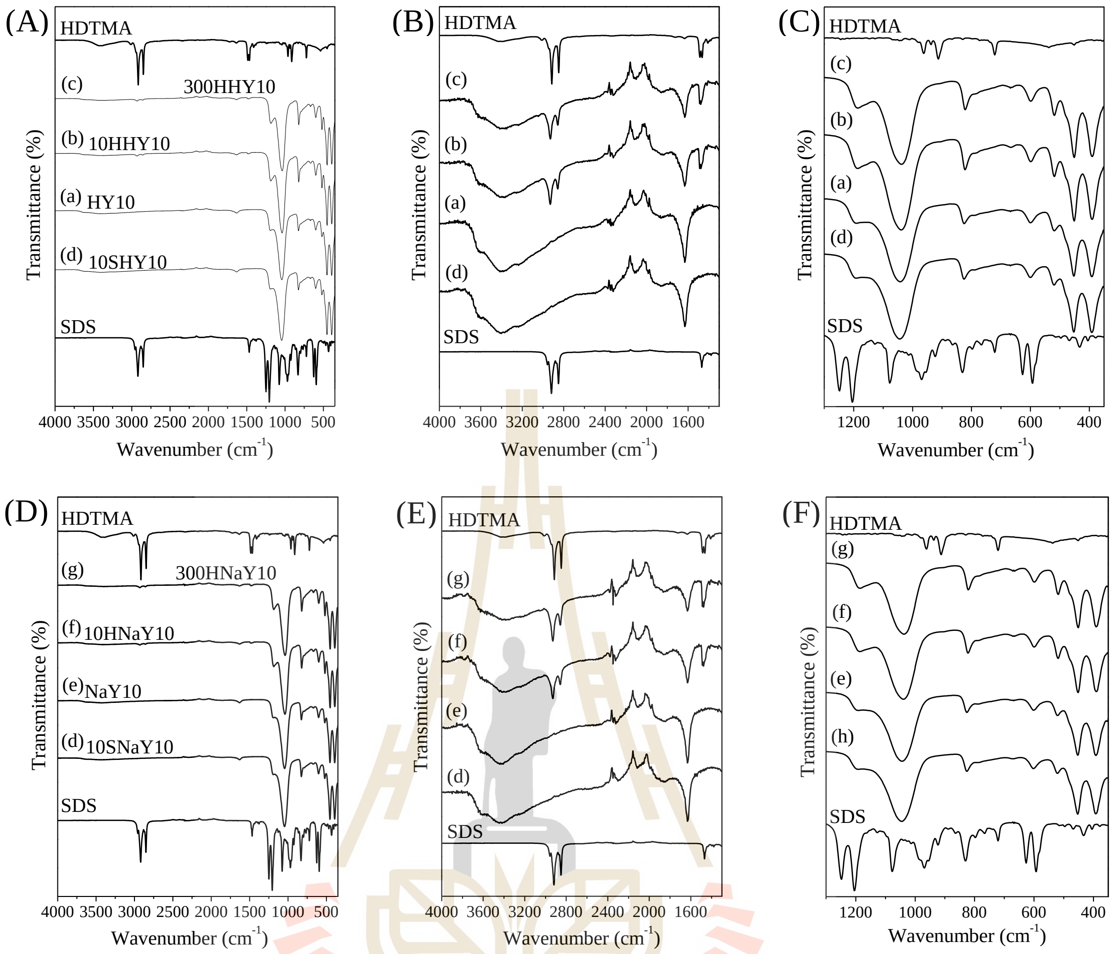

Figure 4.1 ATR-FTIR spectra of unmodified and modified (A–C) HY10 and (D–F) NaY10 in the range of (A and D) 350–4000 cm^{-1}, (B and E) 1300–4000 cm^{-1} and (C and F) 350–1300 cm^{-1}.

However, the FTIR-ATR profiles of SZY10 show the different peak from SZY100 in the surfactant region. The peaks of asymmetric C–H stretching and C–H bending vibrations of 10SZY10 clearly disappear indicating that SDS does not attach on the surface of ZY10 because highly negative charges of their frameworks repulse the negative head groups of SDS.

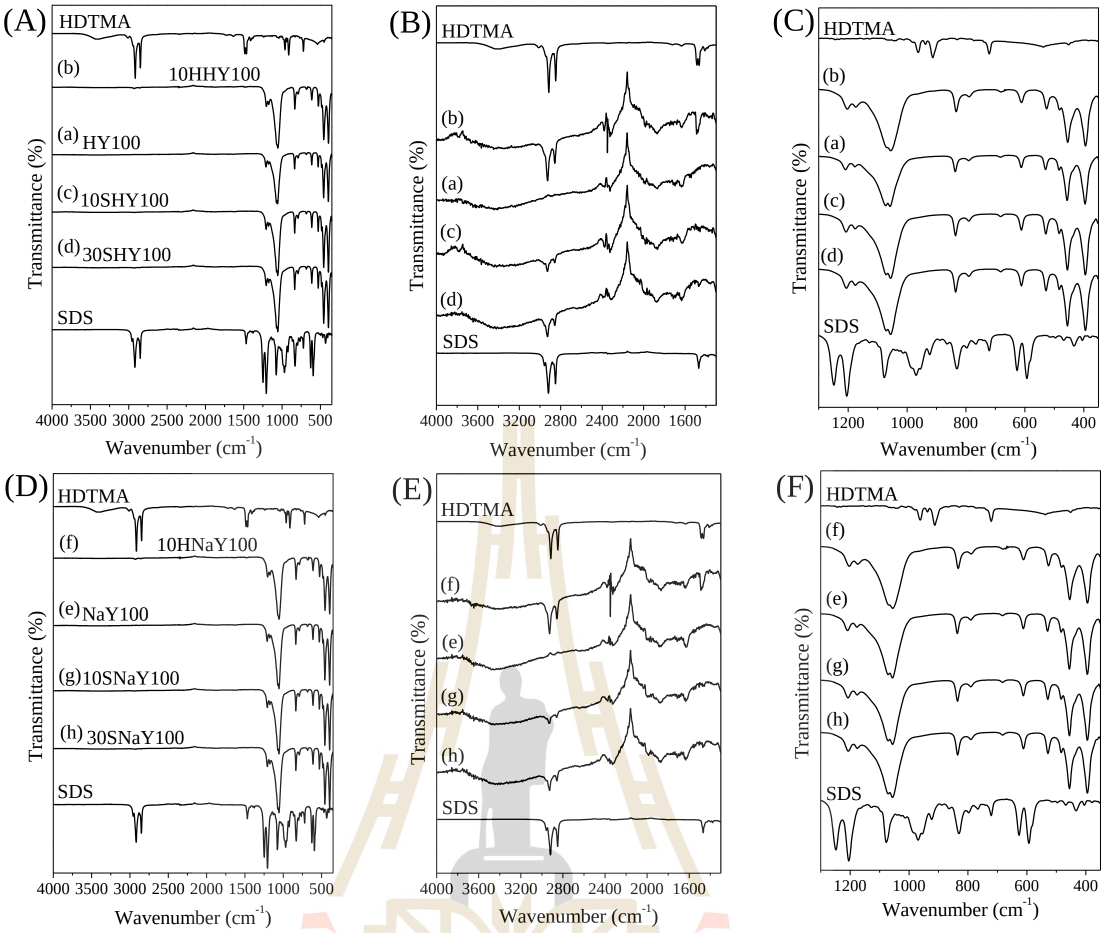

Figure 4.2 ATR-FTIR spectra of unmodified and modified (A–C) HY100 and (D–F) NaY100 in the range of (A and D) 350–4000 cm^{-1}, (B and E) 1300–4000 cm^{-1} and (C and F) 350–1300 cm^{-1}.

4.4.1.2 XRD pattern

Figure 4.3 shows the similar diffraction patterns of the adsorbents before and after the surfactant modifications. The intensity of the peaks decreases when the zeolites were modified with HDTMA and SDS suggesting that the surfactants adsorb mainly on the external surface of the adsorbents without causing any significant change in the zeolite structure.

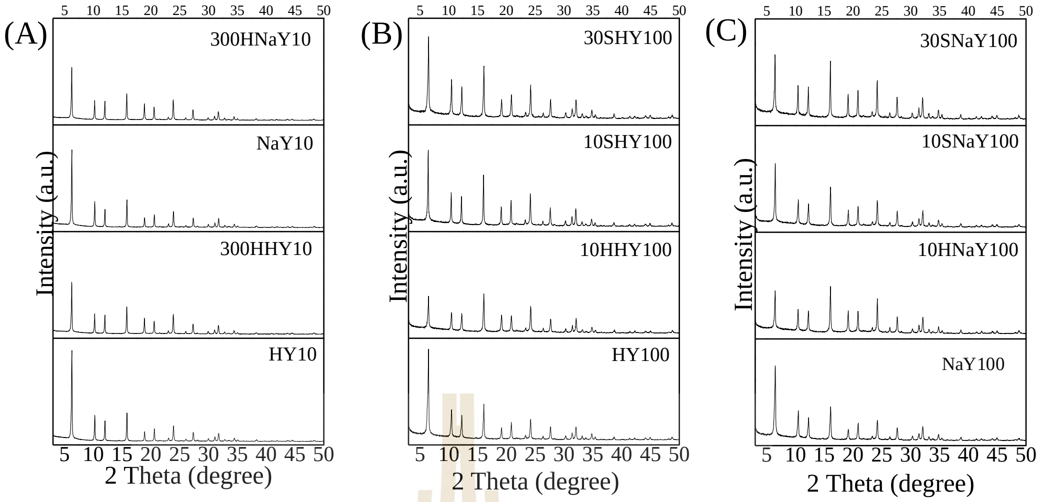

Figure 4.3 XRD patterns of unmodified and modified zeolite (A) HY10 and NaY10 (B) HY100 and (C) NaY100.

4.4.1.3 Particle sizes analysis

The particle size of zeolite after modification seems to be reduced when their surfaces were modified with the surfactants (Table 4.1 and Table 4.2).

Table 4.1 Particle size of zeolite Y10 adsorbents.

adsorbents	particle sizes (nm)	adsorbents	particle sizes (nm)
HY10	9.21	NaY10	7.45
1HHY10	6.61	1HNaY10	6.30
10HHY10	5.32	10HNaY10	4.89
300HHY10	6.39	300HNaY10	6.03
1SHY10	8.24	1SNaY10	5.81
10SHY10	7.78	10SNaY10	5.81

Table 4.2 Particle size of zeolite Y100 adsorbents.

adsorbents	particle sizes (nm)	adsorbents	particle sizes (nm)
HY100	2.72	NaY100	1.75
1HHY100	1.90	1HNaY100	1.60
10HHY100	2.10	10HNaY100	1.45
1SHY100	1.95	1SNaY100	1.92
10SHY100	1.79	10SNaY100	1.47

This result contrasts to our expectation that at high and suitable HTDMA concentration admicelles are formed on the surface of the zeolite resulting in extending the particle size.

4.4.1.4 Determination of chemical composition

To confirm surfactant loading on the zeolite surface, we determined Na, S and Cl percent composition by WD-XRF, and percent N by CHN/S analysis. The results for all adsorbents are shown in Table 4.3 and Table 4.4. Table 4.3 shows the percentages of each element in unmodified zeolite differing from those of the modified zeolites. The percentage of Na^+ in HNaY10 is decreased with an increase in concentration of HDTMA (from 10 to 300 mM) due to cationic head group of HDTMA exchanged with extra-framework cation of zeolite as well as in the HNaY100 (Table 4.4). Na^+ ion was not found in 10HNaY100, indicating that HDTMA was loaded on zeolite by a cation exchange process between quaternary ammonium cation and Na^+ completely. A similar process is expected to occur with HY100. Therefore, HDTMA attaches to the zeolite surface by electrostatic interactions. In addition, a large quantity of Cl and N was detected in both ZY10 and ZY100 compared to unmodified zeolite. These results suggest that HDTMA molecules exist increasingly on zeolite surface when HDTMA loading level is increased. Particularly, the percentages of Cl^- ions illustrate that they act as counter ions for HDTMA, which forms admicelles on the zeolite surface.

In the case of SDS modification, consideration of the Na and S percentages assists to deduce the achievement of SDS modification. The results were found that the percentages of Na and S in SZY100 increased with increasing SDS concentration, but S did not detect in SZY10 suggesting that SDS binding to the zeolite surface is different from that of HDTMA. It is possible that SDS attaches to the zeolite surface via hydrophobic interaction between zeolite and SDS. Thus, SDS can attach on the surface of ZY100 more than ZY10. Additionally, Na^+ ions counterbalancing negatively charged head groups of SDS admicelles and S were increased with an increase in SDS concentration.

Table 4.3 Chemical composition of ZY10 adsorbents (w/w %).

Samples	Na^a	Cl^a	N^b	S^a
HY10	N.D.	0.05	0.12	N.D.
10HHY10	N.D.	0.09	0.55	N.D.
300HHY10	0.06	0.43	0.83	N.D.
10SHY	0.31	N.D.	0.21	0.07
NaY10	0.72	N.D.	0.20	N.D.
10HNaY10	0.61	N.D.	0.72	N.D.
300HNaY10	0.09	0.50	0.83	N.D.
10SNaY10	0.98	0.30	0.18	N.D.

Table 4.4 Chemical composition of ZY100 adsorbents (w/w %).

Samples	Na[a]	Cl[a]	N[b]	S[b]
HY100	N.D.	N.D.	0.14	N.D.
10HHY100	N.D.	2.15	0.60	N.D.
10SHY100	0.19	N.D.	N.D.	0.60
30SHY100	0.28	N.D.	N.D.	0.66
NaY100	0.13	N.D.	0.14	N.D.
10HNaY100	N.D.	1.82	0.61	N.D.
10SNaY100	0.25	0.31	N.D.	0.64
30SNaY100	0.35	0.17	N.D.	0.82

[a] Data from WD-XRF.

[b] Data from CHN/S analyzer.

4.4.1.5 Thermogravimetric analysis

The thermal behavior of the surfactant-modified zeolite and the unmodified zeolite was evaluated using thermogravimetric analysis. The profile of unmodified zeolite is clearly different from modified zeolite in both ZY10 and ZY100 (Figure 4.4 and 4.5). TG and DTG thermograms of HY10 and NaY10 (Figure 4.4A and C) show only a single DTG peak at approximately 75 °C, resulting from the loss of weakly bound water molecules. The thermograms of 300HHY10 and 300HNaY10 (Figure 4.4B and D) show three sharp peaks. The first peak can be attributed to the loss of weakly bound water. The decomposition of HDTMA shows a sharp peak at approximately 320 and at around 590 °C. At the lower temperatures (around 320 °C) represents the initial decomposition phase, due to decomposition of HDTMA bound to neighboring molecules, via a hydrophobic interaction. The final phase occurring at the higher temperature of 590 °C, corresponds to decomposition of HDTMA bound strongly to the zeolite surface by electrostatic interactions (Lin and Zhan, 2012).

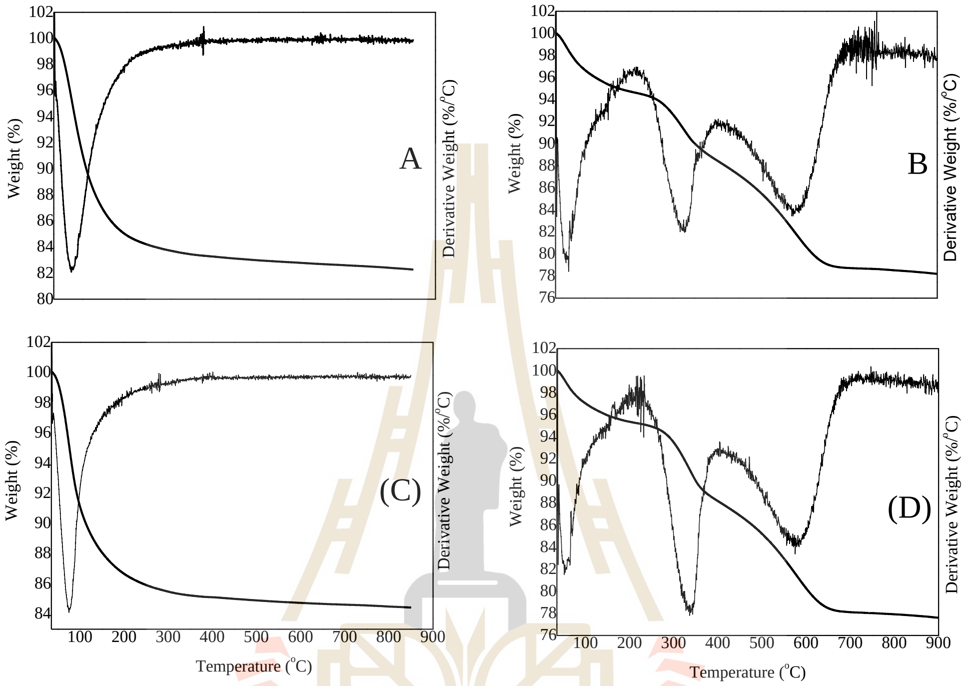

Figure 4.4 Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of (A) HY10, (B) 300HHY10, (C) NaY10 and (D) 300HNaY10.

The TG and DTG thermograms of HY100 and NaY100 (Figure 4.5A and E) are similar to HY10 and NaY10. A single DTG peak occurs around 46 °C, resulting from loss of weakly bound water molecules. The thermograms are different when considering between modification with HDTMA and SDS. Figure 4.5B shown the thermogram of HDTMA-modified HY100 and Figure 4.5C and D are thermograms of SDS-modified HY100. The first peak at approximately 40–50 °C and the second peaks at around 170–200 °C appeared in both HDTMA- and SDS-modified zeolite. The first peak can be attributed to the loss of weakly bound water and the second peak corresponds to the loss of hydrating water strongly bound to the zeolite framework and the ionic head of the surfactants. The decomposition of HDTMA (Figure 4.5B and F) shows three peaks, at approximately 275, 320 °C and a broad peak at around 590 °C. The change at the lower temperatures (275 and 320 °C) represents the initial decomposition phase, due to decomposition of HDTMA bound to neighboring molecules via a hydrophobic interaction. The final phase occurring at the higher temperature of 590 °C, corresponds to decomposition of HDTMA bound strongly to the zeolite surface by electrostatic interactions (Lin and Zhan, 2012). The decomposition of SDS appears clearly two ranges, with the first range centered at around 325 °C, and the second, a broad band centered at approximately 500 °C. The lower-temperature range corresponds to decomposition of SDS bound by a hydrophobic tail to tail interaction. The second range corresponds to decomposition of SDS bound to the zeolite surface via a Brønsted acidic site on the zeolite. Modified NaY100 shows the similar TG and DTG curve to modified HY100 indicating that SDS is formed as admicelles on the zeolite surface in the same as HDTMA arrangement. Table 4.5 and Table 4.6 summarize the percent mass of water and surfactant for all samples over various temperature ranges. It was found that HDTMA loadings are similar for both H-form and Na-form of zeolite Y. Likewise, SDS loading is similar for both H- and Na-forms of the zeolites. However, the result of ZY10 modified with 300 m MHDTMA (300HHY100) is different from ZY100 modified with 10 mM HDTMA (10HHY10). It was found that percentage of the surfactant bound in the outer surface of 10HHY10 is higher than that bound on the outer surface of 300HHY100, indicating that the surfactant with concentration of 300 mM does not yet form complete bilayer of 300HHY10.

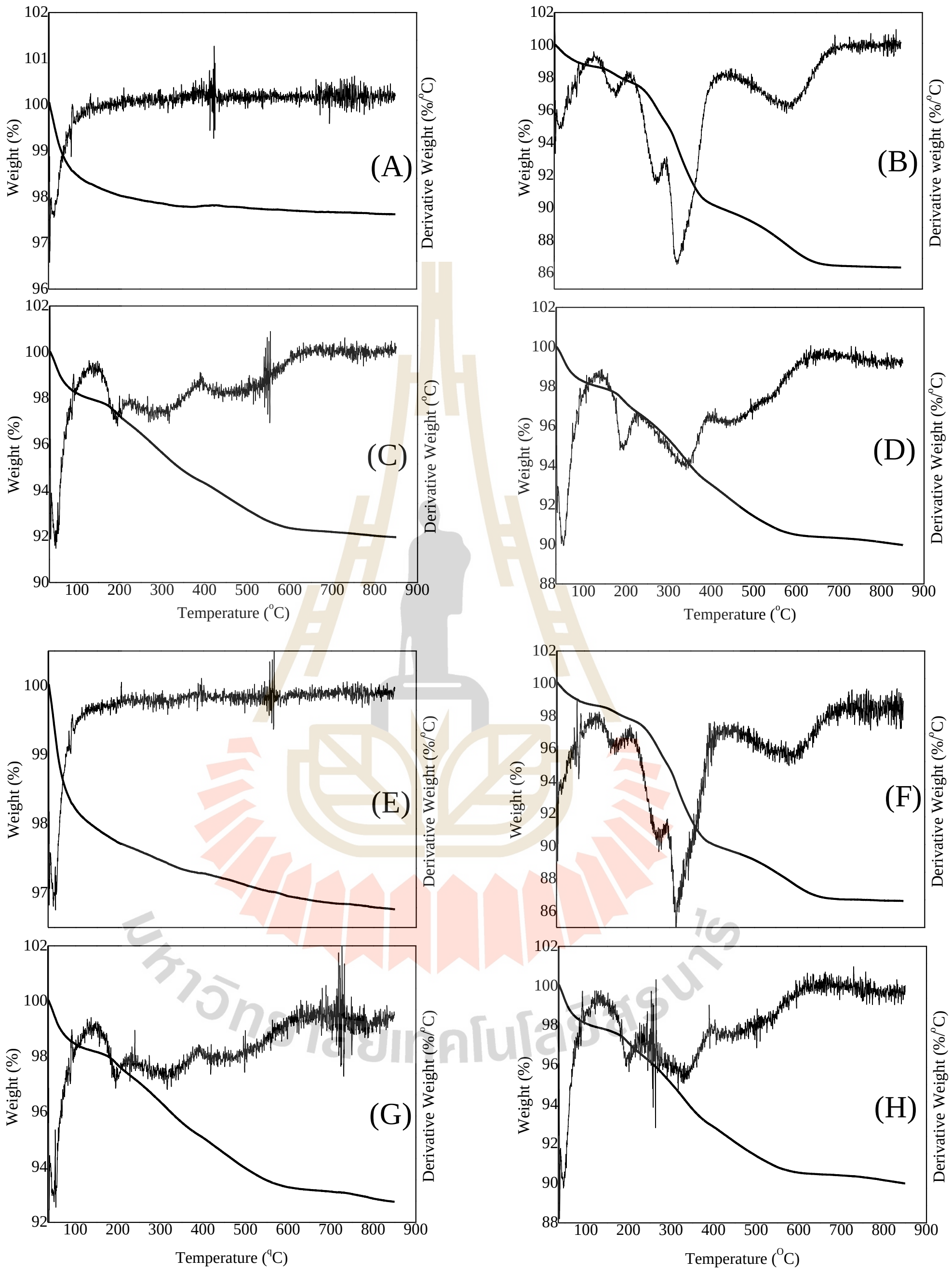

Figure 4.5 Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of (A) HY100, (B) 10HHY100, (C) 10SHY100 (D) 30SHY100, (E) NaY100, (F)10HNaY100, (G) 10SNaY100 and (H) 30SNaY100.

Table 4.5 The percent composition of water and surfactants of zeolite Y10.

Adsorbents	Weakly-bound water (%)	Strongly-bound water (%)	Surfactant-bound to neighboring molecules (%)	Surfactant-bound to zeolite surface (%)
	35–150 °C	150–400 °C	150–400 °C	400–700 °C
HY10	13.31	3.43	-	-
300HHY10	4.55	-	6.95	9.77
NaY10	11.92	2.96	-	-
300HNaY10	4.05	-	7.77	10.07

Table 4.6 The percent composition of water and surfactants of zeolite Y100.

Adsorbents	Weakly-bound water (%)	Strongly-bound water (%)	Surfactant-bound to neighboring molecules (%)	Surfactant-bound to zeolite surface (%)
	35–100 °C	100–200 °C	200–400 °C	400–700 °C
HY100	1.52	0.45	-	-
10HHY100	1.15	0.98	7.60	3.84
10SHY100	1.80	0.99	2.91	2.11
30SHY100	1.76	1.11	4.12	2.69
NaY100	1.80	0.48	-	-
10HNaY100	1.19	0.93	7.75	3.39
10SNaY100	1.55	0.77	2.62	1.94
30SNaY100	1.91	1.01	4.24	2.44

4.4.1.6 Chemisorption or Temperature-program desorption (TPD)

The strength and density of surface acid sites were studied by NH_3-TPD. NH_3 is a polar molecule with permanent electric dipole moment of $\mu = 1.30$ D (Dima and Rees, 1990). There are some interactions between NH_3 molecules and Na^+ cations when these cations are present in zeolite. NH_3 can adsorbed on other cations with different ion-exchange levels. Nevertheless, this interaction is not so strong as the interaction between NH_3 molecules and protonic sites. Thus, the corresponding peak appears for lower temperature and the peak associated with this interaction is bigger when the Na^+ level is higher (Costa, Lopes, Lemos, and Ribeiro, 1999). The profile in Figure 4.6 is corresponding to the information of Costa et al. (1999). NaY10 has high level of Na^+ more than NaY100, thus the acid site density of NaY100 is lower than NaY10 (Table 4.7). Nevertheless, zeolite in H-form shows the peak of acidic site shifted to higher temperature.

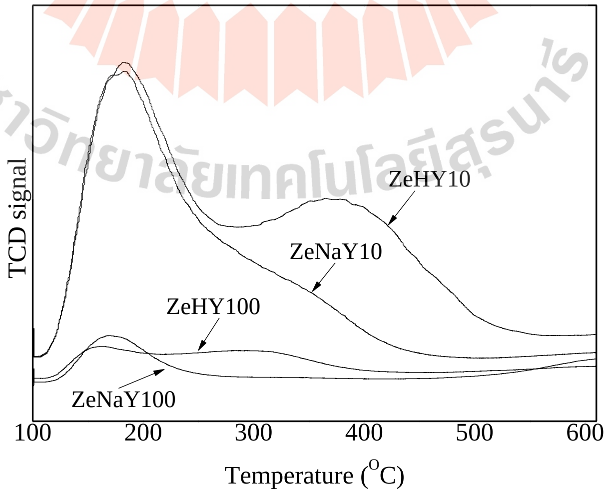

Figure 4.6 TPD profile of NH_3 of adsorbents.

Table 4.7 Densities of acid site.

Adsorbents	Quantities of acid site (mmol/g)	
	Peak 1	Peak 2
HY10	0.809	0.810
NaY10	0.730	0.328
HY100	0.060	0.116
NaY100	0.096	0.023

4.4.1.7 Surface characteristics of unmodified and modified zeolite

Table 4.8 and Table 4.9 summarize the surface characteristics of adsorbents, including the BET surface area, external surface area, micropore surface area, total pore volume and the average pore diameter of ZY10 and ZY100. From the results, it is apparent that the BET surface areas for surfactant-modified zeolites in both H- and Na-form, are smaller than those of the unmodified zeolites. After modification, the average pore size of the zeolites increases while the pore volume decreases. Partially covering or blocking of smaller pores results in an increase in apparent average pore size that causes the total pore volume decreased. This result is consistent with a report by Patdhanagul and Chao (2010). In the case of ZY10 (Table 4.8), a decreasing of surface area of HHY10 is not significantly different from HNaY10. The surface area of ZY10 drastically decreases with an increase in the concentration of HDTMA up to 10 mM, whereas the surface area of SZY10 decreases insignificantly with an increase in the concentration of SDS. This result suggests that SDS attaches inconveniently on the surface of ZY10 compared to HDTMA. In the case of ZY100 (Table 4.9), the surface area of ZY100 has a tendency to decrease with increasing the concentration of surfactants. The ratio of the surface area of 10HHY100 and 10HNaY100 is more significantly decreased than that of the other adsorbents suggesting that HDTMA tends to arrange itself on external surfaces and at pore openings.

Table 4.8 Surface characteristics and ZY10 porosity were determined by BET and *t*-plot analysis.

Adsorbents	S_{BET} (m^2 g^{-1})	S_{micro} (m^2 g^{-1})	S_{ext} (m^2 g^{-1})	S_{micro}:S_{ext}	V_t (cm^3 g^{-1})	D_a (nm)
HY10	752	668	84	8.0:1	0.42	2.23
1HHY10	709	635	74	8.6:1	0.42	2.39
10HHY10	62	19	43	0.4:1	0.14	8.75
300HHY10	52	17	35	0.5:1	0.15	11.53
1SHY10	750	686	64	10.7:1	0.44	2.32
10SHY10	743	678	65	10.4:1	0.45	2.43
NaY10	847	760	87	8.7:1	0.48	2.26
1HNaY10	719	641	78	8.2:1	0.43	2.41
10HNaY10	86	29	66	0.4:1	0.16	7.19
300HNaY10	41	5	36	0.1:1	0.13	13.19
1SNaY10	880	782	98	8.0:1	0.51	2.34
10SNaY10	761	695	66	10.5:1	0.46	2.41

Table 4.9 Surface characteristics and ZY100 porosity were determined by BET and *t*-plot analysis.

Adsorbents	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)	S_{ext} ($m^2\ g^{-1}$)	S_{micro}:S_{ext}	V_t ($cm^3\ g^{-1}$)	D_a (nm)
HY100	744	596	148	4.0:1	0.55	2.97
0.5HHY100	741	577	164	3.5:1	0.56	3.01
5HHY100	575	456	119	3.8:1	0.43	2.99
10HHY100	299	173	126	1.4:1	0.33	4.47
30HHY100	281	159	122	1.3:1	0.33	4.66
0.5SHY100	727	585	142	6.0:1	0.53	2.89
10SHY100	548	402	146	2.8:1	0.45	3.31
30SHY100	492	326	122	2.7:1	0.42	3.45
NaY100	797	631	166	3.8:1	0.61	3.04
0.5HNaY100	707	543	164	3.3:1	0.54	0.05
5HNaY100	554	416	138	3.0:1	0.43	3.12
10HNaY100	318	184	134	1.4:1	0.35	4.37
30HNaY100	286	155	131	1.2:1	0.34	4.80
0.5SNaY100	735	590	145	4.1:1	0.51	2.75
10SNaY100	587	432	155	2.8:1	0.49	3.37
30SNaY100	466	346	120	2.9:1	0.42	3.57

Comparing the BET data between SZY10 and SZY100, the result shows that SDS is proper to modify the surface of ZY100 better than that of ZY10, while the surface of HZY10 contains the higher quantity of HDTMA molecule than that of HZY100.

4.4.1.8 Effect of surfactant loading level for adsorption of non-ionic pesticides

Atrazine, cyanazin, linuron and carbofuran are the pesticides that occur in neutral form at ambient condition. The natural of these pesticides trends to adsorb on hydrophobic surface more than hydrophilic surface of adsorbent. The adsorption data in Figure 4.7–4.10 show that the pesticides were removed by HZY100 better than HZY10. Using a low concentration of HDTMA can help to improve negligible adsorption capacity of ZY10 for adsorb atrazine, linuron and carbofuran, but it had no effect for ZY100. However, the used of HDTMA at high concentration over 5 mM resulting to decrease the adsorption capacity of all adsorbent for adsorb pesticides. The adsorption results of SDS-modified zeolite (SZY10 and SZY100) shown in Figure 4.7–4.10 indicated that that the concentration of SDS has no effect on the removal of the pesticides.

When compared the molecular weight of linuron and carbofuran effect on the adsorption of ZY10 (Figure 4.9 and 4.10). it was found that linuron was adsorbed on ZY10 more than carbofuran. It suggests that a smaller structure of linuron is easier to enter the pore of zeolite than carbofuran.

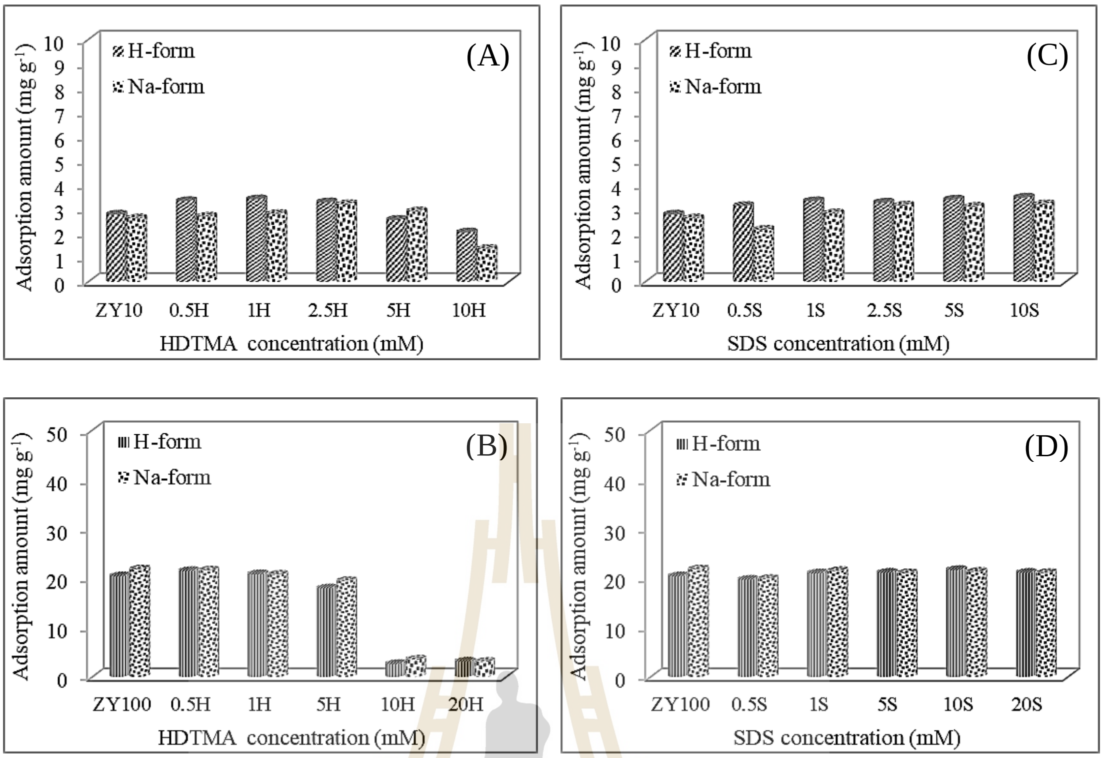

Figure 4.7 Effect of surfactant concentration loading on adsorption capacity of atrazine on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and (D) SZY100 at initial concentration 10 and 25 ppm for ZY10 and ZY100, respectively.

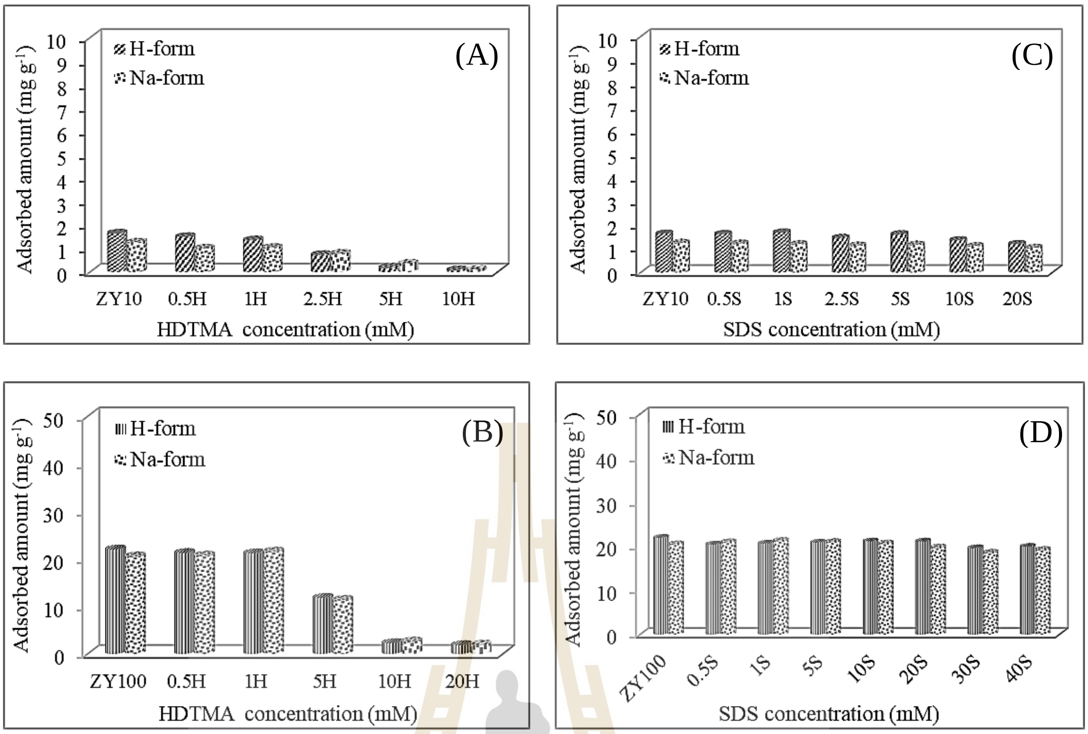

Figure 4.8 Effect of surfactant concentration loading on adsorption capacity of cyanazin on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 10 and 25 ppm for ZY10 and ZY100, respectively.

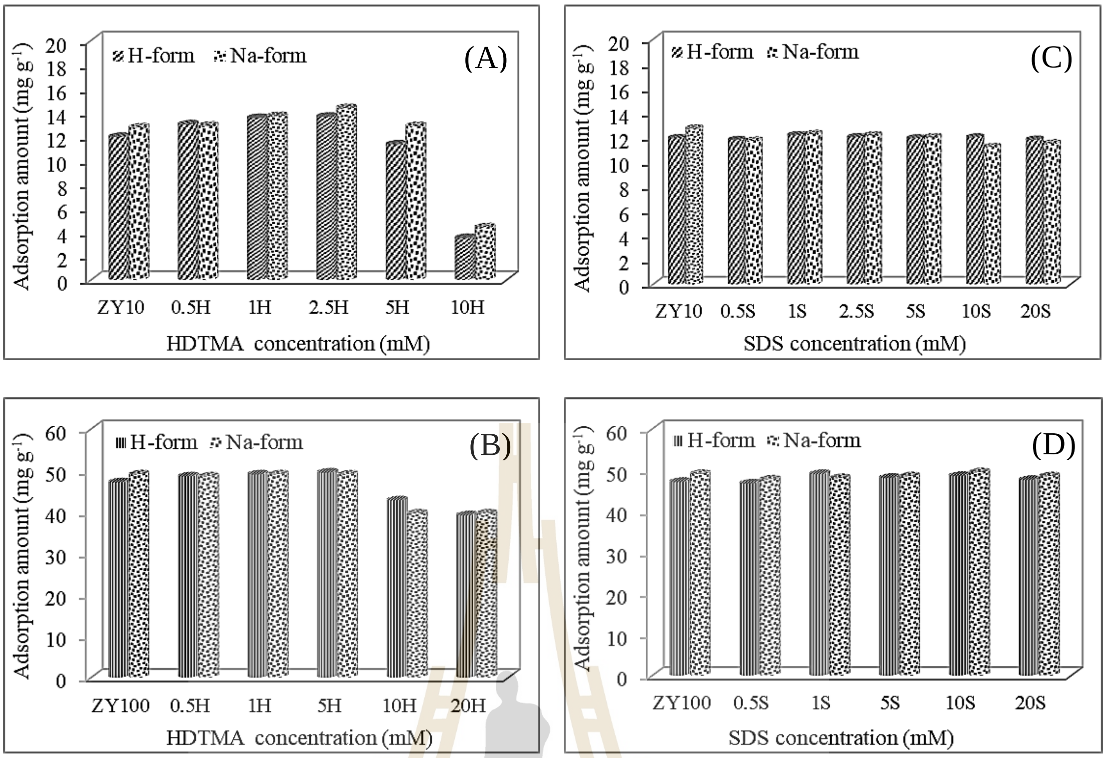

Figure 4.9 Effect of surfactant concentration loading on adsorption capacity of linuron on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 25 and 50 ppm for ZY10 and ZY100, respectively.

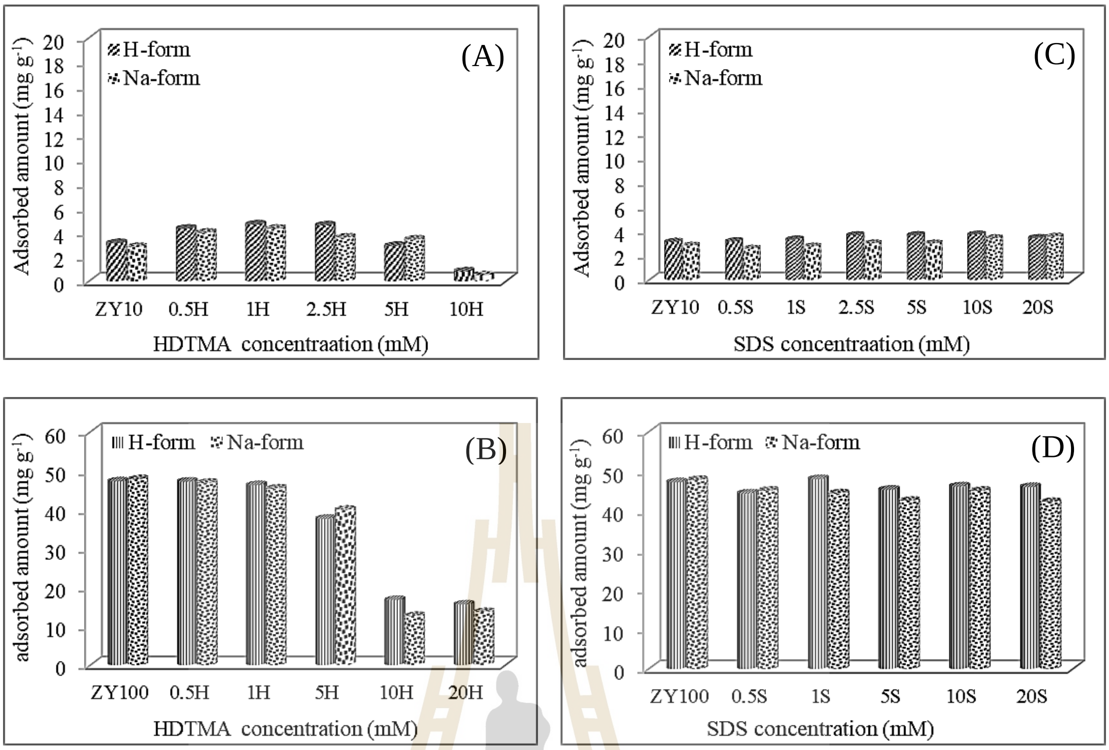

Figure 4.10 Effect of surfactant concentration loading on adsorption capacity of carbofuran on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 25 and 50 ppm for ZY10 and ZY100, respectively.

4.4.1.9 Effect of surfactant loading level for adsorption of ionic pesticides

Paraquat and 2,4-D are classified as ionic pesticides which are cationic and anionic pesticides at study condition, respectively. In addition, the adsorption capacity of the other pesticides such as difenzoquat (DQ^+) and bentazon by the zeolites and the modified zeolites was investigated as well. The figure 4.11−4.14 show that the quantities of the pesticides adsorbed on the surfactant-modified zeolites at various surfactant concentrations. The figures show that the extent of the adsorption ability is dependent on the surfactant loading level and the method used to modify the adsorbents. The adsorption capacities of the modified zeolite for removal of 2,4-D and bentazon (Figure 4.11 and 4.12) show the different value in contrast with PQ^{2+} and DQ^{+} (Figure 4.13 and 4.14).

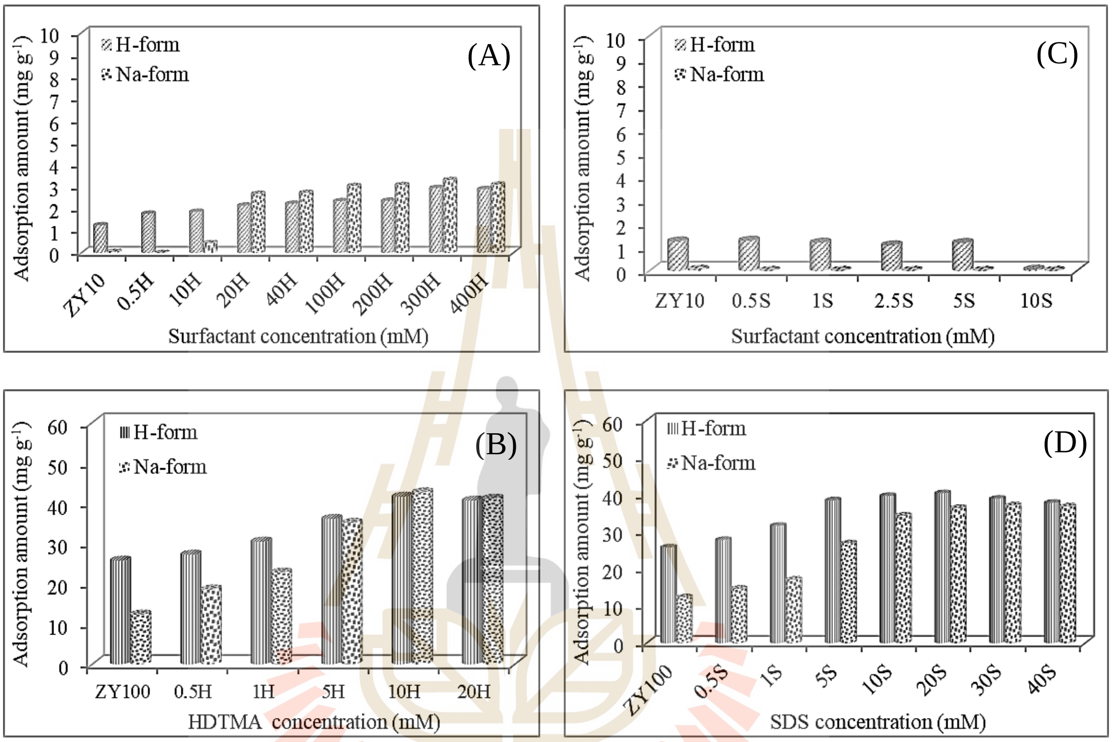

Figure 4.11 Effect of surfactant concentration loading on adsorption capacity of 2,4-D on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 10 and 50 ppm for ZY10 and ZY100, respectively.

The removal of the acidic pesticides (2,4-D and bentazon) by HZY10 and HZY100 is better than that by ZY10 and ZY100 (Figure 4.13 and 4.14). The effect of HDTMA loading level on 2,4-D removal by HZY10 and HZY100 shown in Figure 4.13A and B reveals that an increase in concentration of HDTMA can improve the adsorption capacity due to the positive head group of HDTMA bilayer able to interact with the negative charge of 2,4-D. In addition, it was found that, the adsorption capacity of HDTMA-modified zeolite in H-form is higher than that in Na-form at the low concentration of HDTMA, but the adsorption capacity of Na-form trends to increase or equal to or over H-form when the concentration of HDTMA is increased. This result reveals that the HDTMA-modified zeolite can adsorb 2,4-D better than unmodified zeolite and HDTMA modification of zeolite in Na-form assists to improve the adsorption capacity better than H-form. However, the result of bentazon adsorption differs from the case of 2,4-D adsorption. It was found that the surface of both ZY10 and ZY100 with high HDTMA in admicelle form brings a decrease in the adsorption capacity.

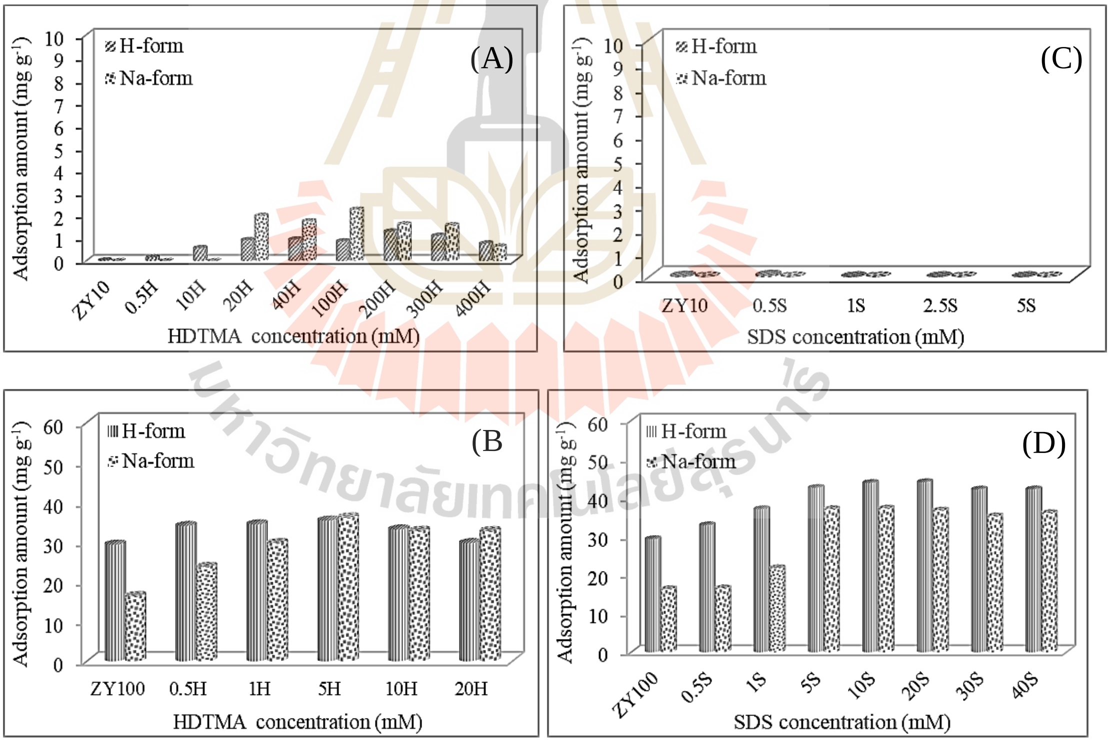

Figure 4.12 Effect of surfactant concentration loading on adsorption capacity of bentazon on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 10 and 50 ppm for ZY10 and ZY100, respectively.

In the part of SDS modification (Figure 4.11D and 4.12D), the result was found that the surface of SZY100 can adsorb 2,4-D and bentazon in a larger amount than that of ZY100. The formation of SDS in admicelles increases a proper site to adsorb these pesticides.

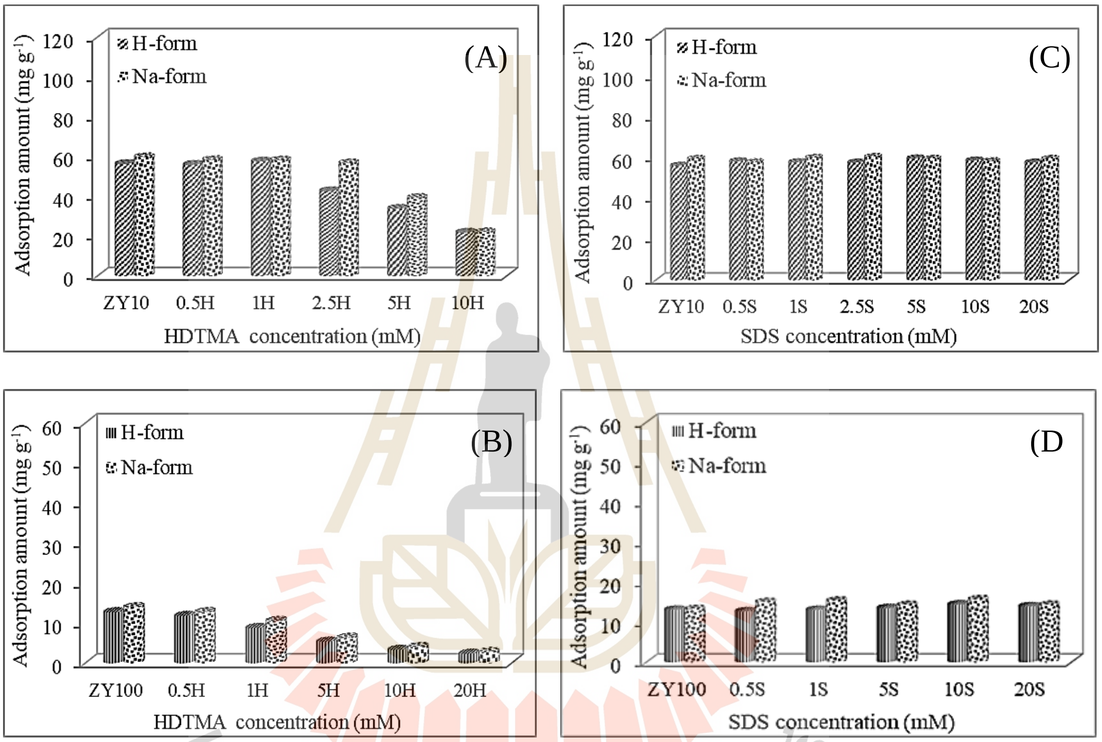

Figure 4.13 Effect of surfactant concentration loading on adsorption capacity of PQ^{2+} on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 75 and 50 ppm for ZY10 and ZY100, respectively.

In the case of PQ^{2+} adsorption result (Figure 3.13), it was found that HDTMA modification with high concentration until it forming a bilayer affects the reduction of the adsorption capacity of both HZY10 and HZY100, because the positive head group of HDTMA bilayer repels the positive charge of PQ^{2+}. An increase in SDS concentration loading does not enhance the PQ^{2+} adsorption, because of SDS negligible to attach on ZY10 surface. In the case of ZY100, the result can deduce that an arrangement of SDS in admicelle form keeps a space for PQ^{2+} to penetrate to interact with SZY100.

The DQ^{+} adsorption results shown in Figure 4.14 reveals that the modification of zeolite with HDTMA results to a decrease in the adsorption capacity when the HDTMA concentration was increased. Whereas, SDS modification does not affect the improvement of the adsorption ability for removal of DQ^{+} in both ZY10 and ZY100.

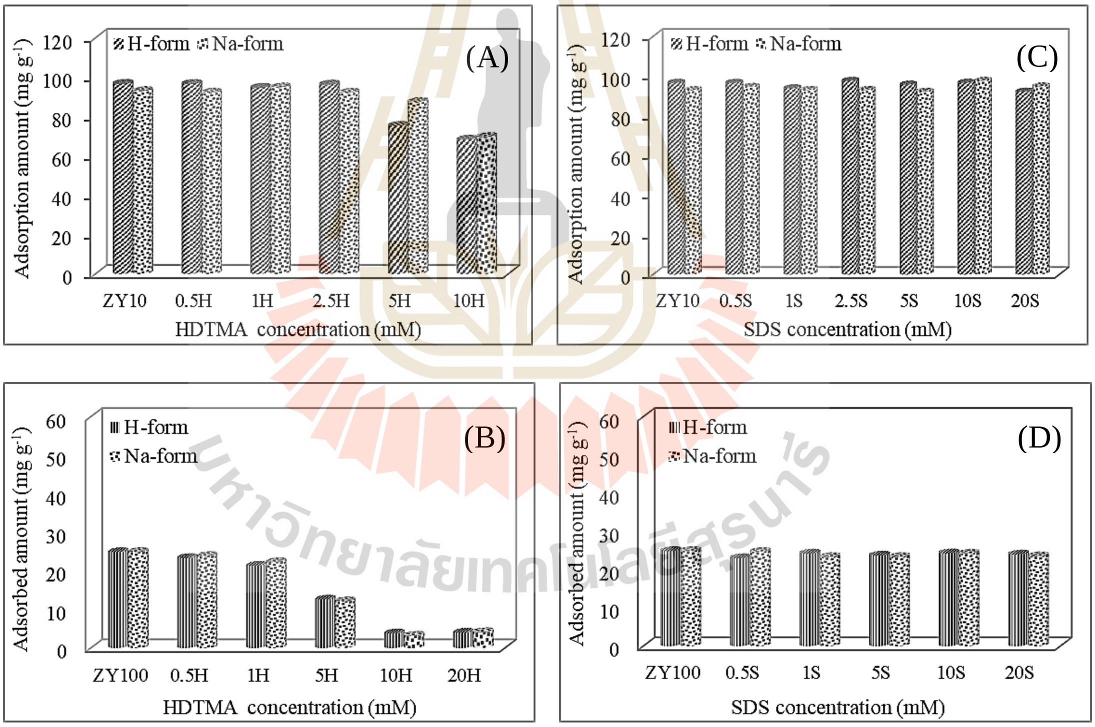

Figure 4.14 Effect of surfactant concentration loading on adsorption capacity of DQ^{+} on various adsorbent as (A) HZY10, (B) HZY100, (C) SZY10 and SZY100 at initial concentration 75 and 50 ppm for ZY10 and ZY100, respectively.

When considered the result between paraquat and difenzoquat, the adsorption value of difenzoquat is higher than that of paraquat. This could be explained that difenzoquat is monovalent cation while paraquat is divalent cation. Difenzoquat ion per active site of modified zeolite is 1:1, while paraquat ion per active site is 1:2. Accordingly, an amount of adsorbed DQ^+ per a certain amount of active site is larger than that of adsorbed PQ^{2+}.

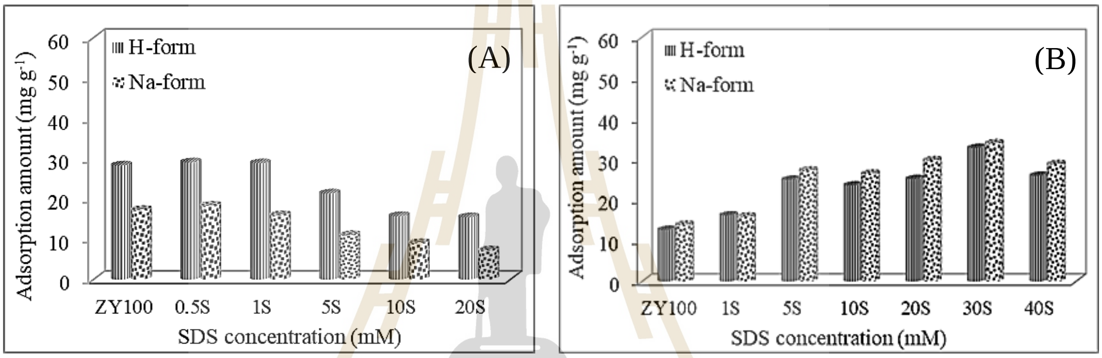

Figure 4.15 Effect of surfactant concentration loading on adsorption capacity of (A) 2,4-D and (B) PQ^{2+} on SDS-modified ZY100 at initial concentration 50 ppm. Adsorbents were dried in desiccators 3−5 days before use.

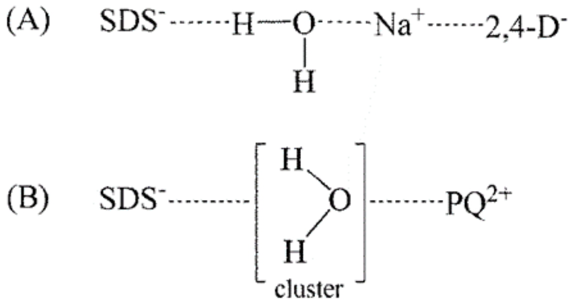

Figure 4.16 A proposed adsorption model of pesticides on SZY when prepared by (A) drying in oven at 110 °C and (B) drying in desiccators.

Drying procedure during preparation of SDS-modified zeolite affects adsorption capacity. SZY100 exhibits greater adsorption capacity toward 2,4-D when the adsorbents are dried in an oven at 110 °C for 3 h, compared with drying in a desiccator for 3–5 days (Figure 4.15). However, SZY100 adsorption capacity toward PQ^{2+} is greater after drying in a desiccator compared to an oven drying at 110 °C. Water molecules adsorbed on the zeolite play an important role in adsorption capacity; when the adsorbents are dried at 110 °C, weakly bound water molecules are removed, leaving behind highly-polarized water molecules that are bound to negatively charged groups on SDS. Highly polarized water molecules provide suitable binding sites for Na^+, facilitating coordination between sodium and the 2,4-D anion. However, drying in a desiccator tends to retain a cluster of water molecules around the negative SDS head group, weakening interactions between SDS and Na^+ ions, and consequently, Na^+ dissociates more easily from active sites. Hence, after desiccator drying, PQ^{2+} can adsorb to the modified zeolite via ion exchange with Na^+, while oven drying favors coordination with 2,4-D anions via interaction with coordinated Na^+.

Consequently, the HHY100/HNaY100 modified zeolites exhibit the greatest adsorption efficiency toward 2,4-D. HY100 modified with 10 mM HDTMA (10HHY100) exhibited the greatest performance toward 2,4-D and was selected for further 2,4-D adsorption studies.

4.5 Conclusions

Modification of zeolites HY and NaY (Si/Al mole ratio of 10 and100) with an appropriate amount of HDTMA or SDS resulting in changing the surface properties of zeolite. HDTMA can change the negative surface to positive surface by using high concentration of HDTMA as arrangement in admicelle form. At high concentration of SDS the negative charge presents on the ZY100 surface due to negative head group of SDS exposed to the solution. However, modification of HDTMA can improve the adsorption capacity of ZY10, but not for ZY100. Moreover, in the case of SDS-modified zeolite, water content affects the pesticide adsorption capacity. At low water content, the adsorbent is more effective in the adsorption of 2,4-D, while high water content favors PQ^{2+} adsorption.

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CHAPTER V

EFFICIENCY OF UNMODIFIED AND MODIFIED ZEOLITE FOR REMOVAL OF 2,4-D AND PARAQUAT FROM AQUEOUS SOLUTION

5.1 Abstract

The work in this section purposes to study the efficiency of selected adsorbents for removal 2,4-D and paraquat. The result was found that the greatest adsorption values for 2,4-D and PQ^{2+} occurred at pH 3 and pH 11, respectively. 10HZY promotes a high activity to remove 2,4-D more than ZY at pH over 3.0, while 30SZY shows a better capacity more than ZY at pH less than 9.0. The equilibrium adsorption data can be fitted well with the Langmuir isotherm model and the adsorption kinetics follows a pseudo-second order model.

5.2 Introduction

An application of zeolite could be expanded by functionalization of the zeolite surface. Surface properties, such as surface charge and hydrophobicity, this achievement can be controlled by organic functionalization of the internal and external surface. The negative surface charge of zeolite Y is proper to modified with HDTMA cationic surfactant, and also can interact with anion of SDS at the same time. The hydrophobic part of zeolite surface can attach with the hydrophobic tail of surfactants. The surface charge and hydrophobicity depend on the concentration of surfactant loading level. At a concentration lower than CMC, an arrangement of surfactants is in a form of hemimicelle, and they can form to admicelle when the concentration of surfactant is higher than the CMC value. The result from the chapter IV indicates that ZY10 is achieved to modify with HDTMA only while ZY100 can be modified by both HDTMA and SDS. This section purposed to study a parameter of pH and contact time, kinetics and adsorption isotherm to evaluate the capacity of the selected adsorbent.

5.3 Experiment

5.3.1 Materials

Zeolite 350HUA and 385HUA as a high-silica zeolite as HSZ-300 series was obtained from Tosoh corporation. Reagent grade paraquat dichloride hydrate (98% purity), 2,4-D (99.9% purity), SDS, and HDTMA were obtained from Sigma. A stock of PQ^{2+} solution was prepared by calculating the mass of PQ^{2+} from paraquat dichloride.

5.3.2 Batch adsorption study

5.3.2.1 Effect of surfactant loading

The adsorption efficiency of pesticides depends on the formation of surfactant on the surface of adsorbents. Thus, the first parameter related to the extraction evaluation in this study is the effect of the concentration of surfactant added to the medium. The experiment was performed by keeping the desired concentration of pesticides constant (depending on the type of pesticide) and varying the concentration of each surfactant. The modified-zeolites are treated with various concentrations of the surfactant of 0.5, 1, 5, 10 and 20 mM. For this purpose, 10 mg of adsorbent samples were added into 125 mL conical flasks with 10 mL of pesticides aqueous solution. The experiments were carried out at ambient temperature for 24 h on a shaker equipped at 130 rpm. After that the suspensions were centrifuged at 3000 rpm, for 10 min and filtered (using nylon syringe filter) before using in the next step. The residual paraquat, and 2,4-D concentration were finally determined using a UV-Vis spectrophotometer at the wavelength of the maximum adsorption of 257 and 283, respectively. The pesticides adsorption capacity and the removal efficiency for each adsorbent at present time were calculated with equation (1) and (2), respectively.

$$\frac{q}{t} = \frac{(C_o - C_t)V}{m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where C_o and C_t are the concentrations of adsorbates in aqueous solution at initial time and at time t, respectively (mg L^{-1}); V is the volume of adsorbate solution (L); m is the mass of adsorbent (g); qt is the amounts of pesticide adsorbed at time t (mg g^{-1}).

5.3.2.2 Optimum contact time and adsorption kinetics study

Batch adsorption experiments were performed for removal of pesticides at ambient temperature, and without adjusting pesticide solution pH values. Adsorbents were treated with pesticide solutions in a ratio of 1 g adsorbent/1 L pesticide solution. The mixtures were continuously shaken, while aliquots of supernatant were withdrawn for analysis at various time intervals, until the determined adsorption rate was constant.

5.3.2.3 Effect of the pH

The effect of pH on the adsorption of each pesticide on unmodified and modified zeolites Y was investigated over the pH range of 2.0 to 12.0 (depending on the type of pesticide). Pesticide solutions were prepared by dissolving a suitable amount of pesticides in distilled water. The pH of the solution was adjusted by adding with 0.1 or 0.01 mol L^{-1} of HCl or NaOH solutions before performing the adsorption experiment. The adsorbent was contacted with pesticide solution at solid/liquid ratio as 10 mg/10 mL. The mixture was placed on a water shaker bath at 30 °C until it reached to equilibrium, and then it was filtered. The filtrates were analyzed for residual pesticide concentration. Duplicate test was performed in all cases.

5.3.3.4. Adsorption isotherm

Adsorption experiments were performed by a batch equilibration procedure using a 125 mL conical flask with a mixture comprising an adsorbent/pesticide solution ratio of 10 mg/10 mL. Experiments were conducted at optimum pH values for each pesticide, and at pH 6.0. The initial concentration ranges for 2,4-D and PQ^{2+} were 50–250 ppm at optimum pH, and 20–150 ppm at pH 6.0. The adsorbent–pesticide mixture was placed on a water shaker bath at 30 °C until it reached equilibrium, and then centrifuged and filtered. Filtrates were analyzed for traces of residual pesticide. All experiments were performed in duplicate.

5.3.2.5 Study the multifunctional possibility of modified zeolite Y for simultaneous adsorption of various pesticides.

Modified zeolites Y was added to the quaternary mixture solution (using appropriate concentration ratio of 2,4-D: atrazine: diuron: paraquat). The suspensions were shaken at ambient temperature, for 24 h at 130 rpm, and then filtered using a 0.45 μm membrane. The concentrations of each pesticide were determined by HPLC. All the experiments were performed in duplicate and average value was presented.

5.4 Results and Discussions

5.4.1 Effect of initial pH

The capacity of zeolite adsorbent varies with initial pH of aqueous solution. Changes in pH of solution affect the speciation of the adsorbent species, the adsorbent surface charge, and the degree of pesticide ionization (Bakhtiary, Shirvani, and Shariatmadari, 2013; Nejati, Davary, and Saati, 2013). To optimize pH for the pesticide adsorption, the absorption experiments were performed by adding the adsorbents into the pesticide solutions and adjusting pH using 1.0 and 0.1 M HCl or NaOH (Figure 5.1). Figure 5.1 reveals that the adsorption capacity toward 2,4-D is similar for both H- and Na-form adsorbents, but that there are significant differences in adsorption capacity between modified and unmodified zeolite. When pH ≤ pK_a (2,4-D), this pesticide exists mainly in neutral form, with some in anionic species present. Neutral 2,4-D molecules adsorb to ZY and SZY100 in preference to HZY100 adsorption. For pH values greater than pK_a, 2,4-D exists predominantly in anionic form in solution. The anions preferentially adsorb to the positively charged surface of HZY100. Therefore, at high pH, HZY100 exhibits greater adsorption capacity than the others. However, HZY100 adsorption performance decreases with increasing pH because of competition between OH^- and 2,4-D anions. ZY100 and SZY100 adsorption efficiency decreases significantly, approaching zero at pH 6.0, as negatively charged adsorbent surfaces repel 2,4-D anions. All adsorbents exhibit increasing adsorption capacity with increasing pH for PQ^{2+}, with the greatest capacity occurring at pH 11.0 (Figure 5.1).

At pH values less than 9.0, SZY100 adsorption capacity is greater than that of ZY100, which is a result of stronger interactions between PQ^{2+} and negative head groups on SDS. At pH values greater than 6.0, ZY100 adsorption efficiency significantly exceeds that of SZY100, probably due to greater increases in the surface negative-charge on ZY100 compared to SZY100.

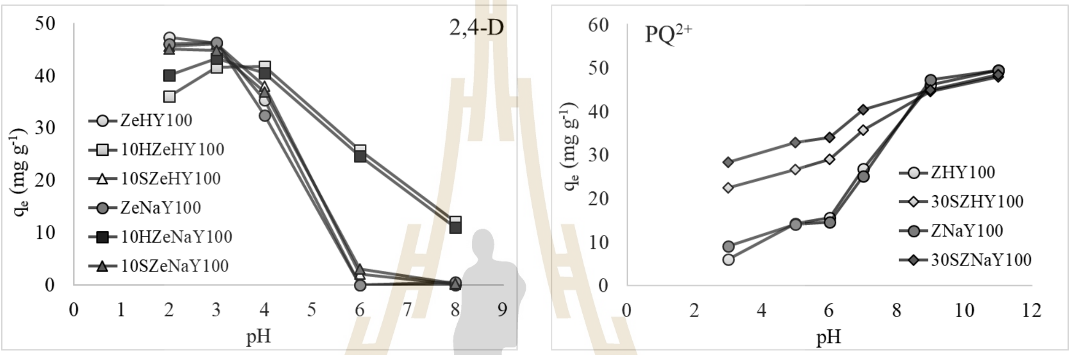

Figure 5.1 Effect of initial pH of solution on adsorption capacity of 2,4-D and PQ^{2+}. The initial concentration of pesticides is 50 ppm.

5.4.2 The study of adsorption kinetics

To find the optimum adsorption contact times, the experiments of pesticides adsorptions onto unmodified and modified zeolites were performed at room temperature (28.0±2.0 °C) with a fixed initial pesticide concentration of 50 ppm. The adsorptions of 2,4-D and PQ^{2+} on all adsorbents as a function of time are shown in Figure 5.2. The results reveal that the pesticide adsorption increases rapidly with contact time at the initial period, then it is gradually slow down until reaching an equilibrium. This can be explained that at the initial stage the adsorbent contains a large amount of available active sites for pesticide molecules and at the later stages the numbers of vacant surface sites and concentration of pesticides decrease resulting in a decrease in the adsorption rate. Figure 5.2 show the time consumed during the adsorption of the pesticides with each adsorbent until reaching to the equilibrium. The data indicate that the adsorption capacity of all adsorbents rapidly increased in the initial time and remained nearly constant after 5h for 2,4-D and 6h for PQ^{2+}. However, to ensure that the adsorptions of all adsorbents reached the equilibrium, the experiment was carried out for 6 and 8 h for 2,4-D and PQ^{2+}, respectively.

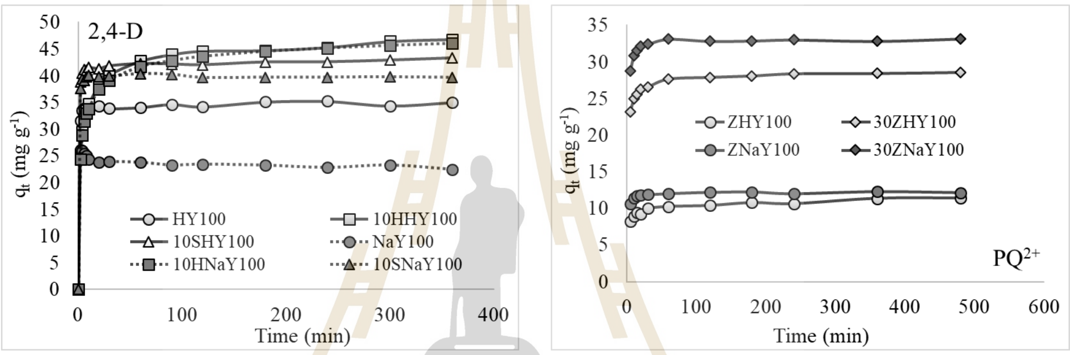

Figure 5.2 Adsorption kinetics of ZY100 and MZY100 on 2,4-D and PQ^{2+} removal at an initial concentration 50 ppm (non-adjusted pH; adsorbent dosage, 1 g/1 L, room temperature).

Adsorption kinetics results for each adsorbent are given in Figure 5.2. A plot of adsorbed pesticide versus time shows that HDTMA coverage on the surface of zeolite affects an increase in equilibration time. To elucidate the process for adsorption of pesticides, we selected pseudo-first and second order models that fit the kinetic data. The linear form of the pseudo-first order model is given as follows equation 3 (Yuh-Shan, 2004);

$$log\ (q_e - q_t) = log\ q_e - \frac{k_1}{2.303} t \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where q_e and q_t are pesticide adsorption capacities of the adsorbent at equilibrium (mg g^{-1}) and at any given time t (min), respectively; and k_1 is the rate constant for the pseudo-first order kinetics model (min^{-1}). The linear form of the pseudo-second order model is given as follows equation 4 (Ho and McKay, 1999);

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{k_2 q_e^2} \qquad \text{……………………(4)}$$

where q_e and q_t are the pesticide adsorption capacities of an adsorbent at equilibrium (mg g^{-1}) and at time t (min), respectively; and k_2 is the rate constant of the pseudo-second order kinetic model (g mg^{-1} min^{-1}). Calculated q_e values are in good agreement with the pseudo-second order model (see Figure 5.3), with an R^2 value close to, or equal to 1. Tables 5.1 and 5.2 summarize calculated parameters. The values of q_e, calculated by linear regression analysis are in good agreement with experimental values for both 2,4-D and PQ^{2+} adsorption. The best fit of the pseudo-second order kinetic model suggests that the adsorption of pesticides occurs by a chemisorption mechanism, riven by electrostatic attraction between pesticide and adsorbent (Moradi, 2014; Shariati, Faraji, Yamini, and Rajabi, 2011).

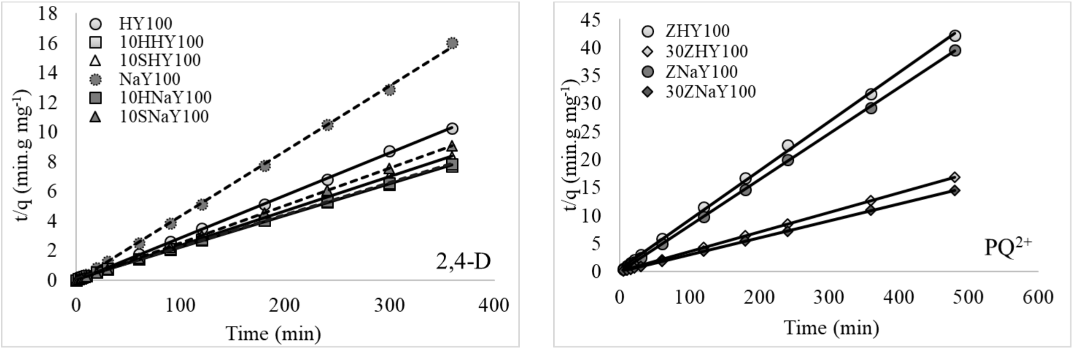

Figure 5.3 Pseudo-second order profile of unmodified and modified ZY100.

Table 5.1 Pseudo-second order constants for removal of 2,4-D and by ZY100 and MZY100.

Adsorbents	2,4-D			
	q_e (exp) (mg g^{-1})	q_e (mg g^{-1})	k_2	R^2
HY100	35.0	34.8	0.062	0.9998
10HHY100	46.8	46.7	0.006	0.9996
10SHY100	43.3	43.1	0.027	0.9999
NaY100	22.5	22.8	0.035	0.9996
10HNaY100	46.0	46.1	0.006	0.9997
10SNaY100	39.7	39.7	0.155	1.0000

q_e (exp) data from experiment.

Table 5.2 Pseudo-second order constants for removal of PQ^{2+} by ZY100 and MZY100.

Adsorbents	PQ^{2+}			
	q_e (exp) (mg g^{-1})	q_e (mg g^{-1})	k_2	R^2
HY100	11.39	11.4	0.015	0.9990
30SHY100	28.55	28.6	0.017	1.0000
NaY100	12.15	12.2	0.122	0.9999
30SNaY100	33.15	33.11	0.041	1.0000

q_e (exp) data from experiment.

5.4.3 Study of adsorption isotherms

Optimal adsorption of 2,4-D and PQ^{2+} occurs at pH 3.0 and 11.0, respectively. Adsorption isotherms reveal that increased pesticide concentrations result in increased adsorption capacity (Figure 5.4).

Langmuir and Freundlich adsorption isotherms describe sorption behavior between liquid and solid phases at equilibrium, and permit determination of adsorption capacity. The data for adsorption of both pesticides by ZY100 and MZY100 zeolites were fitted into two commonly used isotherm models.

The Langmuir isotherm is used to model monolayer adsorption; it is applicable to homogeneous adsorption on a surface (Bayrak, 2006). The linear form of the model is applied to quantitatively evaluate sorption performance equation 5;

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where C_e is the equilibrium concentration of pesticide in the bulk solution (mg L^{-1}); q_e is the amount of pesticide adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}); q_m is the maximum adsorption capacity (mg g^{-1}); and K_L is the Langmuir constant (L mg^{-1}); A dimensionless constant separation factor or equilibrium parameter; R_L is defined using equation 6 (Bayrak, 2006; Vimonses, Lei, Jin, Chow, and Saint, 2009);

$$R_L = \frac{1}{1 + K_L C_0} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where C_o is the maximum initial concentration of pesticide solution (mg L^{-1}). R_L indicates the favorability of the adsorption process ($0 < R_L < 1$); an unfavorable process has $R_L > 1$.

The Freundlich isotherm model is an empirical equation, appropriate for describing adsorption on heterogeneous surfaces, or multilayer sorption (Ng, Losso, Marshall, and Rao, 2002). The Freundlich isotherm is given as equation 7;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \text{........................(7)}$$

where K_F ((mg g^{-1})(L $mg^{-1})^{1/n}$) and n are Freundlich constants; K_F is related to the adsorption capacity of the adsorbent, while the n value is related to the intensity of adsorption which indicates the favorability of adsorption.

The adsorption data fit the Langmuir isotherm model better than the Freundlich isotherm model for all adsorbents. The linear adsorption isotherm parameters are shown in Tables 5.3 and 5.4. High K_L values indicate that all the adsorbents have high affinities for pesticides removal, while R_L values between 0 and 1 indicate highly favorable adsorption. Therefore, pesticides preferentially adsorb to ZY100 and MZY100 surfaces with monolayer adsorption.

However, water quality criteria for protection of aquatic life requires a pH value in the range of 6.0–9.0 (Chiaudani and Premazzi, 1988), and the pH range for most natural waters is 6.0–8.5 (Tariq, Ali, and Shah, 2006). Our adsorption isotherms were also obtained at pH 6, suggesting our adsorbents are appropriate for application to water resource and environmental management. Figure 5.5 shows that the adsorption capacities of our surfactant-modified zeolites exceed the capacity of unmodified zeolite at pH 6.0, and this isotherm differs from that obtained optimal pH. Thus, our surfactant-modified zeolite is advantageous for removal of pesticides from natural water sources because of its ability to adsorb both of the studied pesticides over a broad pH range (Figure 5.4). Tables 5.3 and 5.4 show the Langmuir and Freundlich maximum adsorption capacities for 2,4-D and PQ^{2+} obtained from this work. The table confirms that zeolite Y and surfactant-modified Y zeolites are effective adsorbents for the removal of both 2,4-D and PQ^{2+} from aqueous solution.

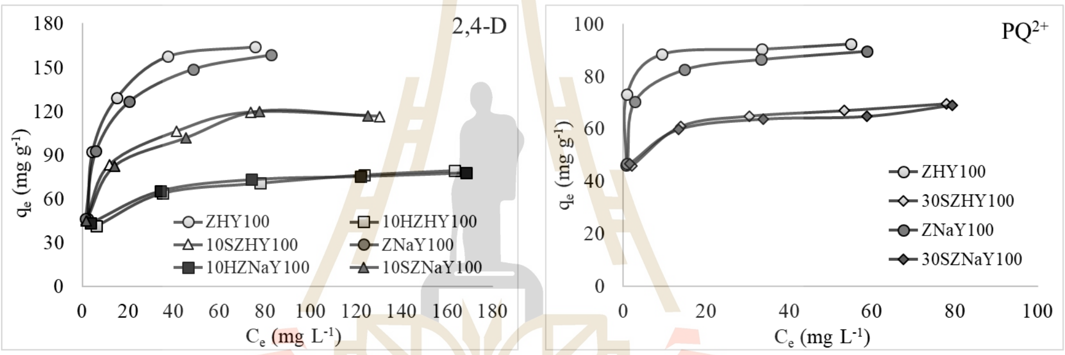

Figure 5.4 Adsorption isotherms of 2,4-D at pH 3.0 and PQ^{2+} at pH 11.0.

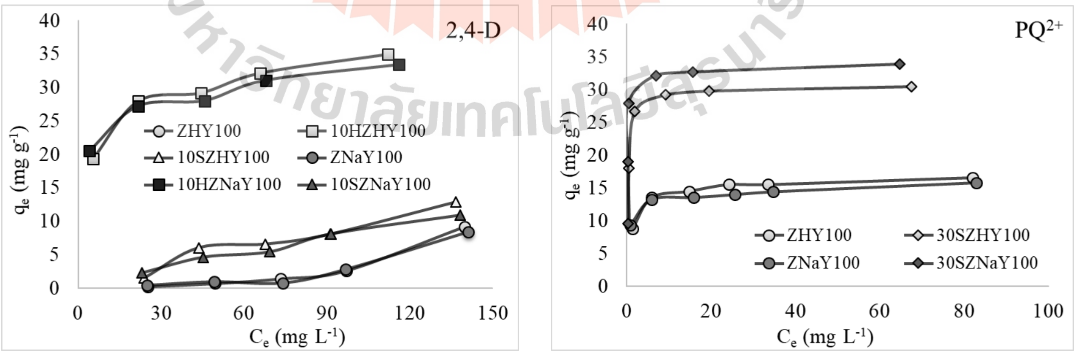

Figure 5.5 Adsorption isotherms of 2,4-D and PQ^{2+} at pH 6.0.

Table 5.3 Langmuir and Freundlich isotherm modeling of 2,4-D adsorption by ZY100, 10HZY100, and 10SZY100, at pH 3.0.

Adsorbents	Langmuir				Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	$K_F{}^*$	1/n	R^2
HY100	175.44	0.1857	2.11×10^{-2}	0.9989	45.33	0.3324	0.8465
10HHY100	82.64	0.1078	3.58×10^{-2}	0.9981	29.79	0.1970	0.9808
10SHY100	120.48	0.2478	1.59×10^{-2}	0.9991	43.88	0.2236	0.9528
NaY100	166.67	0.2020	1.94×10^{-2}	0.9976	48.42	0.2912	0.9532
10HNaY100	80.00	0.1778	2.20×10^{-2}	0.9991	35.97	0.1576	0.9801
10SNaY100	121.95	0.1885	2.08×10^{-2}	0.9970	42.28	0.2279	0.9762

* Unit of K_F is (mg g^{-1})(L mg^{-1})$^{1/n}$

Table 5.4 Langmuir and Freundlich isotherm modeling of the PQ^{2+} adsorption by ZY100 and, 30SZY100 at pH 11.0.

Adsorbents	Langmuir				Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	$K_F{}^*$	1/n	R^2
HY100	92.59	1.9286	3.44×10^{-3}	0.9999	61.00	0.1178	0.6742
30SHY100	70.42	0.4948	1.33×10^{-3}	0.9993	42.98	0.1156	0.9688
NaY100	90.91	0.9091	7.03×10^{-3}	0.9997	53.00	0.1438	0.8609
30SNaY100	68.97	0.5215	1.26×10^{-3}	0.9977	45.44	0.0943	0.9775

* Unit of K_F is (mg g^{-1})(L mg^{-1})$^{1/n}$

5.4.4 Study property of zeolite as multifunctional adsorbents

The efficiency of the modified zeolite for using as multifunctional adsorbent can be considered as follows. When considered the result from the adsorption of single pesticide, it seems that SDS-modified zeolites are proper to use as the multifunctional adsorbent (see Table 5.5), although their adsorption capacities cannot be improved with increasing SDS loading.) However, when considered the results of the study of simultaneous adsorption of four pesticides shown in Table 5.5. It indicates that unmodified HY100 has the highest total adsorption value with around six folds more than the others.

Table 5.5 Adsorption capacity of adsorbents for simultaneous removal of the pesticides.

adsorbents	adsorption capacity (mg g^{-1})				
	atrazine	diuron	2,4-D	PQ^{2+}	Total
HY100	79.6	78.1	6.8	16.3	180.8
NaY100	1.9	28.6	16.8	0	47.3
1HHY100	4.6	24.2	13.6	3.9	46.3
10SHY100	0	11.3	14.6	8.8	34.7
30SHY100	15.1	26.5	16.3	11.6	69.5

5.5 Conclusions

Modification of ZY100 with HDTMA and SDS can enhance the adsorption capacity for removal of 2,4-D and PQ^{2+} depending on the arrangement of the surfactant and water content. The adsorption properties of the adsorbents are also dependent on pH of the solution. An increase in solution pH results in a decrease in 2,4-D adsorption capacity, but PQ^{2+} adsorption capacity increased. At optimum pH (pH 3.0 for 2,4-D and pH 11.0 for PQ^{2+}), the maximum adsorption capacity of the unmodified zeolite is greater than that of the modified zeolites. However, in the pH range of 4–8, the surfactant-modified zeolites are more effective. Additionally, the adsorption of the pesticides fits very well to the Langmuir isotherm model and adsorption kinetics follows a pseudo-second order model, suggesting that mainly electrostatic interactions exist between pesticide and adsorbent.

5.6 References

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CHAPTER VI

CONCLUSIONS

The adsorption processes were conducted with the condition of natural pH of pesticides as around 3–6, thus, PQ^{2+} exists in cationic form and 2,4-D is in both anionic and neutral molecules, while diuron, linuron and atrazine are in neutral form. HY10 zeolite is the best adsorbent to adsorb PQ^{2+}. HY500 and HY100 are appropriate to remove diuron, linuron and 2,4-D. However, the results indicate that HY100 can adsorb PQ^{2+} more than HY500 and suitable to use as an adsorbent in simultaneous adsorption of various pesticides. Using the adsorbents to adsorb the pesticides with analytical grade and commercial grade provides the similar result in the case of PQ^{2+}, atrazine and diuron, but, it has difference in HY zeolite with low Si (HY10) and high Si (HY100 and 500). HY10 can adsorb a commercial grade of 2,4-D more than HY100 or HY500, which is in contrast to the case of analytical grade of 2,4-D. After modification of HY to Na-form and modification with HDTMA and SDS surfactants, it was found that the modified zeolites affect the removal capacity of some pesticides. Countercation Na$^+$ obviously affects the adsorption of 2,4-D, while the surfactant-modified zeolite apparently affects the adsorption of 2,4-D and PQ^{2+}. The arrangement of HDTMA on the HY100 surface as admicelles enhances the PQ^{2+} adsorption. In the case of SDS-modified zeolite, it was found that water content plays an important role in the removal of the pesticides. Zeolite lacking of water shows the high adsorption capacity for 2,4-D, which is in contrast to the PQ^{2+} adsorption.

In addition, pH is an important parameter influencing the adsorption capacity. An increase in the initial pH of the solution results in increasing the removal of PQ^{2+}, on the other hand the removal of 2,4-D is decreased. However, it seems that pH of the solution has no effect on the adsorption of the other pesticides such as diuron, linuron and atrazine. Nevertheless, the study of the adsorption isotherms of these adsorbents seems to fit well with Langmuir model more than Fruendlich suggesting that the most pesticides adsorb on the surface of zeolite as a monolayer. In addition, all modified zeolites were used to adsorb DQ^{+}, carbofuran, bentazon and cyanazin, as well. The adsorption profile of carbofuran, bentazon and cyanazin are not different from the previous study of 2,4-D, diuron and atrazine, respectively, except in the case of DQ^{+}. The adsorption value of DQ^{+} is higher than that of PQ^{2+} around 2-folds according to the different in valency.

APPENDICES

APPENDIX A

PARTICLE SIZE ANALYSIS

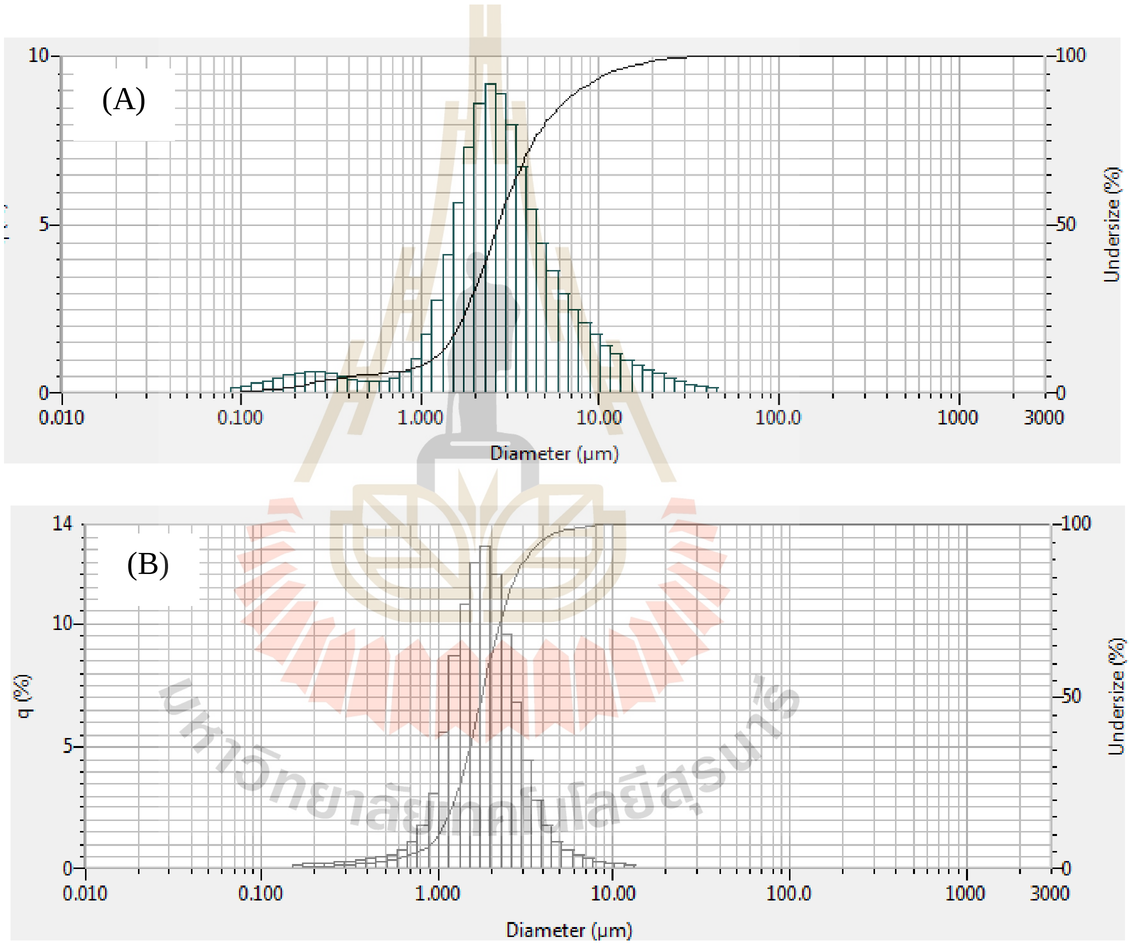

Figure A1 Profile of particle size analysis of (A) HY100 and (B) 10HHY100.

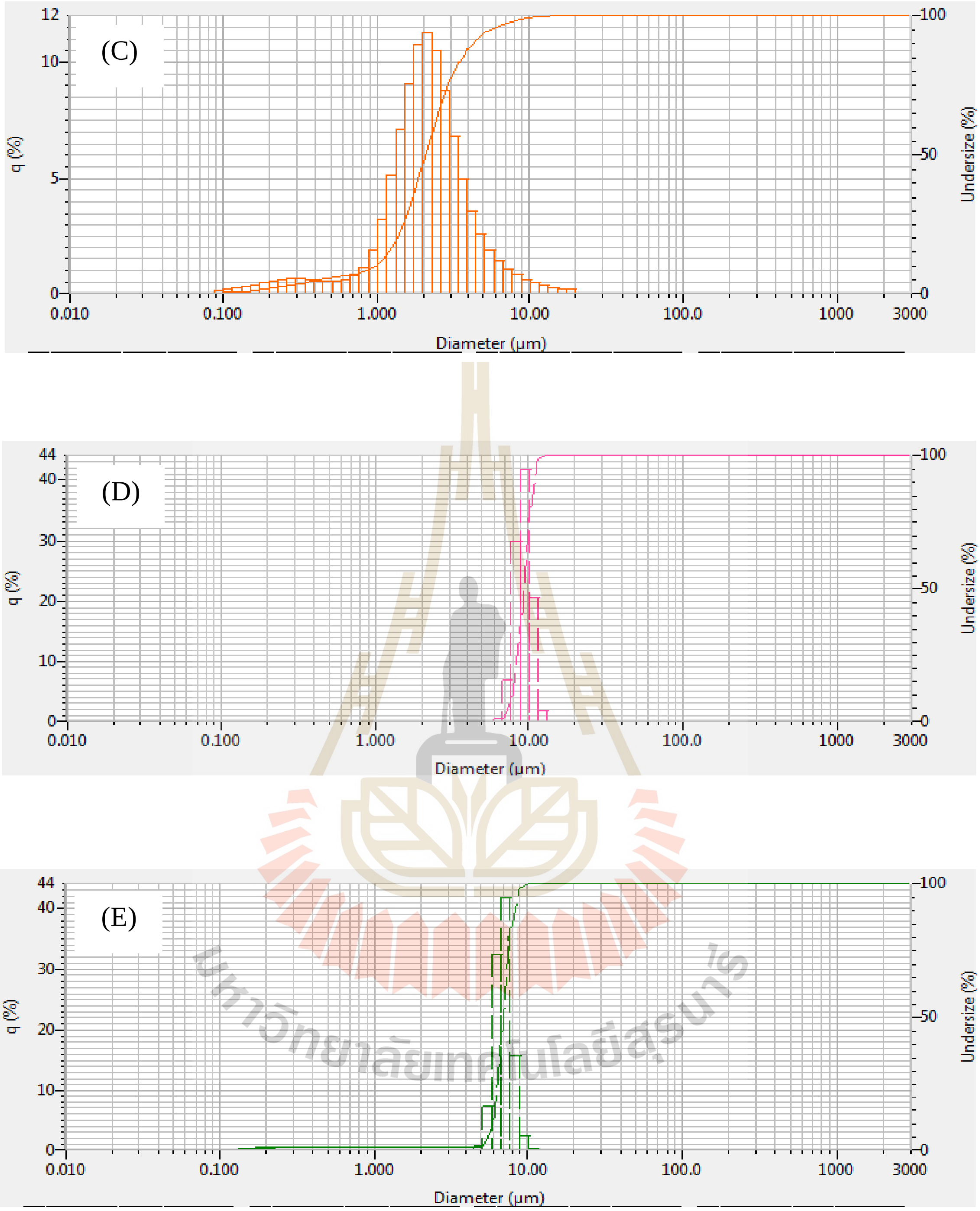

Figure A1 Profile of particle size analysis of (C) 10SHY100, (D) HY10 and (E) 300HHY10 (Continued).

APPENDIX B

HPLC ELUSION PROFILE

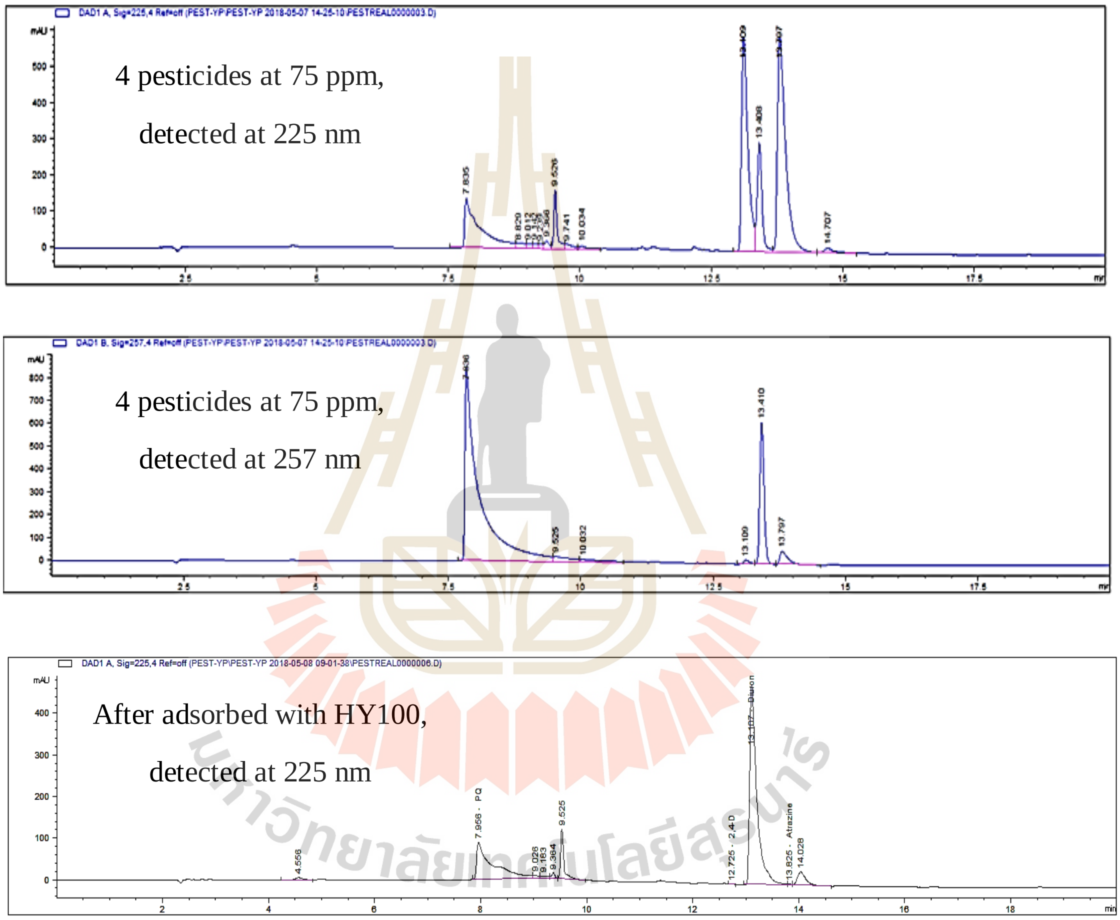

Figure B1 HPLC elusion profile of 4 pesticides in mixture solution (at concentration 75 ppm/each pesticide) detected with UV-Vis detector.

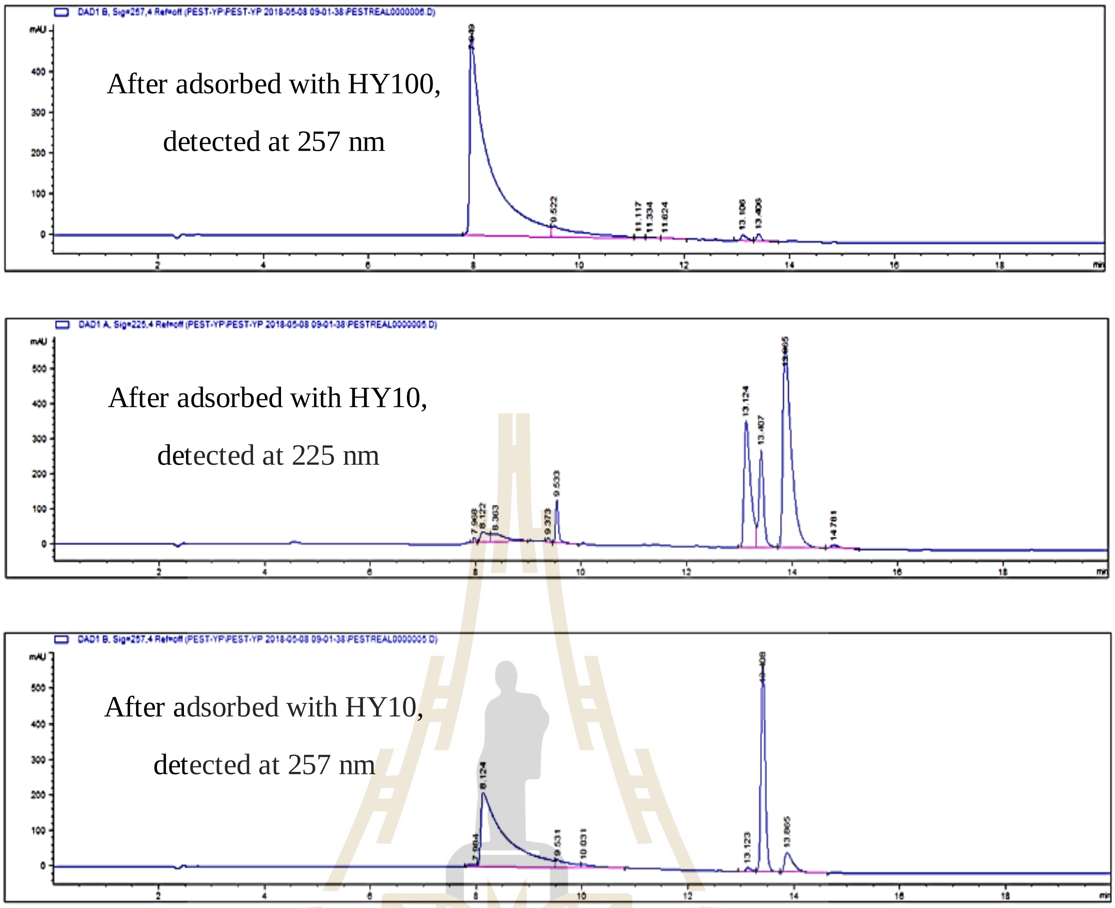

Figure B1 HPLC elusion profile of 4 pesticides in mixture solution (at concentration 75 ppm/each pesticide) detected with UV-Vis detector (Continued).

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