การสังเคราะห์ซีโอไลต์จากเถ้าโรงไฟฟ้าชีวมวล โดยใช้กระบวนการไฮโดรเทอมอล และการประยุกต์ใช้ซีโอไลต์ที่สังเคราะห์ได้

นางสาวพีรดา บวรธรรมทัศน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SYNTHESIS OF ZEOLITE FROM ASH OF BIOMASS POWER PLANT BY USING HYDROTHERMAL PROCESS AND APPLICATION OF SYNTHETIC ZEOLITE

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	SYNTHESIS OF ZEOLITE FROM ASH OF BIOMASS POWER PLANT BY USING HYDROTHERMAL PROCESS AND APPLICATION OF SYNTHETIC ZEOLITE
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พีรดา บวรธรรมทัศน์ : การสังเคราะห์ซีโอไลต์จากเถ้าโรงไฟฟ้าชีวมวล โดยใช้กระบวนการไฮโดรเทอมอล และการประยุกต์ใช้ซีโอไลต์ที่สังเคราะห์ได้ (SYNTHESIS OF ZEOLITE FROM ASH OF BIOMASS POWER PLANT BY USING HYDROTHERMAL PROCESS AND APPLICATION OF SYNTHETC ZEOLITE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.มนัสกร ราชากรกิจ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. สิรวัลภ์ เรืองช่วย, 107 หน้า.

เถ้าลอยจัดเป็นปัญหาสำคัญของโรงไฟฟ้าชีวมวล อย่างไรก็ตามเถ้าลอยเหล่านี้สามารถนำมาประยุกต์ใช้ให้เกิดประโยชน์ได้หลายวิธี ซึ่งการสังเคราะห์ซีโอไลต์ก็นับเป็นวิธีหนึ่งที่สามารถเพิ่มมูลค่าให้เถ้าลอยได้ งานวิจัยนี้มุ่งเน้นการศึกษาสภาวะที่เหมาะสมในการสังเคราะห์ซีโอไลต์โดยกระบวนการไฮโดรเทอร์มัล ภายใต้ความดันบรรยากาศ วัตถุดิบที่ใช้ในการทดลองคือเถ้าลอย 3 ชนิดได้แก่ เถ้าแกลบ เถ้าชีวมวลจากโรงไฟฟ้า 3 เถ้าชีวมวลจากโรงไฟฟ้า 4 ซึ่งจะทำการแปรผันสภาวะในการสังเคราะห์ซีโอไลต์ดังนี้ ชนิดของสารละลายด่าง ความเข้มข้นสารละลายด่าง อุณหภูมิในการทำปฏิกิริยา และระยะเวลาในการทำปฏิกิริยา ผลการทดลองสามารถสรุปได้ว่าซีโอไลต์ที่สังเคราะห์ได้จากเถ้าลอยทั้ง 3 ชนิดคือซีโอไลต์ P สภาวะที่เหมาะสมต่อการสังเคราะห์ซีโอไลต์จากเถ้าลอยที่ได้จากเชื้อเพลิงประเภทแกลบล้วนคือ การใช้โซเดียมไฮดรอกไซด์ความเข้มข้น 3 โมลาร์ ทำปฏิกิริยาที่อุณหภูมิ 99±1 องศาเซลเซียส เป็นเวลา 24 ชั่วโมง และสำหรับเถ้าลอยจากเชื้อเพลิงชีวมวลอีก 2 ชนิด สภาวะที่เหมาะสมคือ การใช้โซเดียมไฮดรอกไซด์ความเข้มข้น 2 โมลาร์ ทำปฏิกิริยาที่อุณหภูมิ 99±1 องศาเซลเซียส เป็นเวลา 24 ชั่วโมง โดยซีโอไลต์ที่สังเคราะห์ได้จากเถ้าแกลบล้วน เถ้าชีวมวลจากโรงไฟฟ้า 3 เถ้าชีวมวลจากโรงไฟฟ้า 4 มีค่าความสามารถในการแลกเปลี่ยนแคลเซียมไอออน 381.08 264.34 และ 261.96 มิลิกรัมแคลเซียมคาร์บอเนตต่อซีโอไลต์ 1 กรัม ตามลำดับ และเมื่อนำไปประยุกต์ใช้เป็นตัวดูดซับตะกั่วในสารละลายสังเคราะห์ พบว่าประสิทธิภาพในการการดูดซับตะกั่วของซีโอไลต์ที่ได้จากเถ้าทั้ง 3 ชนิดมีค่าเท่ากับ 82.43% 74.68% และ 61.70% ตามลำดับ ที่ pH 5 ความเข้มข้นของตะกั่วเท่า 1000 มิลลิกรัมต่อลิตร

สาขาวิชา การจัดการสิ่งแวดล้อม (สหสาขาวิชา) ลายมือชื่อนิสิต พีรดา บวรธรรมทัศน์
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PEERADA BOWORNTHAMMATUS: SYNTHESIS OF ZEOLITE FROM ASH OF BIOMASS POWER PLANT BY USING HYDROTHERMAL PROCESS AND APPLICATION OF SYNTHETIC ZEOLITE. THESIS PRINCIPAL ADVISOR: ASST. PROF. MANASKORN RACHAKORNKIJ, Ph.D., THESIS CO-ADVISOR: SIRAWAN RUANGCHUAY, Ph.D., 107 pp.

Unlike biomass, combusted biomass in the form of fly ash from biomass power plant may pose a major problem in waste management. Nonetheless, they have high potential for applications, especially in construction material industry. Zeolite production is one of the potential applications for obtaining high value products from these fly ashes. This study focused on synthesis of zeolite using hydrothermal process under atmospheric pressure. A matrix of experiments was designed for three different sources of fly ash; namely, pure rice husk, biomass from power plant No. 3, and biomass from power plant No. 4. Zeolite synthesis was carried out under varied experimental conditions that include type of basic solution, concentration of alkali, temperature, and reaction time. Phase analysis via X-ray diffraction spectrometry (XRD) identified zeolite P as a major phase in the synthetic zeolite samples from the three recipes. The optimum condition for the pure rice husk ash treatment was with 3 M NaOH, 99±1°C, and 24 hours of reaction time. Those for Biomass 3 and Biomass 4 were obtained at 2 M NaOH, 99±1°C, and 24 hours. Zeolites synthesized at the optimum conditions for each recipe of fly ash had cation exchange capacities of 381.08, 264.34, and 261.96 $mgCaCO_3/g$ zeolite, respectively. The synthetic zeolites produced from the abovementioned optimum conditions were then tested for heavy metal treatment application. Maximum removal efficiency for lead (Pb) of the three biomass recipes were 82.43%, 74.68%, and 61.70%, respectively, at initial lead concentration of 1000 mg/L and pH 5.

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LIST OF ABBREVIATIONS

°C	Degree Celsius
°F	Degree Fahrenheit
α cage	Alpha cage
β cage	Beta cage
ε_p	Particle porosity
ρ_p	Particle density
A	Angstrom
AAS	Atomic Adsorption Spectrometer
AC	Activated carbon
Al_2O_3	Aluminium oxide
$Al_2O_3.SiO_2$	Alumino-siliate
AlO_4	Aluminiumtetraoxide
ASTM	America Society for Testing and Materials
B3	Biomass fly ash from power plant 3
B4	Biomass fly ash from power plant 4
BET	Brunauer–Emmett-Teller
C_2H_2	Acetylene
$CaCl_2.2H_2O$	Calcium Chloride Dihydrate
Ca-form	Calcium form
CaO	Calcium Oxide
CEC	Cation exchange capacity
C_e	Equilibrium concentration
CO_2	Carbon dioxide
C_o	Initial concentration
Conc.	Concentration
d	Diameter
d_p	Pore diameter
E_a	Activation energy
EDTA	Ethylene diamine tetraacetic acid
FCC	Fluid catalytic cracking

g/cm^3	gram per cubic centimeter
HNO_3	Nitric acid
$J.mol^{-1}.K^{-1}$	Joule per mole per kelvin
K	Kelvin
K-form	Potassium form
K_2O	Potassium oxide
KOH	Potassium hydroxide
kJ/mol	kilojoule per mole
L	Liter
LOI	Loss on Ignite
LTA	Lind type A
M	Molar
ML	Million
MT/yr	Metric ton per year
MW	Mega watt
M.W.	Molecular weight
mg $CaCO_3$/g	milligram as calcium carbonate per gram
min	minute
mmHg	millimeter of mercury
mol	mole
Na-form	Sodium form
Na_2AlO_2	Sodium aluminate
Na_2O	Sodium oxide
Na_2SiO_2	Sodium silicate
NaOH	Sodium hydroxide
NOx	Nitrogen oxide
NZ	Natural zeolite
nm	nanometer
OH^-	Hydroxide ion
PP#3	Power Plant 3

PP#4	Power Plant 4
Pb(II)	Divalent lead ion
$PbCO_3$	Lead carbonate
$Pb(NO_3)_2$	Lead nitrate
PbS	Lead sulfide
$PbSO_4$	Lead sulfate
pm	Pico meter
R	Rice husk ash
R^2	Linear regression
rpm	Round per minute
SBU	Secondary building unit
SEM	Scanning Electron Microscope
SSA	Specific surface area
S_g	Surface area
SiO_2	Silica dioxide
SiO_4	Silicontetraoxide
SO_2	Sulfur dioxide
ton/yr	ton per year
US$/ton	US dollar per ton
USEPA	U.S. Environmental Protection Agency
VOC	Volatile organic content
Wt	Weight
XRD	X-ray diffraction spectrometer
XRF	X-ray fluorescence spectrometer
ZB3	Zeolite from biomass ash plant 3
ZB4	Zeolite from biomass ash plant 4
Z-Na	Zeolite sodium form
ZR	Zeolite from rice husk
Zeolite NaP	Zeolite sodium P
Zeolite NaP1	Zeolite sodium P one

CHAPTER I

INTRODUCTION

1.1 Introduction

Thailand is developing in the industrial sector especially now. The development causes the electric energy using greatly. The important power resources are the kind of coals, oil and natural gas. These fuels are non-renewable energy. Even though, these are giving high value and adding the capital in the production. These fuels still cause the environmental effect as well, for examples: acid rain, global warming and etc. Thus, we should seek the energy or the other fuels for using them such as energy from sun, wind, water, and biomass. These fuels are renewable energy, availability and environmental friendly. They are not adding the capital in the production.

Energy of biomass is appropriate for Thailand. Because Thailand is an agricultural country where is rich in biomass resources. Biomass is an important renewable energy source for the rural area in Thailand. Biomass fuels are not trades. It is a basic energy for cooking and heating in rural household. Now, biomass can be used to generate the electricity for industries like agro-industries, food industries, wood industries which use biomass fuel for energy resource as main source. Furthermore, biomass fuels are environmental friendly because it can be reduced, reused, and recycled. However, burning these substances will cause ashes greatly. These ashes will effect to area. Even though, these ashes can apply and gain more advantages at the present such as steel mills, composition of cement, fertilizer, soil improvement, light weight brick, and zeolite.

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth metals (principally sodium, potassium, magnesium and calcium). They have a lot of porous structure and high the skin area. Zeolites have many useful purposes. They can perform ion exchange, filtering, odor removal, chemical sieve, and gas absorption tasks. From these properties make zeolite to be popular and to prevent in many countries extensively. It is also high valuable for industrial. A lot of raw materials are used to synthesize zeolite. In case of biomass ashes are counted to the interesting raw material. Because of the elements and the structure of biomass ashes can be synthesized zeolite. One of purpose of this research is to convert the biomass ash into the utilities material, zeolites.

Lead is also commonly heavy metal which found in water; drinking water, ground water, and waste water. It is highly toxic to human, plant and animal. Normally, the removals of lead are precipitation, solvent extraction, ion exchange, and adsorption on activated carbon. These treatments do not suitable for developing countries. Therefore the other aim of this research is to use synthetic zeolite from biomass ash to adsorb lead in synthetic water. Due to the important properties of zeolites are chargeable and high areas.

1.2 Objectives

The main objective of this research is to synthesize zeolite from ash of biomass power plant by using hydrothermal process in optimum condition. The sub-objectives are as follows:

1.2.1 To analyze physical and chemical composition of biomass ashes for synthesis of zeolite
1.2.2 To study parameters having an effect on properties of zeolite
1.2.3 To analyze characteristic of zeolite by both of physical and chemical properties
1.2.4 To study absorption of lead on zeolite between synthetic zeolite in laboratory, natural zeolite on the market and activated carbon
1.2.5 To evaluated the economic of synthetic zeolite

1.3 Hypotheses

Ashes from biomass power plant can apply to a starting material in the synthesis of zeolite. And synthetic zeolites have high effective to adsorb lead in solution.

1.4 Scope of the study

1.4.1 Collection of biomass ash samples was done at Thai Power Supply Co., Ltd. In Chachoengsao province, Thailand.

1.4.2 Type of zeolite was determined by X-ray Diffraction Spectrometer (XRD).

1.4.3 The optimal conditions for synthetic zeolite form biomass ash were determined by the cation exchange capacity (CEC) which is titrated with EDTA.

1.4.4 The synthetic zeolites from optimal condition were analyzed morphology by Scanning Electron Microscope (SEM) and specific surface area by Brunauer–Emmett-Teller (BET).

1.4.5 Adsorption study was done in batch experiments.

1.4.6 Concentration of lead would be determined by Atomic Absorption Spectrophotometer (AAS).

1.5 Benefits of this study

Fly ash is waste from biomass power plant. It is a big problem for generating plant. However, biomass will be utilized. Zeolite is one way for increasing value of them. Zeolites are wildly use in many industrials especially industry of detergent in Thailand. The important properties of zeolite are ion exchange, adsorption, and molecular sieve. In this research, synthetic zeolite from biomass will be use as adsorption materials to treat lead in solution. They will be improved to potentially replace of more expensive conventional methods such precipitation and carbon adsorption.

CHAPTER II

THEORECTICAL BACKGROUND AND LITERATURE REVIEW

The electric generation provides the production and delivery of electrical power to areas that need electricity. The important power resources are the kind of coals, oil and natural gas. These fuels are nonrenewable energy and are giving high value and adding the capital in the production. Besides, these fuels still cause the environmental effect as well, for examples: acid rain, global warming and etc. Thus, the suitable fuels for electric generation should be renewable energy, availability and environmental friendly such as energy from sun, wind, water, and biomass.

Biomass is an important renewable energy source for the rural areas in Thailand. Biomass fuels are not trade, and mostly home grown. Nowadays, biomass materials can be use to generate electricity and heat that have substantially lower environmental impact than traditional fossil fuels. (Seksan et al., 2007)

2.1 Biomass power plants

In recent years, scientists have found many new ways to generate electricity from biomass. The original method was to burn plant material and use the heat created to boil water and generate steam. Biomass fuels produced electricity by thermal conversion technology for burning biomass fuels which includes the following:

- Mass burn stoker boilers
- Stoker boilers (stationary sloping grate, travelling grate, and vibrating grate).
- Fluidized bed boilers (bubbling and circulating).
- Gasification with combustion in a close-coupled boiler.
- Pulverized fuel suspension fired boilers.

Each of these technologies has advantages and disadvantages. All have been commercially proven with biomass. Stoker boilers are widely in use but are not always the most appropriate choice. For example, rice husks are most easily fired in fluidized beds or gasified because the lower operation temperatures reduce the risk of slugging. Stoker and suspension-fired units may also be used, but precautions should be taken to minimize slugging potential. Fluidized beds are good choices in general because they can tolerate wide variations in fuel moisture and size. Suspension firing is not suitable for most biomass fuels because they are usually difficult to grind. Gasification may be a suitable choice, but lacks widespread technical and commercial acceptance (National Energy Policy Office, 2000).

2.1.1 Biomass fuel

Biomass is plant matter such as trees, grasses, agricultural crops or other biological material. It can be used as a solid fuel, or converted into liquid or gaseous forms, for the production of electric power, heat, chemicals, or fuels (The National Renewable Energy Laboratory, 2007). Biomass composition is divided into (Energy for Environmental Foundation, 2007):

- Moisture: Most of the biomass contains considerably high moisture content because it comes from agricultural by-products. The biomass that is suitable for combustion should have less than 50 per cent of moisture.

- Combustible substance: Combustible substance consists of volatiles matter and fixed carbon. The biomass that contains a great amount of volatiles matter is highly combustible.

- Ash: Most of biomass contains 1-3 per cent of ash except for rice husk that has around 10-20 per cent of ash, which causes problem in combustion and dumping.

The main agriculture residues in Thailand consist of rice husk, bagasse, palm oil waste, wood waste.

1. Rice husk

Rice husk is produced during paddy milling. Information on this resource is given in Table 2.1. Rice husk constitutes about 23 percent of the paddy weight. It has a heating value of 13,500 kJ / kg. Rice husk has been used as fuel for power plants in Thailand.

2. Bagasse

Bagasse is the fiber residue remaining after sugar cane has been processed to remove the sugar laden juice. Bagasse properties are given in Table 2.1. Bagasse constitutes 28 to 30 percent of the cane and heating value of 10,000 kJ / kg.

3. Palm oil residue

Palm oil is produced from oil palm trees. Palm oil residues account for about 44 percent of the fresh fruit weight. It gives heating value of 8,400 – 18,250 kJ / kg. Properties of the solid residues are given in Table 2.1.

4. Wood residues

Wood residues include chips, bark, and sawdust produced within various wood processing industries including sawmills, furniture factories, and other industries. Processing of saw logs, and processed wood occurs at sawmills and production plants and is accompanied by residue production of 30 to 60 percent and heating value of 10,000 kJ / kg. The aggregate properties of residues produced in these industries are given in Table 2.1.

Table 2.1 Biomass characteristics

Characteristics	Rice husk	bagasse	palm oil residue	wood waste
Source of biomass	Rice paddy	Sugar cane	Fresh fruit bunches	Saw logs, parawood trees, processed wood
Biomass production rate (percent of source)	23	28 - 30	44	30 - 60
Total biomass availability (million tons/yr)	2.30 – 3.68	2.25 - 3.50	0.47 – 0.74	1.84
Higher heating value (kJ/kg)	14,100	10,000	8,400 - 18,250	10,000

Source: National Energy Policy Office, 2000

For the efficiency of biomass utilization, the plants should install equipment, specially designed according to different components. Characteristics of Biomass fuel impinge electric generation (Energy for Environmental Foundation, 2007):

- **Scattered resources of biomass**

The resources can be categorized into two fashions: The cluster is the wastes from agro-industrial process, which can be obtained from rice mills, sugar refineries, and other factories. Although some biomass such as corncobs harvested by portable machinery and Para wood wastes are potential unexploited biomass resources, the disadvantage is the transportation expense.

- **Size**

Biomass size matters. For example, Para wood wastes from plantations or sawmills are too big to be used as fuel right away due to the low combustibility. They need to be chipped into small pieces first but that costs money ancillary to total expense.

- **Moisture**

Moisture in biomass is a significant factor. Biomass that has high moisture is not suitable for combustion unless they are gasified through the dewatering process or the anaerobic treatment. Wood wastes with 50-60 per cent of moisture can be accumulated until the moisture naturally decreases but that requires spacious storage and if they are stored for too long, they decompose.

- **Contaminants**

The contaminants in biomass - dirt, gravels, rocks and stain - need extra caution especially the alkaline on empty bunches because it leaves sticky stain in the water tube of combustion room.

- **Ash**

The quantity of ash in biomass affects the combustion, especially the rice husk with 16 percent of ash in weight. Therefore the combustion room needs to be designed for easy and efficient ash dumping and cleanup.

Biomass fuels are advantageous for Thailand. Since Thailand is of imported fuel. And biomass is environment friendly. However, biomass fuels an agriculture country, biomass is abundance. Use of low-cost biomass can offset the high cost have some disadvantages. One is high investment cost for modern biomass technology. The other is the fact that conversion efficiency in utilizing biomass as an energy source is generally low (Phongjaroon, 2004).

2.1.2 Case study: Thai Power Supply (TPS) Co., Ltd.

Thai Power Supply Co., Ltd. is located in industrial settlement 304IP2 at Chachoengsao province. Electricity and steam for tenant industries are supplied by many biomass power plants. This study focuses on plant no. three and four. At, Plant three, 10.4 MW of electricity is generated from burning of rice husk, wood wastes, coal, corn cob, sawdust. For plant four, rice husk, wood waste, coal, and palm residues are used to produce 37.15 MW. Both of plant three and four utilize circulating fluidized bed technology for transformation of biomass fuel to heat. The processes are: fuels are prepared for use by crushing. After crushed, the fuels are mixed with air and blown into the boiler to heat water to produce steam. The steam flows into a turbine, which spins a generator to produce electricity. The steam is cooled, condensed back into water, and returned to the boiler to start the process over. Burning biomass produces 99 % fly ash, which is very light, exits the boiler along with the hot gases, is removed by an electrostatic precipitator before dispersed into the atmosphere and get to silo to accumulate.TPS fly ash from silo is utilized for improve soil texture and export to foreign country for steel mill industrial.

2.1.3 Utilization of ash

1. Composition of cement concrete

One of the leading uses for fly ash is in concrete products applications. Fly ash use in concrete improves the workability of plastic concrete, and the strength and durability of hardened concrete. Fly ash is also a cost effective ingredient in concrete because it contributes to the total cementations component in the mix and therefore allows the producer to reduce the amount of cement in a typical mix design.

2. Fertilizer

The benefits from ashes depend on your soil and the rate at which the ashes are applied. Generally, ashes contain potassium, a major plant nutrient plus a number of minor nutrients. Biomass ashes contain all the mineral elements that were in the biomass, except for nitrogen and sulfur which are lost through the burning process. Potassium, calcium and magnesium carbonate or oxides are present in comparatively large amounts giving the ashes a strongly alkaline reaction which can neutralize acid soils. However in soils that are already alkaline, high application rates can be harmful. A further compounding problem is that about 80 to 90 percent of the minerals in ashes are water-soluble, so that high application rates can cause salts to build up in soils, resulting in plant injury. As a plant food, ashes contain 5 to 7 percent potassium and 1to 2 percent phosphorous. They also have 25 to 50 percent calcium compounds.

3. Soil Improvement

Soil Amendment is the chemical and/or mechanical modification of soil properties to improve the engineering performance of soils. The properties that are most often modified are strength, plasticity, density, and water content. Improvements to soil properties expedite construction activities which contribute to savings in time and money. Typically, fly ash is used in conjunction with other materials such as lime, cement, or lime kiln dust to achieve the desired effect.

4. Soil Stabilization to Improve Strength

Fly ash is used to improve the compressive and shearing strength of soils. Fly ash can be used to effectively improve sub-grades, base courses and backfill which reduce lateral earth pressures and improve slope stability on embankments. Several factors should be considered including the in-place soil properties, moisture content at time of compaction, fly ash blend ratio with lime, cement, etc.

5. Soil Stabilization to Control Shrink Swell

Various soils undergo extensive volumetric changes when subjected to fluctuating moisture contents. If not controlled, these volumetric changes can impose loads that cause movement to structures that lead to premature failure. Fly ash reduces the potential of a plastic soil to undergo volumetric expansion by bonding the soil grains which restrict or reduce soil particle movement.

6. Soil Modification to Reduce Water Content

Moisture content of soil must be controlled due to the effect it has on soil density. Soil must be compacted to the maximum practical density to achieve a firm base for overlying structures. Fly ash serves as a drying agent for soils that are too wet to achieve the required density. The drying affect of fly ash in wet soil occurs rapidly which allows the contractor to quickly proceed with construction activities. Fly Ash also makes the soil more resistant to water infiltration.

7. Light weight brick

The Light-weight Concrete blocks are very useful building products, helping to reduce dead weight of the structures and accelerating pace of construction, when used as pre-cast elements for walling and flooring etc. Unfortunately the basic cost of the product has been too high to be offset by the economic gain accruing due to speed and lighter structure. However, one of technologies of producing light-weight concrete has been made to be more environments friendly by incorporating use of fly-ash, as admixture for walling material in residential buildings not only reduces urban environmental pollution but also lowers its construction cost.

8. Zeolite

Fly ash is used as raw material for zeolite synthesis by hydrothermal treatment with base solution under various conditions. Because of fly ash is mainly composed of some oxides derived from inorganic compounds, which remain after combustion. The amounts of the main components of ash are SiO2 and Al2O3, show few variations with the type of biomass. The similar chemical composition of fly ash as same as some volcanic rocks that are called zeolite.

2.2 Zeolite

Zeolites are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, magnesium, calcium, strontium, and barium (Breck D.W., 1974). Zeolite structures are three dimension frameworks which base on network of aluminate (AlO_4) and silicate (SiO_4) tetrahedral linked to each other by sharing all of the oxygen in Figure 2.1

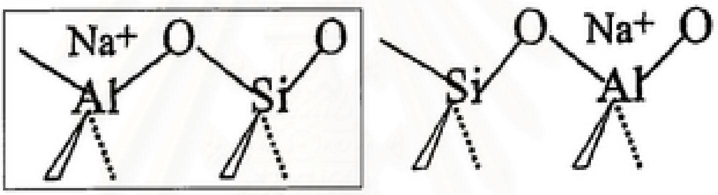


Figure 2.1 Basic structure of zeolite (Robert B., Mirko H., Boris S., 2006)

The empirical formula of a zeolite is of the type:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O,$$

Where: M is any alkali or alkaline earth atom

n is the charge on that atom,

x is a number from 2 to 10 of AlO4 tetrahedral are joined only to SiO_4 tetrahedral

y is a number from 2 to 7 of water molecules are contained in zeolite framework.

2.2.1 Structure of Zeolite

The zeolites comprise the largest group of aluminosilicates with framework structure. They depend on common features of the aluminosilicate framework structures. Normally, each group of zeolite has a common subunit of structure which is a specific array of aluminate (AlO_4) and silicate (SiO_4) tetrahedral. In Classification, the Si – Al distribution is neglected. In Figure 2.2, group of zeolites are single 4-ring (S4R), single 6-ring (S6R), double 4-ring (D4R), double 6-ring (D6R), complex 4-1, T_5O_{10} unit, complex 5-1, T_8O_{16} unit, and complex 4-4-1, $T_{10}O_{20}$ unit. These are called secondary building unit (SBU) (Meier W.M., 1968). In some case, the zeolite framework can be considered in term of polyhedral unit. Some of SBU are probably involved in crystal growth process. Some of polyhedral structures are shown in Figure 2.3.

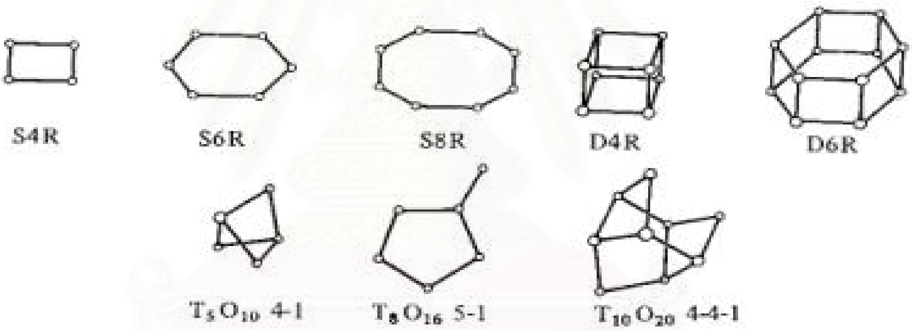


Figure 2.2 The secondary building unit in zeolite structure (Meier W.M., 1968)

α – cage β - cage

Figure 2.3 Some of polyhedral in zeolite framework (Antonio Currao, 2007)

2.2.2 Type of Zeolite

1. Mineral zeolite

Zeolites were first recognized as a new group of minerals consisting of hydrated aluminosilicates of alkali and alkaline earths which discovery of stilbite in1756 (Cronstedt, 1756). Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. The most common of which are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Zeolite minerals have been used in many investigations of zeolite structure and properties. More over, they are widely used in industries where consider of uniformity and purity are essential. Because of zeolites mineral are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. Therefore, synthetic zeolites are synthesized by scientists. Normally, natural zeolites are use in agricultural industry. For example, natural zeolites could remove ammonia in shrimp pond, and soil amendment by ion exchange.

2. Synthetic zeolite

Synthetic zeolites are hydrate aluminosilicates that formed under hydrothermal condition. The term of hydrothermal is used in a broad and includes the crystallization of zeolite from aqueous system which contains the necessary chemical component. Types of synthetic zeolite depend on Si/Al ratio and other condition that use to synthesize. More than 150 zeolites have been synthesized. Some of the more common synthetic zeolites are zeolites A, P, X, Y, and ZMS-5. Synthetic zeolites are pure and low contaminants. For this reason, they are suitable for industrial sectors. The applications of synthetic zeolite depend on type and characteristic of them.

For example, Zeolite A or Linde Type A (LTA) is great of commercial important due to its molecular sieve and ion exchange capacity. The aluminosilicate framework of zeolite A is generated by Si / Al ratio about 1. It has three form; Zeolite 3A is the K-form, having the following composition: $0.4K_2O{\cdot}0.6Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$. Zeolite 4A is Na-form, The unit cell is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$. Finally, zeolite 5A is the Ca-form, the following composition: $0.7CaO{\cdot}0.30Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$ (Beijing Henrky Chemical Materials Co.,Ltd.) Normally, it is synthesized in the Na-form. Zeolite A has been crystallized at temperature ranging from 25 to 150˚C with the crystallization time varying from 14 days to 2.5 hours. The properties are showed in table 2.2

Table 2.2 The properties of zeolite A

Properties	Zeolite A
Si / Al ratio	0.7 – 1.2
Symmetry	cubic
Density	1.99 g/ml
Pore size	4.2 A

Source: D.W. Breck, 1974

Zeolite P is one kind of synthetic zeolite which alway use in detergent industry. It use as builder material in detergent (Sasol Olefins & Surfactants, 2008). Zeolite P is Na-form, unit cell is $Na_6[(AlO_2)_6(SiO_2)_{10}].15H_2O$. Several structurally related zeolite P type has been synthesized including a cubic and tetragonal form. Zeolite P is stable at higher temperatures and has been formed over a temperature range of 60 to 200˚C (D.W. Breck, 1974). The properties are showed in table 2.3

Table 2.3 The properties of zeolite P

Properties	Zeolite P
Si / Al ratio	1.1 – 2.5
Symmetry	cubic or tetragonal
Density	2.01 g/ml
Pore size	3.1 x 4.4 A

Source: D.W. Breck, 1974

2.2.3 Synthesis of zeolite

Zeolites are normally synthesized hydrothermally from basic reaction gels at low temperatures under an autogenously pressure and in the presence of a large excess of water. Most of the highly siliceous zeolites are formed in the presence of organic bases known as templates, introduced in the early 1960's (Barrer R. M.et al., 1961).

Typically alkaline aluminosilicate gels are cooked, usually at temperatures < 200°C and sometimes much less (Milton, 1989) under specified conditions for times ranging up to several days (Barrer, 1989, Jansen, 1991). Such low temperatures favor the formation of the desired open structures, and the results also strongly depend on the thermal history. Different alkaline cations favor different structures; in part, this seems to result from ion-pairing effects, with larger cations favoring larger silicate oligomers by preferential association with them (McCormick *et al.*, 1989). Alkali cations must also influence both nucleation and growth of silicate polymers, as they have a large effect on the crystallization kinetics of even pure-silica structures (Goepper *et al.*, 1992). The crystallized products also strongly depend on Al/Si ratio (Szostak, 1989, Jansen, 1991) and pH, as well as the presence of additional anions. Therefore, the structure and properties of zeolite product are highly dependent on the physical and chemical nature of the reactants used in preparing the reaction mixture, its overall chemical composition, and on the type of cations or organic template and the conditions (temperature, pressure and duration) of the hydrothermal treatment.

The general reaction scheme describing the zeolite synthesis process as show in figure 2.4

$$\mathrm{NaOH} + x\mathrm{Al_2O_3}\cdot y\mathrm{SiO_2} \xrightarrow{\text{Fusion}} \mathrm{Na_2SiO_3} + \mathrm{Na_2AlO_2}$$

$$\mathrm{NaOH\ (aq)} + \mathrm{Na_2Al(OH)_4\ (aq)} + \mathrm{Na_2SiO_3\ (aq)} \xrightarrow{\text{room-temperature}}$$

$$[\mathrm{Na}_x(\mathrm{AlO_2})_y(\mathrm{SiO_2})_z\cdot\mathrm{NaOH}\cdot\mathrm{H_2O}]\ \text{(gel)} \xrightarrow{\text{323–623 K}}$$

$$\mathrm{Na}_p[(\mathrm{AlO_2})_p(\mathrm{SiO_2})_q]\cdot h\mathrm{H_2O}\ \ \text{(crystal in suspension)}$$

Figure 2.4 Synthesis of zeolite process (Keka O., Narayan C. P. and Amar N. S., 2004)

Tongkam (1999), synthesized zeolite from coal fly ash of Mae-Moh power plant by using alkaline hydrothermal process. Variables studied were type of base solution, concentration, temperature, and reaction time. In the result showed that several types of zeolite such as zeolite P, chabazite, nepheline and gismondine were synthesized. The optimum condition was used NaOH solution 2 M, 100°c, and 72 hr that gave the cation exchange capacity (CEC) 619.44 mmol/kg.

Querol et al. (1997a) used KOH and NaOH as activators to synthesize zeolite using both open and closed system. They have carried out experiments from fly ashes of varying compositions, collected from different power plants. Their results have shown higher conversion efficiency of NaOH than that of KOH solutions; even at higher KOH concentrations (1M and 473 K), quartz and mullite could not be dissolved substantially and remained in the fly ash. Higher pH of the solution also showed better zeolite synthesis efficiency. Mainly zeolite NaP1, NaP derivatives and Phillipsites have been synthesized by NaOH and KOH activation.

Fukui et al. (2006) Studied effects of NaOH concentration on the crystal structure and the reaction rate of the zeolite synthesized from fly ash with a hydrothermal treatment method. They used ash and ash mixed with silica powder as raw materials. They found that with a higher NaOH concentration in the hydrothermal treatment, the proportion of phillipsite in the powder product was lower and the proportion of hydroxyl sodalite was higher. And the time elapsed before the start of the crystallization of zeolite was shorter, and the zeolite crystal generation rate was greater. Phillipsite only could be selectively synthesized by using a raw material comprising fly ash with the addition of silica powder even when hydrothermal treatment was performed with high concentration aqueous NaOH solution, and with a higher NaOH concentration, the necessary silica powder mass increases. When phillipsite was selectively synthesized by using a mixture of fly ash and silica powder as a raw material, the phillipsite generation rate increases with a higher NaOH concentration in the hydrothermal treatment liquid, thereby the treatment time could be shortened.

2.2.4 Utilization of Zeolite

Synthetic zeolites are principally used as molecular sieves, catalysts and detergents. As molecular sieves, their major applications include pressure swing absorption gas separators; desiccants, either in cooperation or competition with silica gel and activated alumina, for the removal of water hydrocarbons and other liquids; removal of water and hydrocarbons in double glazing and brake system and the dry of industrial gases. In a similar way zeolites can absorb ions and molecules and thus act as a filter for odor control, toxin removal and as a chemical sieve.

1. Commercial and Domestic

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules, as traps for molecules so they can be analyzed. Zeolites have the potential of providing precise and specific separation of gases including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include: noble gases, N_2, and formaldehyde (http://www.mineralszone.com/minerals/zeolites.html, 2005).

2. Petrochemical industry

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogen forms of zeolite are prepared by ion-exchange which is powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. Catalytic cracking uses a furnace and reactor. First crude oil distillation fractions are heated in the furnace and passed to the reactor. In the reactor the crude meets with a catalyst such as zeolite. It goes through this step three times, each time getting cooler. Finally it reaches a step known as separator. The separator collects recycled hydrogen. Then it goes through fractionators and becomes the final item (http://www.chemguide.co.uk/physical/catalysis/petrochem.html, 2002).

3. Agriculture

In agriculture, zeolites are used as a soil treatment. It provides a source of potassium. The zeolite can serve a similar function of fertilizer and micronutrients. Zeolites can also act as water moderators, in which they will absorb up to 55% of their weight in water and slowly release it under plant demand. This property can prevent root rot and moderate drought cycles (http://www.zeolite.ca/agriculture.htm, 2007).

4. Heating and refrigeration

Zeolites can be used as solar thermal collectors and for adsorption refrigeration. In these applications, their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability is exploited. This hygroscopic property coupled with an inherent exothermic reaction when transitioning from a dehydrated to a hydrated form (heat adsorption), make natural zeolites effective in the storage of solar and waste heat energy (http://www.mineralszone.com/minerals/zeolites.html, 2005).

5. Detergents

The largest outlet for synthetic zeolite is the global laundry detergent market. This amounted to 1.44 million metric tons per year of anhydrous zeolite A in 1992**.** Zeolite is used as an ion exchange agent in detergents. Ion exchange agents are chemicals which enhance the cleaning efficiency of surfactants. As an effective and universally accepted environment friendly substitute of zeolite provides the much needed mobility and exchange of certain dissolved ions like calcium and magnesium in hard water. Calcium and magnesium which interfere with the cleaning efficiency of surfactants are removed by zeolite enabling surfactant to clean linen better. The greater calcium and magnesium ion exchange ability of zeolite comes from its unique Sieve like structure. Zeolite depletes calcium ion concentration to 2% of its original level within one minute and magnesium ion within 10 minutes of an average wash cycle (Sekhon B.S. and Manjeet K. S., 2004).

6. Environmental Applications

Many of the gains made by the current generation of environmental technologies are being offset by the growth of industrialized populations. Consequently, new and creative pollution prevention and abatement methods are under investigation. The unique properties and selectivity of zeolites can provide effective solutions for environmental pollution by minimizing the production of pollutants and by secondary treatment of the effluents produced. Several areas in which zeolites show strong environmental potential are (R.G. Bell, 2001):

- Reduction of atmospheric NOx and VOC's
- Process improvements in the chemical industry

2.2.5 Zeolite Market

Zeolite worldwide market is a huge one: the total zeolite market is around 4 - 8 ML MT per year, among which 1 - 2 ML are synthetic zeolite. Figure 2.5, 86% of synthetic zeolite is use in detergent, 10% are catalyst and 4% are adsorbent material.

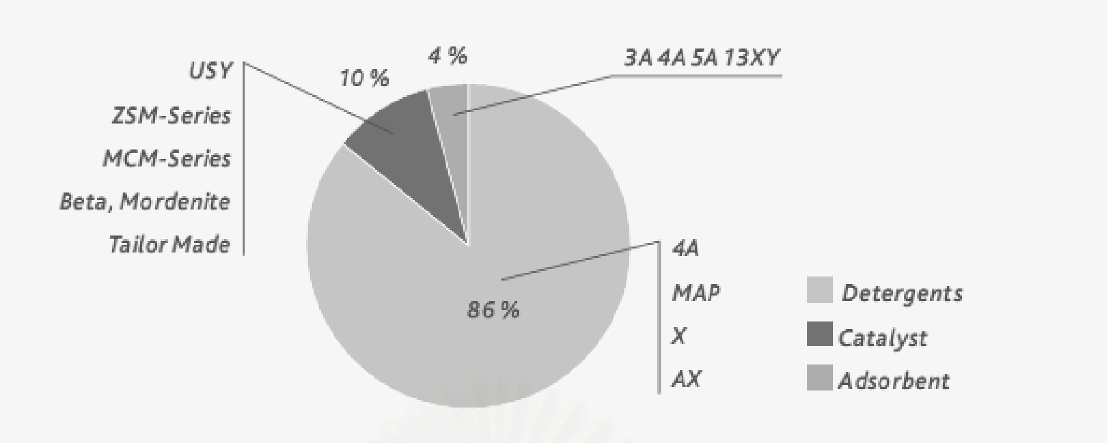


Figure 2.5 Synthetic zeolite world market (Sasol Olefins & Surfactants, 2007)

The largest catalyst market for synthetic zeolites, fluid catalytic cracking (FCC) recently saw the replacement of rare earth zeolites Y with ultra stable zeolites Y: the result is a higher zeolite content in FCC catalysts due to the lower activity of the ultra stable zeolite Y. The total world consumption of FCC catalysts is around 250,000 - 300,000 tons per year and their zeolite content ranges between 5-50%.

The detergent application accounts for around 90% of total synthetic zeolite production, exceeding the 1.2 million ton for year in the world. Sodium zeolite A was developed as a builder for detergents in the early 1970s, and soon as become the builder of choice in laundry detergents. The chronology of the development of detergent builders is given in Table 2.4.

Table 2.4 Chronological development of zeolite builder for detergent

Builder	Year
Zeolite A + triphosphate	1976
Zeolite A + Carbonate + Polycarboxylates	1983
Zeolite A + Crystalline disilicates + polycarboxylates	1994
Zeolite P + Carbonate + Citrate or Polycarboxylate	1994
Zeolite X + Carbonate + Citrate or Polycarboxylate	1997
Zeolite AX (Zeolite X (80%) + Zeolite A (20%)	Recent development

Source: Sekhon B.S. and Manjeet K. S., 2004

2.3 Lead

Lead is transitional element with a symbol Pb. It is a soft and heavy toxic and malleable poor metal. Lead is a toxic metal that was used for many years in products found in and around our homes. Lead may cause a range of health effects, from behavioral problems and learning disabilities, to seizures and death. Children six years old and under are most at risk.The basic information, usefulness in manufacture, adverse effect, and treatment of lead is show in Table 2.5. Lead is a highly toxic metal found in small amounts in the earth's crust. Because of its abundance, low cost, and physical properties, lead and lead compounds have been used in a wide variety of products including paint, ceramics, pipes, solders, gasoline, batteries, and cosmetics. Since 1980, federal and state regulatory standards have helped to minimize or eliminate the amount of lead in consumer products and occupational settings.

Today, the most common sources of lead exposure in the United States are lead-based paint in older homes, contaminated soil, household dust, drinking water, lead crystal, and lead-glazed pottery. While extreme lead exposure can cause a variety of neurological disorders such as lack of muscular coordination, convulsions and coma, much lower lead levels have been associated with measurable changes in children’s mental development and behavior. These include hyperactivity; deficits in fine motor function, hand-eye coordination, and reaction time; and lowered performance on intelligence tests. Chronic lead exposure in adults can result in increased blood pressure, decreased fertility, cataracts, nerve disorders, muscle and joint pain, and memory or concentration problems (ATSDR, 2007).

Table 2.5 The information of lead

Information	Lead
Basic information	
Symbol	Pb
Atomic Number	82
Atomic Mass	207.2 g/mol
Atomic Radius	180 pm
Classification	Post-transition metals or poor metals
Color	Gray
Predominant form	Pb^{2+} or Pb(II)
Number of Proton	82
Number of Neutron	125
Density at 293 K	$11.34\ g\cdot cm^{-3}$
Melting Point	600.61 K or 327.46 °C or 621.43 °F
Boiling Point	2022 K or 749 °C or 3180 °F
Heat of fusion	$4.77\ kJ\cdot mol^{-1}$
Heat of vaporization	$179.5\ kJ\cdot mol^{-1}$
Heat capacity(25 °C)	$26.650\ J\cdot mol^{-1}\cdot K^{-1}$
Half-life	~53,000 years
Natural Source	Mine with zinc, silver and copper The main lead mineral galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$).

Table 2.5 The information of lead (cont.)

Information	Lead
Usefulness in manufacturing	ceramics, pipes, solders, gasoline, batteries, dyes, pigments, paint ,construction material, electrolysis, glassware sheeting, cables, solders, bearings, and cosmetics
Adverse effect	
Chronic exposure	Cancer, Damage the blood forming, nervous, urinary and reproductive systems
Acute exposure	Brain disease may progress to seizure, coma, and death from cardiovascular arrest
Treatment	Chemical precipitation, Ion exchange, Reverse osmosis, Solvent extraction and Adsorption
US-EPA Standard	
Drinking water	0.015 mg/L
Thailand Standard	
Drinking water	0.05 mg/L
Effluent water	0.2 mg/L

Source: Wikipedia, 2008; Lenntech, 2008; US-EPA,2008; PCD,2008; Ruangchuay S., 2005; Riaz Q. , Sohail A., 2005

The adsorption technique has a definite edge over the other techniques. In water containing carbon dioxide and sulfate, solubility of lead is very low (1g/L at pH 8.5-11). At constant pH, the solubility of lead decrease with increase alkalinity. Normally, lead is extremely insoluble, and is present as immobile compounds in the environment. Lead compounds are generally soluble in soft, slightly acidic water. Figure 2.6 show predominance diagram in aqueous solution of lead species.

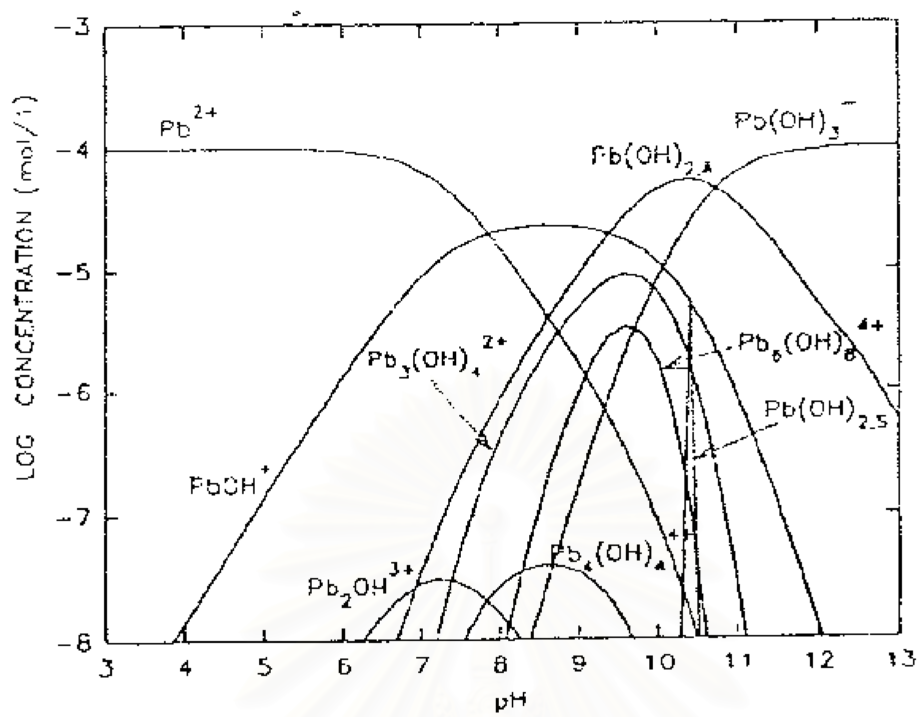


Figure 2.6 Predominance diagram in aqueous solution of lead species (Herreta Urbina and Fuerstenau., 1995)

2.4 Adsorption

2.4.1 Theory of adsorption

There are two basic methods for removal of solids from wastewater. These can be most easily grouped as biological conversion and non-biological or physical -chemical removal processes. One of the physical-chemical processes in use is adsorption.

The phenomenon of absorption was first observed by C.W. Scheele for gases in 1773.Subsequently it was also observed for solutions by Lowitz in 1785. Further significant work in this field was done by Kraemer (1930).

The term sorption, which includes both adsorption and absorption, is a general expression for a process in which component moves from one phase to be accumulated in another, particularly for cases in which the second phase is solid. Adsorption involves the inter-phase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases such as liquid-liquid, gas-liquid, gas-solid or liquid- solid interfaces. In wastewater treatment, we are more concerned with liquid-solid interface.

It is now recognized as a significant process in most of the water, waste water and air treatment technologies. Adsorption on solids particularly on activated carbon has become a widely used operation for purification of water and wastewater. The material which gets adsorbed is adsorbate and the material responsible is adsorbent.

2.4.2 Causes and types of adsorption (Weber, Walter J., 1972, Benefield, Larry D. *et.al*., 1982)

Adsorption from a solution onto a solid occurs as a result of one of the two characteristic properties for a given solvent-solute-solid system or a combination thereof. The primary driving force for adsorption may be consequence of Lyophobic (solvent disliking character) of the solute relative to the particular solvent or of high affinity of the solute for the solid. For majority of the systems encountered in water and wastewater treatment practice, adsorption results from the combined action of the two forces.

The degree of solubility of a dissolved substance is the most significant factor in determining the intensity of the first of the two above forces. Here, "Degree of solubility" can be thought of as the extent of chemical compatibility between the solvent system and a solute.

The more substance likes the solvent system (the more hydrophilic in the case of aqueous solution) the less likely it is to move towards an interface to be adsorbed. Conversely, Hydrophobic i.e. water disliking substances are more likely to be adsorbed from aqueous solution. A large no of organic contaminants have a molecular structure which is made up of both hydrophilic and hydrophobic groups. In this case, the hydrophobic part of the molecule tends to be active at the surface and undergo adsorption, whereas the hydrophilic part tends to stay in the solution phase if at all possible.

The second primary driving force for adsorption results from a specific affinity of the solute for the solid. According to the most plausible of present concepts adsorption, this surface phenomenon may be predominately one of electrical attraction of the solute to the adsorbent, of Van der Waals attraction, or of a chemical nature. The first type falls within the reaction of ion-exchange and is often referred to as exchange adsorption. Exchange adsorption is a process in which ions of one substance concentrate at surface as a result of electrostatic attraction to charged sites.

Adsorption occurring as a result of Van der Waals forces is generally termed physical adsorption. If the adsorbent undergoes chemical interaction with the adsorbent the phenomenon is referred to as chemical adsorption or chemisorptions.

Most adsorption phenomena are combination of the three forms of adsorption, i.e. the several forces which influence different types of adsorption often interact to cause concentration of a particular solute at an interface. Thus it is generally not easy to distinguish between physical & chemical adsorption.

2.4.3 Adsorption mechanism

There are essentially three consecutive steps in the adsorption of materials from solution by porous adsorbents such as granular activated carbon. These are explained as follows:

1. Flux diffusion

This is the first step in the adsorption process. It is the transport of the adsorbate through a surface film to the exterior of the adsorbent. Film, penetration, boundary layer, and other theories have been postulated to explain mass transfer in the region separating a turbulent bulk solution and a solid surface. However, the fluid mechanics of this region are not well defined. Boundary layer theory accounts for a velocity distribution and is more realistic than film theory, which assumes a laminar film surrounding the particle. The term “Film Diffusion” is used generally to describe the resistance to mass transfer at the surface of the particle. However, use of this term is not intended to imply the existence of a definable film nor is it meant to restrict treatment of the data to the film theory.

2. Pore diffusion

The second of the three consecutive steps in sorption by porous adsorbents, with the exception of a small amount of adsorption that occurs on the exterior surface of the adsorbent after transport across the exterior film, is the diffusion of the adsorbate within the pores of the adsorbent.

3. Uptake

The final step in adsorption of the solute is on the interior surfaces bounding the pore and capillary spaces of the adsorbent.

2.4.4 Factors of adsorption

There are six factors for adsorption process (Weber, Walter J., 1972, Benefield, Larry D. *et.al.*, 1982)

1. Surface area

Adsorption is a surface phenomenon, as such the extent of adsorption is a property of specific surface area. A specific surface area can be defined as that portion of total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of a solid adsorbent is greater when the solid is more finely divided and the more porous.

Since the extent of surface reaction will vary with available surface area, adsorption rate should exhibit a monotonic increase with some function of the inverse of the diameter of the adsorbent particles. It the mechanism of uptake is one adsorption on external sites of a non-porous adsorbent, the rate should vary reciprocally with 1st power of the diameter, for a given mass of adsorbent.

The adsorption capacity of a non porous adsorbent should also vary as the inverse of the particle diameter, which for highly porous adsorbent should be relatively independent of particle diameter. However, for porous material such as activated carbon, the breaking up of large particles to form smaller particles can in some situation serve to open some tiny sealed channels in the carbon, which might then become available for adsorption.

Both the rate and extent of adsorption by particle of a fixed size should vary approximately linearly with the dosage of adsorbent over a range of doses that do not result in great differences in the concentration of solute remaining in bulk solution phase. If there are large differences in the concentration of residual solute, then it is necessary to introduce a second variable for both rate and capacity for adsorption.

2. Nature of adsorbent

As we have seen earlier, the hydrophobic or hydrophilic property and the solubility of a solute are to a large extent controlling factors for adsorption equilibrium. The effect of a solute’s chemical character on its uptake from solution can be described by two related general rules.

Lundelius’ rule: According to Lundelius the extent of adsorption of a solute is inversely proportional to its solubility in the solvent from which adsorption occurs. This can be explained by postulating the necessity of breaking some form of solute-solvent bond before adsorption can occur. The greater the solubility is the stronger the solute-solvent bond and smaller the extent of adsorption. However there are exceptions to Lundelius rule.

Traube’s rule: This is a special case of Lundelius rule. The solubility of any organic compound in water decreases with increasing chain length because the compound becomes more hydrocarbon-like as the number of Carbon atoms become greater. Adsorption from aqueous solution increases as a homologous series is ascended, largely because the expulsion of increasingly large hydrophobic molecule from water permits an increasing number of water-water bonds to reformed.

Molecular size: It is also of significant importance, as it relates to rate of uptake of organic solutes by porous active carbon if the rate is controlled by intra particle transport. In this case the reaction generally will proceed more rapidly, the smaller the adsorbate molecule within a given class of compound.

Many components of water and wastewater either exist as or have the potential of existing as ionic species. Acids such as sulphonated alkylbenzenes, fatty acids, phenolic species, amines and many pesticides are a few of the materials and classes of materials which have the property of ionizing under appropriate pH condition. It is seen that with increasing ionization the adsorption of many different types of organic acids is decreased.

The bulk of observations relative to ionization effects on adsorption seem to make a generalization that as long as the compounds are structurally simple, adsorption is less for charged species and more for neutral species. As compounds become more complex the effect of ionization goes on decreasing.

A general rule for prediction of the effect of solute polarity on adsorption is that a complex polar solute will prefer the phase which is more polar. In other words a polar solute will be strongly adsorbed from a non-polar solvent by a polar adsorbent, but will much prefer a polar solvent to a non-polar adsorbent.

3. pH

The pH of a solution from which adsorption occurs may, for one or more number of reasons, influence the extent of adsorption Since hydrogen and hydroxide ions are adsorbed quite strongly the adsorption of other ions is influenced by the pH of the solution. Also since the degree of ionization governs the adsorption, the pH has a significant effect.

In general adsorption of a typical organic solution from water is increased with decreasing pH. In many cases this may result from neutralization of negative charges at the surface of carbon with increasing hydrogen ion concentration thereby reducing hindrance to diffusion and making available more of the active surface of the carbon. This effect varies with different types of the carbon because the charges at the surfaces of carbon depend on the composition of raw materials and the technique of activation.

4. Temperature

Adsorption reactions are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature. Small variations in temperature tend not to alter the adsorption process to a significant extent.

The total amount of heat evolved in an adsorption of a definite quantity of solute on an adsorbent is termed as heat of adsorption DH. While the temperature dependence of equilibrium capacity for adsorption is defined by the parameter DH the dependence of rate of adsorption is expressed in terms of activation energy $E_{a.}$ Although energy parameters E_a and DH are useful tools for delineating the nature of adsorption mechanisms, normal temperature variations generally have only minor effects on adsorption process in water and wastewater treatment.

5. Adsorption of Mixed Solutes

In the adsorption of water and wastewater the material to be adsorbed commonly will be a mixture of many compounds rather than a single one. The compounds may:

1. Mutually enhance adsorption
2. Act relatively independently
3. Interfere with one another.

Mutual inhibition of adsorption capacity can be predicted to occur provided:

1. Adsorption is confined to a single or a few molecular layers
2. Adsorption affinities of the solutes do not differ largely
3. There is no specific interaction between solutes enhancing adsorption.

Mutually depressing effects on rates of adsorption can be predicted because the adsorption of one substance will tend to reduce the number of open sites, and the "concentration" of adsorbent available as a driving force to produce adsorption of the other substance reduces.

Experimental data obtained for both rates of adsorption and adsorption capacities on carbon for mixed solutions indicate that each solute competes in some way with the adsorption of the other.

6. Nature of the Adsorbent

The physico-chemical nature of the adsorbent has profound effects on both rate and capacity of adsorption. Every solid is a potential adsorbent, but the surface characteristics of each material make it different and also decide whether or not it is effective.

It is in this context that we must set aside good adsorbents from the rest of the candidates. The surface area of activated carbon is approximately 1000 m^2 /g. Such a high surface area is achieved by activation whose procedure is discussed separately. Alternative adsorbents, i.e. other than activated carbon, have been tried and this project exclusively deals with the study of such adsorbents. These materials can be pretreated coals, fly ash, metal oxides, wood dust, peat, coconut pith, seed shells, etc. It is the common experience of many researchers that though quite effective these alternative materials are generally less efficient in water and wastewater treatment than activated carbon. To focus on this aspect is the very essence of our work.

2.4.5 Rates of Adsorption

There are three consecutive steps in the adsorption of materials from solution by porous adsorbents such as granular activated carbon.

1. The transport of the adsorbate through a surface film to the exterior of the adsorbent.
2. Sorption by porous adsorbents.
3. Adsorption of the solute on the interior surfaces bounding the pore and capillary spaces of the adsorbent.

Under certain operating conditions, the transport of the adsorbate through the "surface film" or boundary layer to the adsorbent is the rate-limiting step (continuous flow systems through carbon beds). If sufficient turbulence is provided, transport of the adsorbate within the porous carbon controls the rate of uptake (batch reactor with a high degree of agitation).

2.4.6 Adsorbents

The properties of commercial porous adsorbent are showed in Table 2.6. Characteristics desirable in an adsorbent include:

1. High selectivity to enable sharp separations
2. High capacity to minimize the amount of adsorbent needed
3. Favorable kinetic and transport properties for rapid adsorption
4. Chemical and thermal stability, including low solubility in the contacting fluid, to preserve the amount of adsorbent and its properties
5. Hardness and mechanical strength to prevent crushing and erosion
6. A free-flowing tendency for ease of filling or emptying vessels
7. High resistance to fouling for long life
8. No tendency to promote undesirable chemical reactions
9. The capability of being regenerated when used with commercial feedstock that contain trace quantities of high-molecular-weight species that are strongly adsorbed and difficult to desorbs
10. Relatively low cost

Table2.6 Representative properties of commercial porous adsorbent

Adsorbent	Nature	Pore diameter, d_p, nm	Particle porosity, ε_p	Particle density, ρ_p, g/cm^3	Surface area, S_g, m^2/g	Capacity for H_2O vapor at 25 °C and 4.6 mmHg, Wt %, (dry basis)
Activated alumina	Hydrophilic, amorphous	1.0 - 7.5	0.50	1.25	320	7
Silica gel:	Hydrophilic - hydrophobic, amorphous					
Small pore		2.2 – 2.6	0.47	1.09	750 - 850	11
Large pore		10.0 - 15.0	0.71	0.62	300 – 350	—
Activated carbon:	Hydrophobic, amorphous					
Small pore		1.0 – 2.5	0.4 - 0.6	0.5 – 0.9	400 – 1200	1
Large pore		> 3.0	—	0.6 - 0.8	200 – 600	—
Molecular-sieve carbon	Hydrophobic	0.2 – 1.0	—	0.98	400	—
Molecular-sieve zeolite	Polar-hydrophilic, crystalline	0.3 – 1.0	0.2 – 0.5	—	600 - 700	20 – 25
Polymeric adsorbents	—	0.4 - 2.5	0.4 – 0.55	—	80 – 700	—

Source: http://www.unisa.net.unisa.edu.au/Information/100050info/01%20-%20Adsorption%20notes.doc. 2008

2.4.7 Adsorption isotherm

At position of equilibrium, there is a defined distribution of solute between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process; it may be a function of the concentration of the solute, the concentration and nature of competing solutes, the nature of the solution, and so on. Adsorption isotherm express the amount of solute adsorbed per unit weight of solids adsorbent as a function of the concentration of solute remaining in solution at equilibrium. Equations that are often used to describe the experimental Isotherm data were developed by Freundlich, Langmuir and Brunauer, Emmett & Teller (BET).

2.4.7.1 Freundlich isotherm

The Freundlich adsorption isotherm is an adsorption isotherm which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. Empirical equation is given in Equation 2.1. This equation is a special case for heterogeneous surface energies. The linear from of the Freundlich isotherm is given by Equation 2.2.

$$Q = K_f C_e^{(1/n)} \qquad 2.1$$

$$\log q = \log K_f + 1/n\ (\log C_e) \qquad 2.2$$

Where q is the amount of sorbate adsorbed per unit weight of adsorbent, C_e is equilibrium concentration of adsorbate in solution and K_f and n are the Freundlich constants that associate with adsorption capacity and adsorption intensity, respectively. The values of $1 < n < 10$ represent favorable adsorption (Treybal, 1988, Daniela s. and Doina B.,2005)

2.4.7.2 Langmuir isotherm

The Langmuir isotherm was developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. The assumptions are uniform energies of adsorption on the surface. Maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface (Weber, Walter J., 1972, Benefield, Larry D. *et.al.*, 1982). Langmuir equation is showed in Equation 2.3. The linearity of Langmuir is Equations 2.3 that is from plotting 1/q vsv1/C_e

$$q = Q_0bC_e / (1+bC_e) \qquad 2.3$$

$$1/q = 1/ Q_0 + 1/b\, Q_0C_e \qquad 2.4$$

Where q is the amount of sorbate adsorbed per unit weight of adsorbent, C_e is equilibrium concentration of adsorbate. Langmuir constant, Q_0 and b are related to maximum adsorption capacity and energy of adsorption through the Arrhenius equation, respectively. Q_0 can be also interpreted as the total number of building site that are available for sorption. When m/x or 1/q is plotted against 1/Ce, a straight line with slope 1/b Q_0 is obtained and intercept is correspond to 1/ Q_0

The essential characteristics of Langmuir isotherm can be expressed in term of a dimensionless separation factor, r, which describes the type of isotherm and is defined by Equation 2.5.

$$r = 1 / (1+bC_0) \qquad 2.5$$

Where b is a Langmuir constant and is the initial concentration of sorbate.

If,	$r > 1$	Unfavorable
	$r = 1$	Linear
	$0 < r < 1$	Favorable
	$r = 0$	irreversible

2.4.7.3 Brunauer, Emmett & Teller (BET) isotherm

Assumptions of Brunauer, Emmett & Teller (BET) isotherm are Uniform energies of adsorption on the surface. (A) A number of layers of adsorbate molecules form at the surface and that the Langmuir Equation applies to each layer. (B) A given layer need not complete formation prior to initiation of subsequent layers; the equilibrium condition will therefore involve several types of surfaces (Weber, Walter J., 1972, Benefield, Larry D. *et.al*., 1982).

CHAPTER III

METHODOLOGY

3.1 Material

Material and chemical use in this study include three types of biomass fly ash, aluminum powder, and synthetic water.

3.1.1 Fly Ash

Biomass ash is the main raw material, Fly ash samples were collected from electrostatic precipitators from TPS power plant at Chachoengsao province. It will be use three different recipes. Each recipe of biomass ash is originate from biomass fuel that shown in table 3.

Table 3.1 Formula of biomass fuel from TPS as of 21/08/2007

Type of biomass	Rice husk	PP#3	PP#4
Rice husk	100%	16%	8%
Bark	0%	31%	33%
Coal	0%	11%	23%
Wood chip	0%	13%	31%
Board residue	0%	6%	0%
Corncob	0%	17%	0%
Wood shavings	0%	3%	0%
Sawdust	0%	3%	0%
Palm residue	0%	0%	5%

Source: Thai Power Supply Co., Ltd., 2007

Biomass fly ash was preserved in suitable containers. They is vary heterogeneous materials. They were dried at 105˚ overnight and sieve to desire particle size of 425 microns before treated with base solution.

3.1.2 Aluminum powder

The formula of aluminum powder is Al_2O_3. It was use as source of aluminum for synthesis zeolite. It is white powdery. It is chemical for analytical grade.

3.1.3 Synthetic water

Synthetic water sample containing Pb(II) was prepared from lead nitrate (Pb(NO3)2). The synthetic water sample was prepared by dissolving known quantity of analytical grade chemical in double distilled water and use as a stock solution. Buffer solution, sodium acetate, was used for contain pH solution on through experiment.

3.2 Experimental Process Diagram

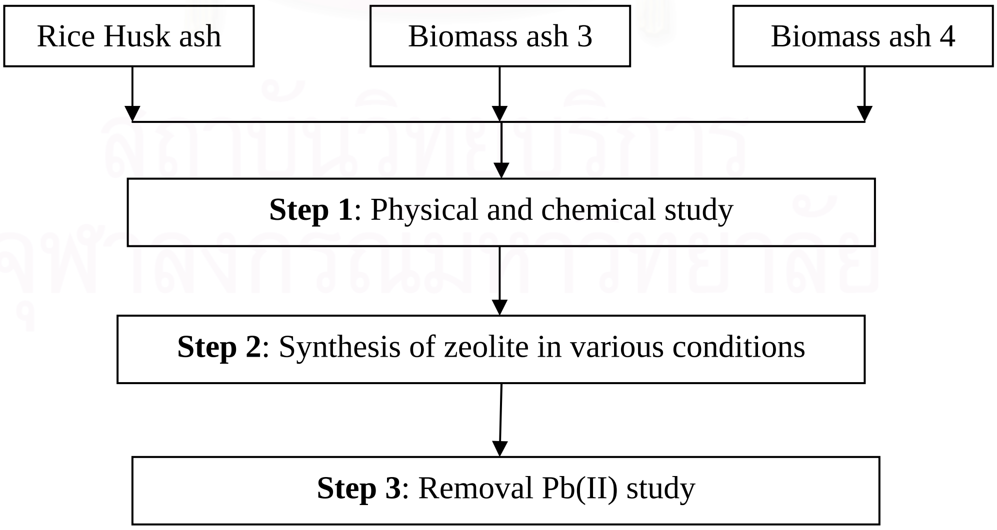


Figure 3.1 Schematic diagram of this research

3.2.1 Study on physical and chemical properties of biomass ash

The physical and chemical properties of ash sample will analyze; Moisture content, loss on ignition (LOI), particle size analysis, chemical compositions, crystal structure, morphology and specific surface area. The methodology is listed as showed in table 3.2

Table 3.2 Methodology for analyzing physical and chemical properties of ash

Parameters	Standard and analyzer
Moisture content	ASTM D2216-98
Loss on ignition (LOI)	ASTM C311-2
Particle size distribution	ASTM D5158-98(2005)
Chemical composition	XRF
Crystal Structure	XRD
Morphology	SEM
Specific surface area	Brunauer–Emmett-Teller analyzer

3.2.2 Study on effect of type of alkaline, concentration of alkaline, temperature, and reaction time for synthesis of zeolite

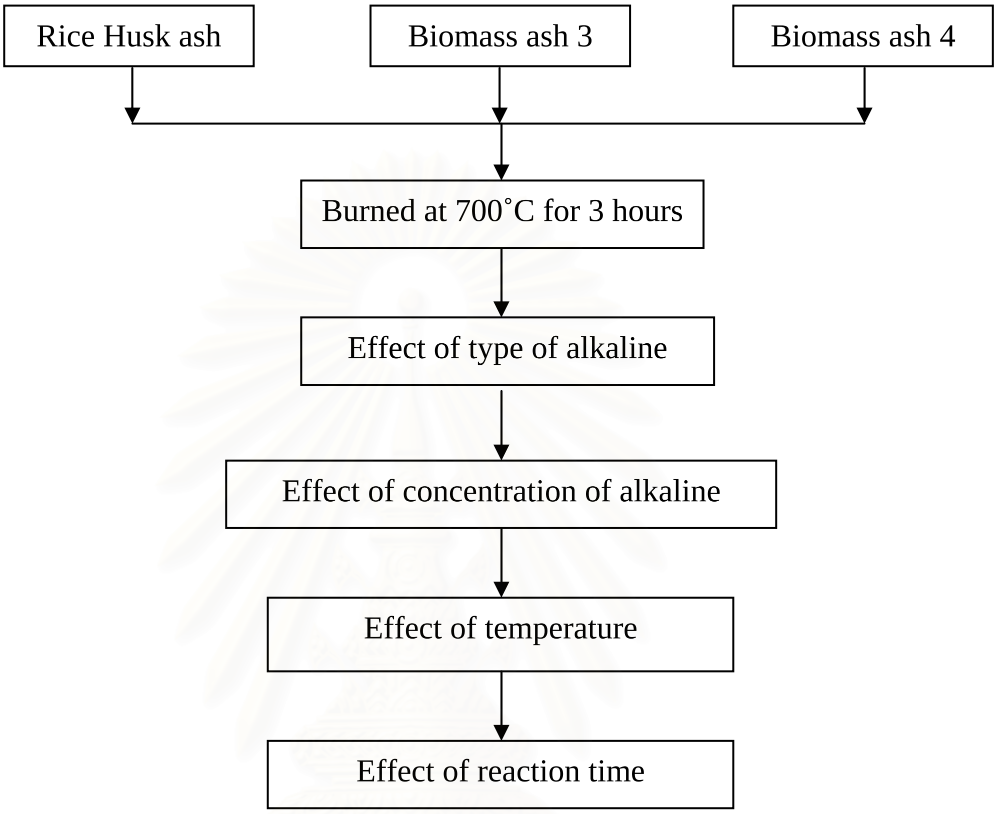


Figure 3.2 Schematic diagram of study effect to synthesis zeolite

Process of zeolite synthesis consists of two parts; part one is sample preparation. Before any treatment, the raw fly ash samples were first be screened through a sieve of 35-mesh size (425 microns) to eliminated larger particles. The unburnt carbon along with other volatile materials present in fly ash was removed by calcination at 700°C for 3 hr. The calcination process was improved amorphous silica structure. Part two is the synthesis of zeolite. The starting materials were ash and aluminum powder of which Si/Al ratio was equal to 1. Therefore, amount of aluminum powder was added depending on amount of silica contained in the ash. These materials could react with alkaline solution and boiled for various periods and stirred in a water bath. After hydrothermal treatment, the reactor was cooled to room temperature. Synthesized products were filtered, washed with distilled water and dried at 105°C overnight. The solid products would be analyzed for cation exchange capacity (CEC) by titration with EDTA. The morphology of the product was identified by XRD and SEM. The specific surface area was analyzed by Brunauer–Emmett-Teller (BET) analyzer. This step was divided into four parts; effect of type of alkaline, concentration of alkaline, temperature, and reaction time. Optimal condition from each step will be used in the next step and will be used for three different ash recipes.

Table 3.3 Conditions for zeolite synthesis

Condition	Part 1	Part 2	Part 3	Part 4
	effect of type of alkaline	concentration of alkaline	temperature	reaction time
Ash	15 g			
Aluminum	Depending on amount of silica in ash			
Alkaline solution	NaOH, KOH	Best alkaline solution from part 1	Best alkaline solution from part 1	Best alkaline solution from part 1
Conc. of alkaline	2M	1, 1.5, 2, 2.5, 3, 5 M	Best Conc. of alkaline from part 2	Best Conc. of alkaline from part 2
temperature	80°C	80°C	70, 75, 80, 99°C	Best temperature from part 3
Reaction time	24 hr	24 hr	24 hr	6, 12, 24, 48, 72 hr

3.2.3 Study on application of synthetic zeolite of removal Pb(II)

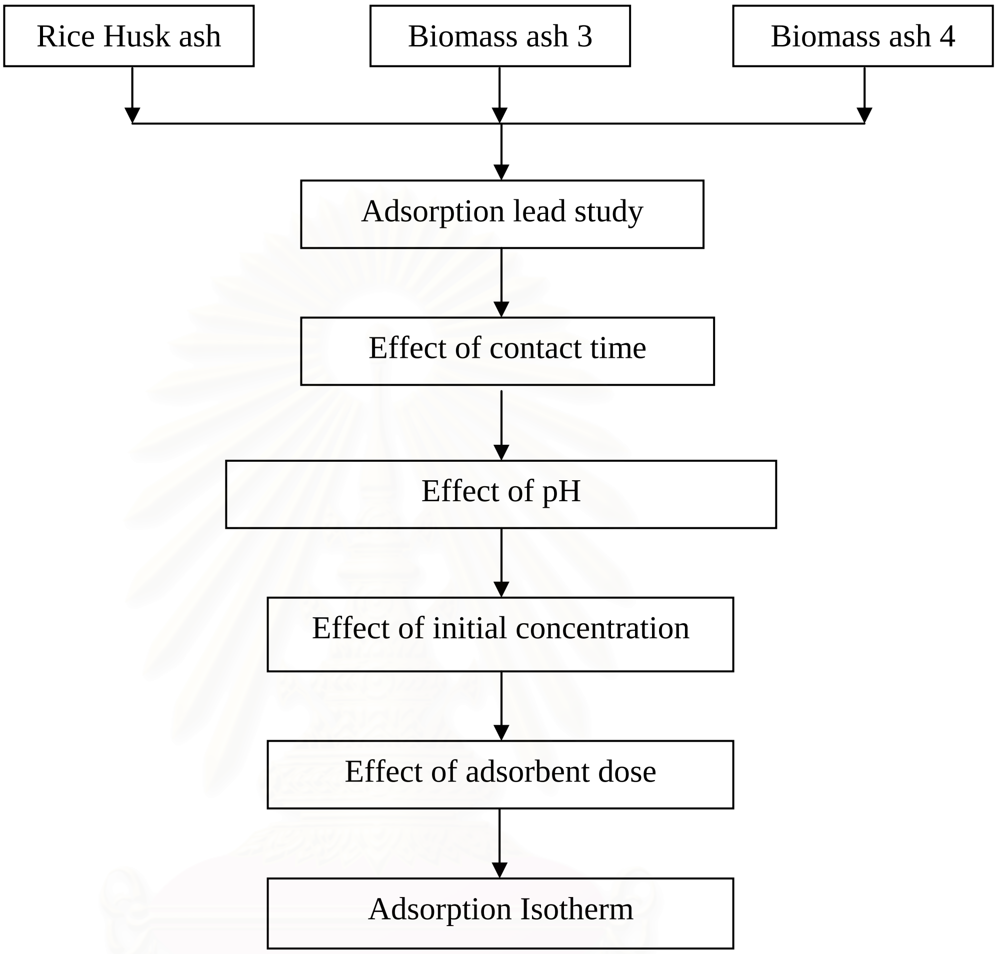


Figure 3.3 Schematic diagram of Pb(II) removal study

Synthetic zeolite is a new and very good filtering medium available for the water purification. The most important property of zeolites is the removal of heavy metals by adsorption and ion exchange. Therefore, this experiment was uses the best of synthetic zeolite for each ash recipe in previous part to adsorb lead of aqueous solution and would be compare them by atomic adsorption (AA) that was used to analyzer. For the conditions were showed in Table 3.4. After that, it was measured pH. It was centrifuged and filtering by Whatman # 42**.** (Kanjana et al., 2007).

Table 3.4 Removal experiments

Factor	Independent variable	Controlled variable
Contact time	3,6,9,12,15,30 min	• Conc. = 10 mg/L • pH = 4 • Dose = 10 g/L
pH	1, 2, 3, 4, 5, and 6	• Conc. = 40 mg/L • Time = optimum • Dose = 10 g/L
Initial concentration	5, 10, 20, 30, 40, 80, 200, 400, 600, 800, and 1000 mg/L	• Time = optimum • pH = optimum • Dose = 10 g/L
Dosage	0.5, 1, 5, 15, and 20 g/L	• Time = optimum • pH = optimum • Conc. = optimum

3.3 Experimental program

3.3.1 Loss on Ignition (LOI)

Loss on Ignition (LOI) is normally used to represent the carbon content in the sample because carbon content will effect to synthesized zeolite. LOI is defined by ASTM C311 as the weight fraction, expressed as percentage, of material that is lost by heating the oven – dried sample at 750 ± 50˚C. LOI is a measurement of unburned carbon remaining in the ash. It can be used as and important indicator of the degree of burnout in material or combustion efficiency.

3.1.2 Particle size analysis

In this study, all three biomass fly ash and zeolite product were subjected to particle size analysis by the air jet sieve method. The air-jet sieve is an instrument using an air-current to agitate the dry sediment particles on the sieve. A single sieve is placed above a rotating vane in an airtight container. The air-jet is blown through the rotating vane and the sieve above the vane. The air and the particles then pass down the sieve on both sides of the vane. The particles are collected on a filter paper. The finest of the sieves is used first and so on until all sieves have been used. The method has been found useful for sieving low density materials and very fine sediments. Materials such as coal, wood and polystyrene particles can be sieved more efficiently.

3.3.3 X-Ray Fluorescence spectrometer

The X-Ray Fluorescence (XRF) method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample, it is the method of choice for field applications and industrial production for control of materials. In this study, raw biomass fly ash was determined the composition of its that use as the raw data for synthesis of zeolite

3.3.4 X-Ray Diffraction spectrometer

X-ray Powder Diffraction (XRD) is an efficient analytical technique used to identify and characterize unknown crystalline materials. Monochromatic x-rays are used to determine the interlunar spacing of the unknown materials. The x-ray spectra generated by this technique, thus, provide a structural fingerprint of the unknown. Mixtures of crystalline materials can also be analyzed and relative peak heights of multiple materials may be used to obtain semi-quantitative estimates of abundances. A glancing x-ray beam may also be used to obtain structural information of thin films on surfaces. In addition, changes in peak position that represent either compositional variation (solid solution) or structure-state information (e.g. order-disorder transitions, etc.) are readily detectable. Peak positions are reproducible to 0.02 degrees. In this research, the analyzer was used to determine the crystal type of raw biomass ash and synthetic zeolite.

3.3.5 Scanning electron microscope

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample. Electronic devices are used to detect and amplify the sign also and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image may be photographed from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor. This research used SEM to scanned the surface of raw fly ash and zeolite product

3.3.6 Specific surface area

Specific surface area is used to represent the fineness of the sample and relate to the rater of interaction with the surrounding. There are several methods to determine it such air permeametry or gas adsorption. This study measured surface area of raw fly ash and zeolite product by Surface Area Analyzer with Brunauer – Emmett – Teller (BET) method

3.3.7 Cation exchange capacity

Cation exchange capacity was determined by exchanging the cation form of material with calcium ion. An accurately weighted sample was stirred with a standard solution of Ca, from CaCl2.H2O dissolved in distilled water and made up to for 15 min and filtered. The filtrate was analyzed for its Ca content by complexometry and the difference is attributed to the exchanged amount.

For the estimation of Ca, the filtrate solution was mixed with 2 ml buffer solution, 5 ml 1 M NaOH, and P&R indicator and immediately titrated with EDTA till the color of the solution changed from pink to blue.

3.3.8 The study of Removal lead

Removal studies were conducted by the batch technique to obtain the data. A series of 50 ml plastic conical tubes were used. The tubes were shaking at room temperature and the shaking speed was 125 rpm. The pH value of solution was adjusted by addition of HNO3 and NaOH. The filtrate was analyzed the lead concentration by AAS. The measurement was made under optimization of wavelength, bandwidth, air/C2H2 flame, detection limit 0.05 mg/L. After adsorption process the filtrate solution was measured pH.

The Adsorption isotherm for Pb(II) onto synthetic zeolite set experiment at the suitable condition found in the experiment. This study used Linear, Langmuir and Freundlich isotherms to describe the lead adsorption onto synthetic zeolite.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Physical and Chemical Characteristic Study

The characteristic of rice husk ash(R), biomass ash 3 (B3) and biomass ash 4 (B4) could be use as general information to determine the possibility of synthetic zeolite. In this study was use material samples from biomass power plant; Thai Power Supply Co., Ltd. in Chachoengsao province, Thailand. Many parameters were presented as follow:

4.1.1 Composition of Ash

The moisture content of ashes are 0.08%, 1.50%, and 1.45% and LOI 4.25%, 5.06%, and 6.11% for Rice husk, Biomass 3, and Biomass 4, respectively. Chemical compositions via XRF analysis are shown in Table 4.1. These have important influence on the potential application of ash. Especially, SiO_2/Al_2O_3 ratio is an important parameter for synthesis of zeolite. It is well known that SiO_2/Al_2O_3 ratio of the precursor solution is crucial to the formation of selected zeolites (Davis, Mark E., Lobo R. F., 1992). The three ash recipes have high SiO_2 but low Al_2O_3. The SiO_2 and Al_2O_3 in the ash might not dissolve completely, therefore the Si/Al ratio in the ash suspension may not be exactly known. To ensure that there was enough Al in the solution, the amount of aluminum added was made equal to unity for synthetic zeolite that has Si/Al ratio of 1.0 by assuming that no Al_2O_3 in ash dissolved but all SiO_2 in ash dissolved. Aluminum powder added was shown in Table 4.2. Crystal structure of three recipes is quartz alpha and cristobalite low that were analyze by XRD. The cation exchange capacity (CEC) of Rice husk, Biomass 3, and Biomass 4 are 7.57, 50.07 and 34.38 respectively.

Table 4.1 Chemical compositions of ash for synthesis of zeolite

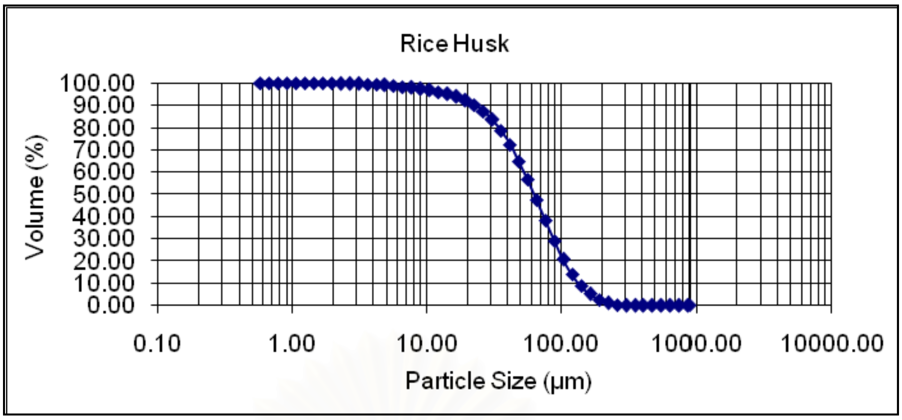
Compounds	Rice husk	Biomass 3	Biomass 4
SiO_2	88.09	73.82	59.67
Al_2O_3	0.19	0.50	7.89
Na_2O	0.07	0.19	0.31
K2O	3.20	4.84	3.99
CaO	0.78	7.10	9.29

Table 4.2 Adding aluminum powder

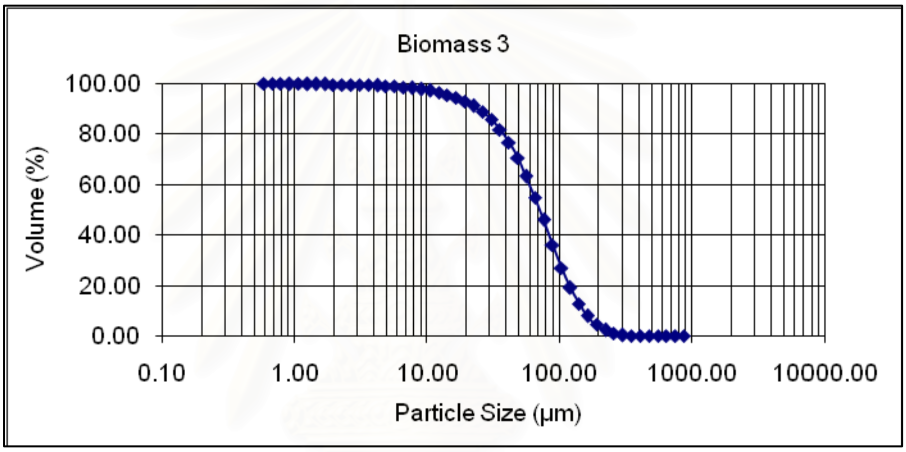
Type of biomass	Amount of aluminum powder (g)
Rice husk	7.14
Biomass 3	6.09
Biomass 4	3.75

4.1.2 Particle Size Distribution

The particle size distribution of rice husk, biomass 3, and biomass 4 ashes were showed in Figure 4.1. Table 4.3 showing particle size of material, indicated that the fineness material was available size according to design.



a



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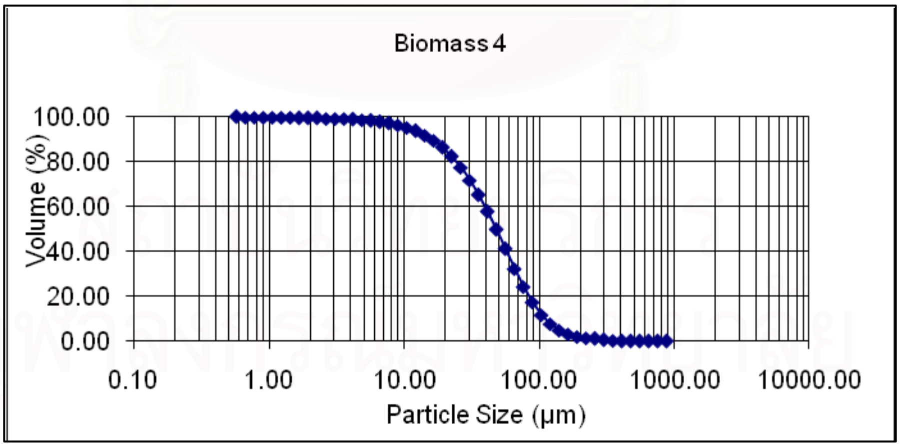


c

Figure 4.1 Particle size Distribution of ash (a) Rice husk (b) Biomass 3 (c) Biomass 4

Table 4.3 Particle size distribution of ashes

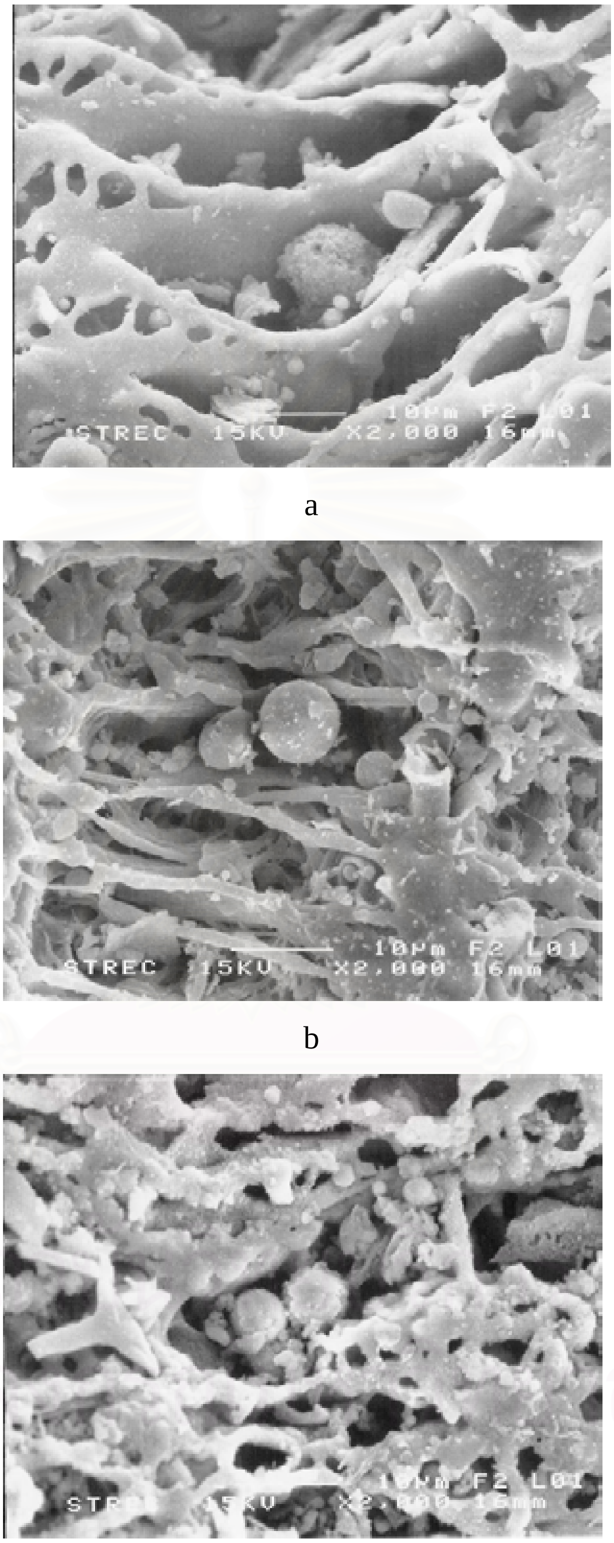
Materials	$d_{50\%}$ (microns)	$d_{90\%}$ (microns)
Rice husk ash	59.14	13.73
Biomass ash 3	71.37	13.55
Biomass ash 4	42.14	8.50

4.1.3 Specific Surface area

From BET analysis results, the specific surface area of rice husk, biomass 3, and biomass 4 ashes are 15.58, 3.78, and 2.44 m^2/g, respectively.

4.1.4 Morphology

Figure 4.2 showed the SEM images of the fly ash at x 2000 magnification for the three difference type; rice husk ash, biomass ash 3 and biomass ash 4, respectively. These photographers clearly revealed the surface texture and different levels of porosity of the material under study. These were evident that the particle of rice husk ash was in form of sheets. For biomass 3 and 4, they had some spherical particle that from coal material. Moreover, they had a lot of branch particle.



a

b

c

Figure 4.2 SEM images (with x 2000 magnification) of fly ash particles (a) Rice husk (b) Biomass 3 (c) Biomass 4

4.2 Synthesis of zeolite

Synthetic zeolites are formed under hydrothermal condition. The term of hydrothermal is used in a broad and includes the crystallization of zeolite from aqueous system which contains the necessary chemical component. Types of synthetic zeolite depend on Si/Al ratio and other conditions that use to synthesize. Synthetic zeolites are suitable for industrial sectors because they are pure and low contaminants. In generally, the important properties of zeolite for commercial aspect are molecular sieve and ion exchange capacity (Breck D.W. C., 1974). Therefore, this research was use cation exchange capacity (CEC) to determine the optimal conditions for synthetic zeolite form biomass ash.

4.2.1 Effect of alkaline

Biomass ash treated with alkaline solution (2 M NaOH or 2 M KOH) was heated at 80˚C for 24 hours. The cation exchange capacity of zeolite products are shown in Figure 4.3 that has direct variation with amount of zeolite product. It can be seen that NaOH was more effective than KOH for all three biomass ash recipes. Because of sodium is main cation composition of LTA which has three forms and zeolite P. Zeolite 3A is the potassium form of the LTA zeolite, having the following composition: $0.4K_2O{\cdot}0.6Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$. Zeolite 4A is the same zeolite, but in the sodium, its formula is: $Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$. Finally, zeolite 5A is the Ca^{2+} exchanged material with the following composition: $0.7CaO{\cdot}0.30Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$ (Beijing Henrky Chemical Materials Co.,Ltd., 2008) Zeolite P is $Na_6(Si_{10}A_{l6}O_{32})\ {\cdot}12H_2O$ that the Na+ exchange material. When ash was treated with KOH and NaOH, they transformed into zeolite 3A, 4A, 5A and P. If they treated with KOH, K_2O is incresing. But they can form in small amount of LTA because the limitation of Na_2O in ash (Table 4.1). The limitation of Na_2O could be eliminated by treating biomass ash with NaOH. Therefore, the quantities of zeolite from treating ash with NaOH have higher than KOH.

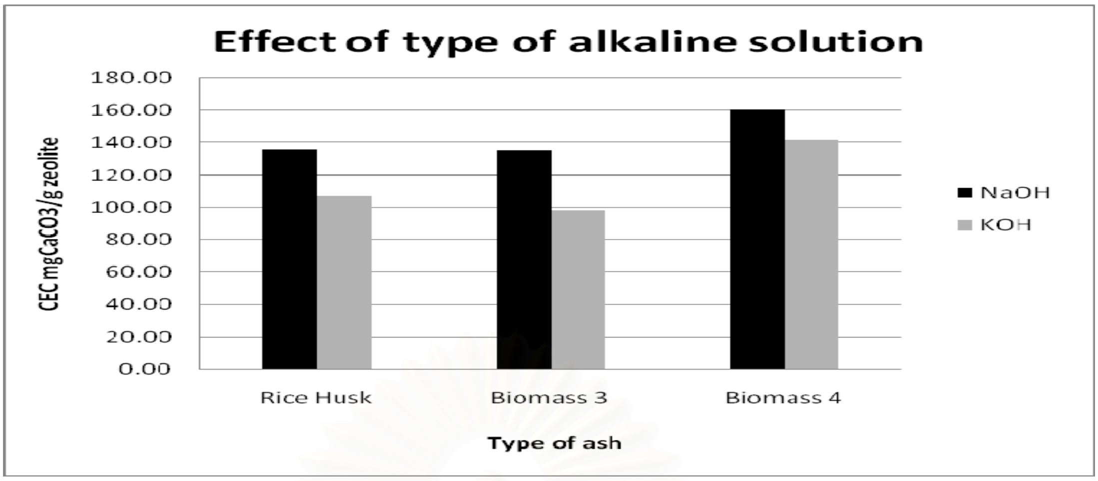


Figure 4.3 The cation exchange capacity of zeolite product of difference alkaline solution

4.2.2 Effect of alkaline concentration

From the previous step, we found that NaOH was suitable for synthesis of zeolite from biomass ash. Moreover, the concentration of NaOH is important to synthesize zeolite. The crystallization of zeolites depends on molar ratios of silica, aluminum and cations. Especially, mole of sodium is more important than other cations because sodium is the main chemical composition for zeolite. Figure 4.4 shows the result of effect of concentration of NaOH determined by CEC. Biomass ash was treated with NaOH in various concentrations and was heated at 80˚C for 24 hours. Rice husk ash contains higher silica content than Biomass 3 and 4. Therefore, it consumed more sodium than other ash. The appropriate concentration for rice husk, biomass3, and biomass4 is 3M NaOH, 2M NaOH, and 2M NaOH respectively. However, the high concentration of NaOH produced excess OH^- concentration. The crystal growth of zeolites would be inhibited by the dissolution stage. Percentage of zeolite crystalline is lower (Breck D.W. C., 1974).

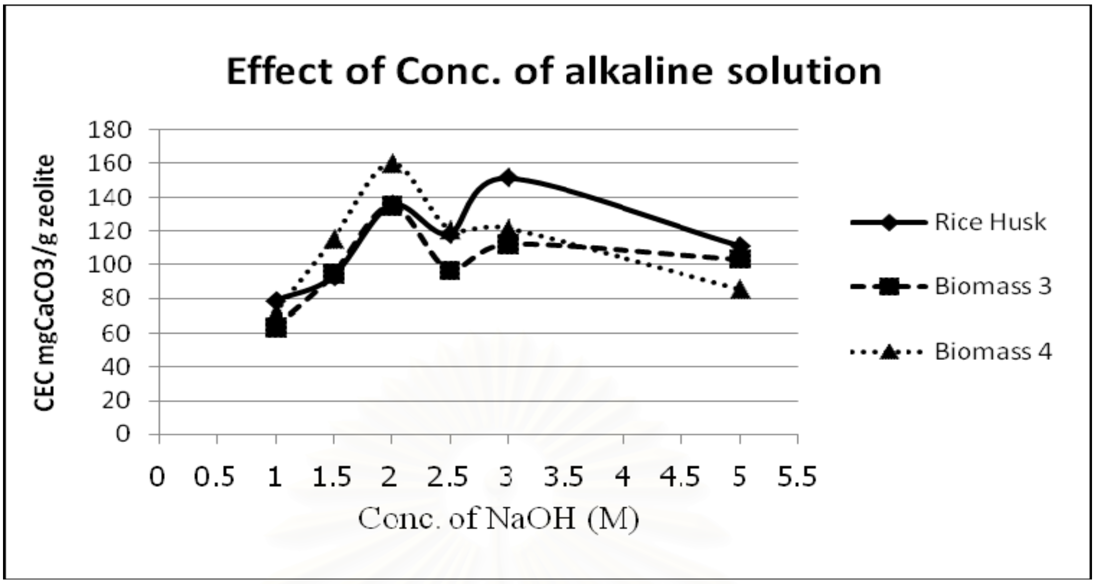


Figure 4.4 The cation exchange capacity of zeolitep of difference concentration of NaOH

4.2.3 Effect of temperature

Another factor that can affect the type of zeolite formed is the curing temperature (Larosa J. L. , Kwan S. , and Grutzeck M. W., 1992). LTA is synthesized at temperature ranging from 25˚C to 150˚C. Zeolite P could be form at 70˚C to 130˚C (Lin CF, Hsi HC, 1995). Normally, its crystalline structures can be formed at 100˚C (Fernandes Machado N. R. C. and Miotto D. M. M., 2005, Tavolaro A., Tavolaro P., 2007). However, the optimal temperature for synthesis of zeolite depends on type of raw materials and the synthesis method. In this research, rice husk and biomass ashes treated with 3M NaOH and 2M NaOH, respectively, were processed at temperature ranging from 70˚C to 99˚C for 24 hr. The results showed the suitable temperature for synthetic zeolite from these ashes is 99˚C which gave highest CEC value (Fig 4.5). The rate of zeolite crystalline increased with temperature increasing, so giving higher CEC value (Breck D.W. C., 1974)

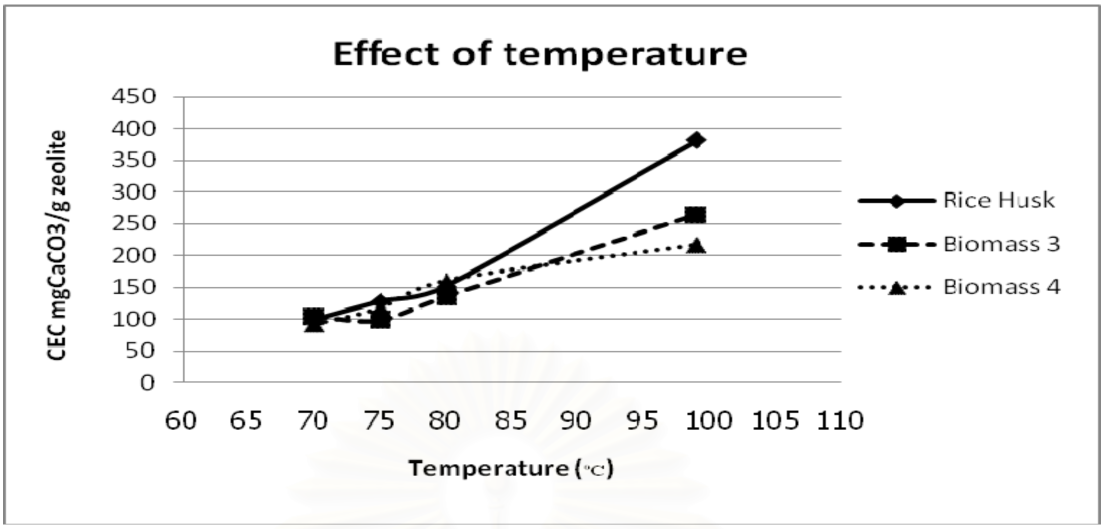


Figure 4.5 The cation exchange capacity of zeolite product synthesized at different temperatures

4.2.4 Effect of reaction time for synthesis of zeolite

The appropriate periods for treating ash in this research are 24 hours (Fig 4.6). The CEC values of treating rice husk ash, biomass 3, and biomass 4 are 381.08, 164.43, 216.96 mg $CaCO_3$/g. The products were analyzed crystal structure by XRF that showed in Figure 4.7. The result showed zeolite P could be synthesized because LTA could be transformed into zeolite P (Breck D.W. C., 1974). Normally, the LTA crystallizes with the aging time varying from 2.5 hours to 14 days. However zeolite A could be change to zeolite P with higher NaOH concentrations, longer reaction times and higher reaction temperatures because of zeolite P is more stable than LTA (Breck D.W. C., 1974).

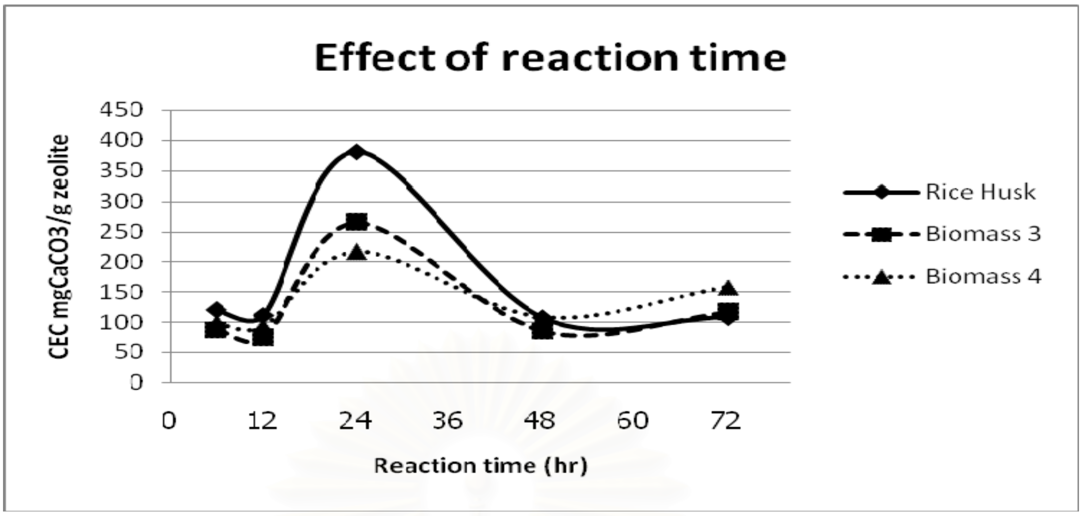


Figure 4.6 The cation exchange capacity of zeolite product of difference crystallization times

4.2.5 The characteristic of Synthetic Zeolite from Optimal Condition

The optimal condition for this research was 3M NaOH for rice husk ash and 2M NaOH for Biomass 3 and 4 at 99˚C for 24 hours. These conditions were gave the product that was determined the structure of product, morphological, Particle size distribution, specific surface area (SSA) and cation exchange capacity (CEC).

4.2.5.1 The Structure of Product

From Figure 4.6 showed the XRD patterns, the treating of three type of biomass ash was converted to zeolite P and contained some quartz from raw material. The Quantitative measure of the crystalline of the synthesized zeolite was made by using the summed heights of major peaks in the X-ray diffraction pattern. The major peaks were selected specifically because they are least affected by the degree of hydration of samples and also by others. Crystalline has been estimated for the synthesized samples by taking the sum of the peak heights of the unknown materials divided by the sum of the peak heights of a standard material that has been assumed to be 100% crystalline i.e. (Keka O., Narayan C. P. and Amar N. S., 2004).

$$\%\ \text{Crystallinity} = \frac{(\text{Sum of the peak heights of unknown material}) * 100}{(\text{Sum of peak heights of standard material})}$$

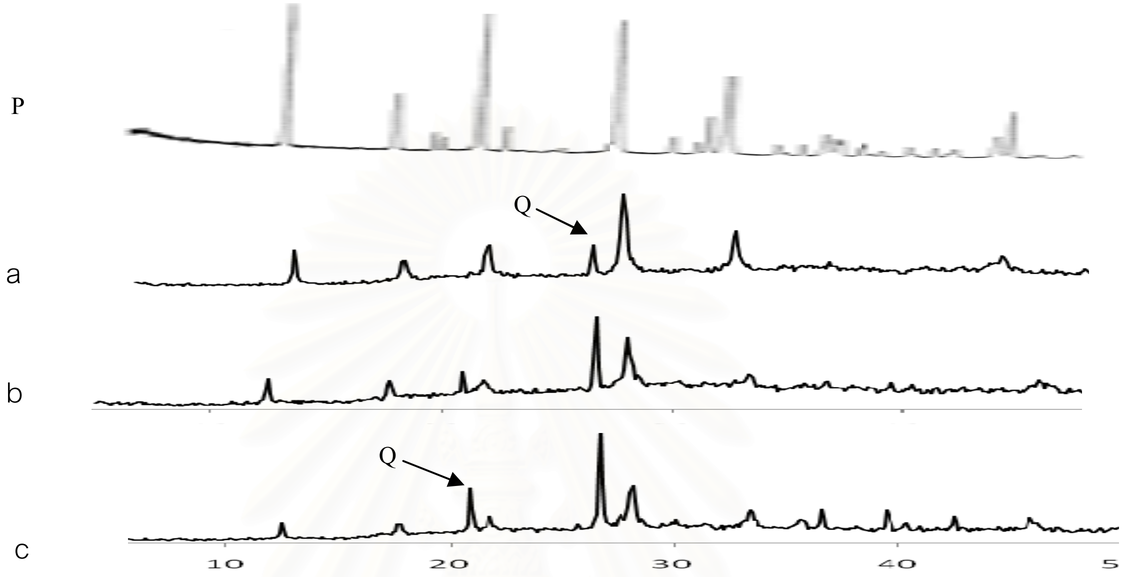
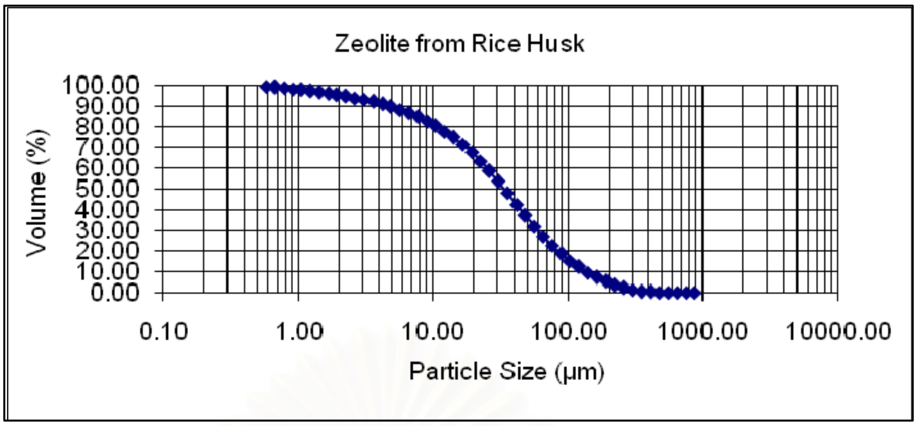


Figure 4.7 XRD pattern of zeolite products a) Rice husk ash, b) Biomass aAsh 3, c) Biomass ash 4. P) standard of zeolite P, Q = Quartz

Therefore, %crystalline of zeolite P were 98.17%, 64.42%, and 62.93% for zeolite from rice husk ash, biomass ash 3, and biomass ash 4, respectively.

4.2.5.2 Particle Size Distribution

Figure 4.8 was exhibited the particle size distributions of synthetic zeolites. The particle size of material was showed in Table 4.3, indicated that the fineness material was available size according to design.



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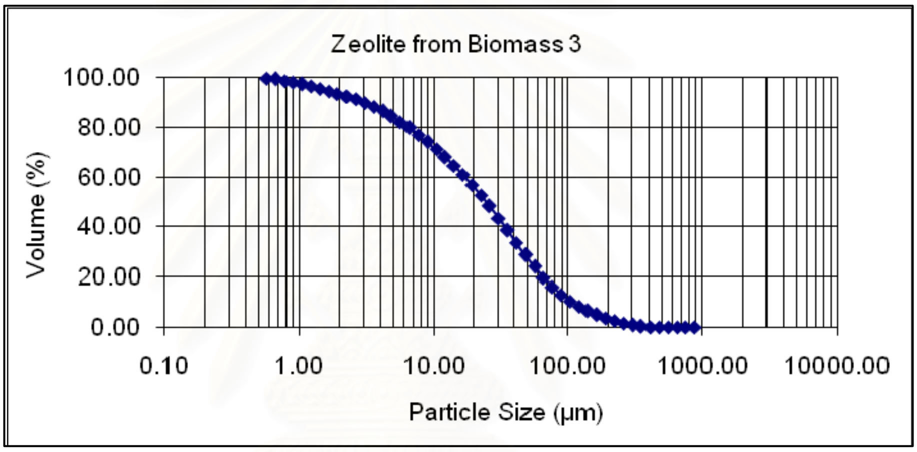

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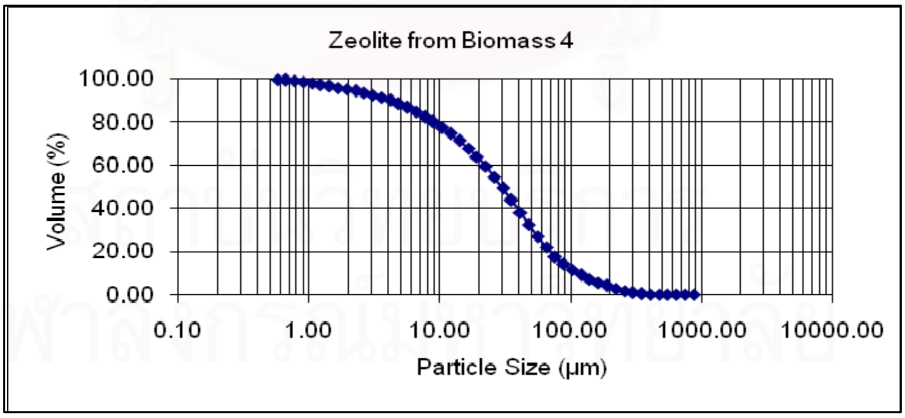

c

Figure 4.8 Particle size sistribution of synthetic zeolite from (a) Rice husk (b) biomass 3 (c) biomass 4

Table 4.4 Particle size distribution of synthetic zeolite

Materials	$d_{50\%}$ (microns)	$d_{90\%}$ (microns)
Zeolite from rice husk ash	32.66	2.96
Zeolite from biomass ash 3	24.23	1.58
Zeolite from biomass ash 4	27.48	2.54

4.2.5.3 Specific Surface Area (SSA) and Cation Exchange Capacity (CEC)

Table 4.5 showed the SSA and CEC value of zeolite products from rice husk ash is higher than biomass 3 and 4. Thus, it is expected that the adsorption of Pb ions will be higher on zeolite from rice husk ash than zeolite from biomass ash 3 and 4

Table 4.5 Properties of zeolite product from ashes

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Materials	SSA (m^2/g)	CEC ($mgCaCO_3/g$)
Zeolite from rice husk ash	99.95	381.08
Zeolite from biomass ash 3	97.18	264.34
Zeolite from biomass ash 4	90.40	216.96

4.2.5.4 Morphology

The SEM image of synthetic zeolites P that fly ash sample treated with NaOH in optimal conditions (Figure 4.9). These photographers revealed the crystal structure of particle of zeolite P from biomass ashes. The crystal structure was not cubic. The particle sizes of ZR is larger than ZB3 but in Figure 4.9a and 4.9b do not followed due to it may be the variation of particle size of sample . For ZB4, The result particle size is moderate compare with other zeolite products. On the other hand in this Figure 4.9c showed smaller crystalline than other one. Because the small crystal of ZB4 was confederated to group of crystals.

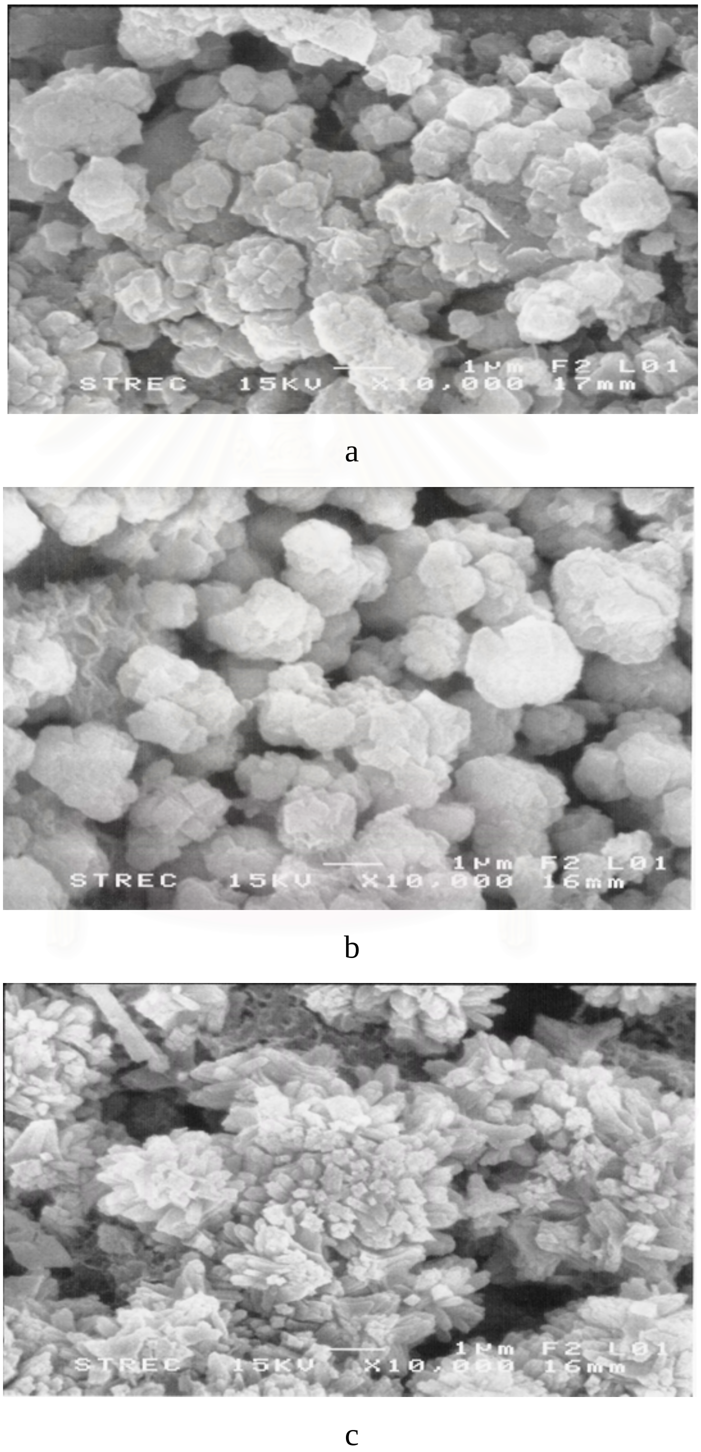


Figure 4.9 SEM images (with x 10,000 magnification) of zeolite particles (a)Rice husk (b) Biomass 3 (c) Biomass 4

4.2.5.5 Yield of zeolite products

Yield calculations are common in chemistry. In order to calculate the theoretical yield, you must first balance the reaction. Then, look closely to determine which reagents are being used in excess and which is the limiting reagent. The overall yield of product depends on the limiting reagent.

After laboratory reaction is complete, they was isolate and measure the amount of product, then compare the actual yield to the theoretical yield to determine the percent yield:

$$\frac{\text{Actual yield (in mole)}}{\text{Theoretical yield (in mole)}} \times 100\% = \%\ \text{yield of product}$$

Calculating percent yield actually involves a series of short calculations. Follow this step-by-step;

- Balance the reaction and determine the stoichiometry or ratios of reactants to products.
- Find the number of moles of each starting material used.
- Determine which reagent is limiting.
- Calculate the moles of product expected if the yield were 100% based on the limiting reagent.
- Calculate the grams of product corresponding to the number of moles expected.

In this study, percent yield of synthetic zeolite P from three types of biomass ash showed in Table 4.6

Table 4.6 % yield of synthetic zeolite P from three types of biomass ash

Materials	% yield of products
Zeolite from rice husk ash	85.19%
Zeolite from biomass ash 3	75.00%
Zeolite from biomass ash 4	63.16%

4.2.6 The comparison between raw biomass ash and synthetic zeolite

The properties of zeolite product compared with raw material that showed in Table 4.7, 4.8, and 4.9. These results are given similar trend for all of them.

The crystalline phases that can be identified in the unmodified fly ash are quartz. These are also present in all the modified ash samples. A secondary phase comprising the zeolite Na-P1 was formed during modification process and can be seen in the 2M NaOH and 3M NaOH-treated samples. Similar observations were made by Singer and Berkgaut (1995), Lin and Hsi (1995), and Querol et al. (1997) who found that zeolite Na-P1 formed at low base concentrations (<3.5 M). Singer and Berkgaut (1995) also noted a decrease in the intensity of the quartz peaks in the XRD pattern as a result of zeolitisation.

The hydrothermal treatment of fly ash with base clearly increases the surface area of the ash. Therefore, synthetic zeolite has higher SSA than raw ash. Lin and Hsi (1995) found a similar increase in SSA although they found the surface area to peak at 3.5M NaOH treatment. The CEC does follow the pattern observed for SSA. But particle sizes are opposite. For morphology, untreated ash are sheets or spherical or branch which become crystal during alkaline treatment.

Table 4.7 The comparison between rice husk ash and zeolite from rice husk ash

Materials	Crystalline Structure	Particle Size (µm)	SSA (m^2/g)	CEC ($mgCaCO_3/g$)	Morphology
Rice husk ash	Quartz alpha Cristobalite low	13.73	15.58	7.57	Sheets
Zeolite from rice husk ash	Quartz Zeolite P	2.96	99.95	381.08	Crystal

Table 4.8 The comparison between biomass ash 3 and zeolite from biomass ash 3

Materials	Crystalline Structure	Particle Size (µm)	SSA (m^2/g)	CEC ($mgCaCO_3/g$)	Morphology
Biomass ash 3	Quartz alpha Cristobalite low	13.55	3.78	50.07	Branch and spherical
Zeolite from biomass ash 3	Quartz Zeolite P	2.96	97.18	264.34	Crystal

Table 4.9 The comparison between biomass ash 4 and zeolite from biomass ash 4

Materials	Crystalline Structure	Particle Size (µm)	SSA (m^2/g)	CEC ($mgCaCO_3/g$)	Morphology
Biomass ash 4	Quartz alpha Cristobalite low	8.50	2.44	34.38	Branch and spherical
Zeolite from biomass ash 4	Quartz Zeolite P	2.54	90.40	216.96	Crystal

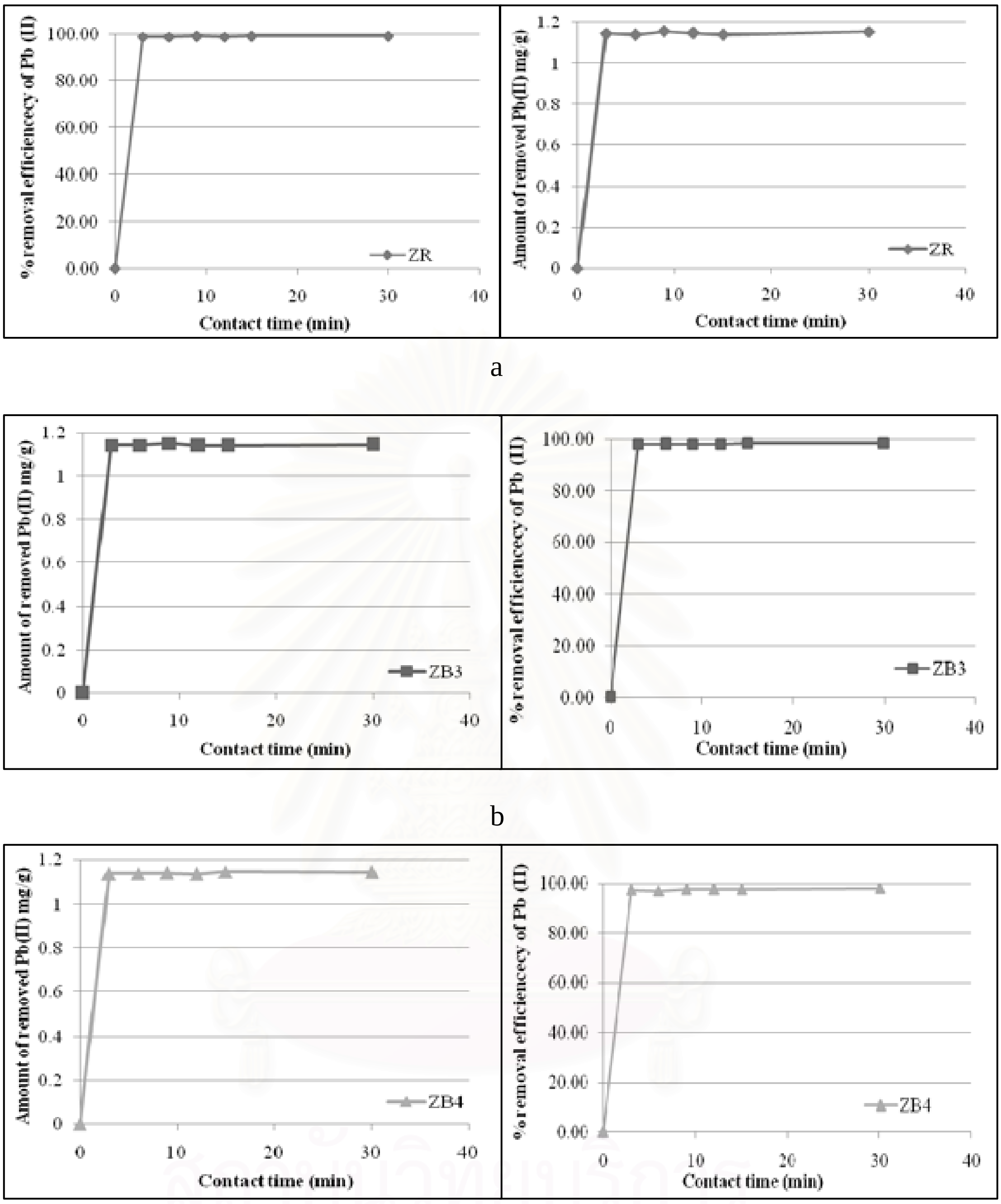
4.3 Removal of lead study

The adsorption process was affected by various parameters such as contact time, pH, concentration of lead solution, and dose of adsorbent. This research was studied these parameters that are given the result as follows:

4.3.1 Effect of contact time

The adsorption for the uptake of lead ions vs. contact time for a fixed adsorbent dose of 10 g/L which were synthetic zeolites from rice husk (ZR), biomass 3 (ZB3) and biomass 4 (ZB4), and with an initial lead ion concentration of 10 mg/L at pH 4.0 are shown in Figure 4.10. These plots indicate that the removal of lead (Pb) and the amount of removal Pb were found to increase with increasing time. After 3 minuets, the removal efficiency of lead was slowly increasing which become constant. The percentages of Pb removal and amounts of removal Pb for all of synthetic zeolite were adsorbed more than 97% and 1.14 mg/g, respectively. Therefore, this study was used contact time of 15 minuets as the equilibrium times for all the next equilibrium experiments at which an equilibrium lead ion concentration (C_e) is presumed to have been attained.

The immobilization of heavy metal ions from aqueous solution on zeolite is complex process consisting of ion exchange and adsorption, since the adsorption kinetics depends on the surface area of the adsorbent, For these reasons, the uptake rate is rapidly to equilibrium. The adsorption of lead ions are quite rapid initially, the rate of adsorption become slower with the passage of time and reaches a constant value. The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents. After the lead ions from bulk solution should travel to the thin liquid film surrounding the adsorbent materials. Then the uptake rate is controlled by the rate which the sorbate is transported from the exterior to interior sites of the adsorbent particle.



a

b

c

Figure 4.10 Effect of contact time on removal of Pb(II) and amount removal of Pb(II) (solution pH 4, Initial Conc. 10mg/L, dose 10 g/L) for (a) Rice husk (b) biomass 3 (c) biomass 4

4.3.2 Effect of pH

The pH level of the aqueous solution is an important variable for the adsorption of metals on the adsorbents. The effect of the pH on the metal adsorption by synthetic zeolite was studied over a pH range of 1-6 for a fixed adsorbent dose of 10 g/L and an initial lead ion concentration of 40 mg/L. The pH was adjusted using dilute nitric acid and sodium hydroxide solutions. The pH was measured before and after the attainment of equilibrium.

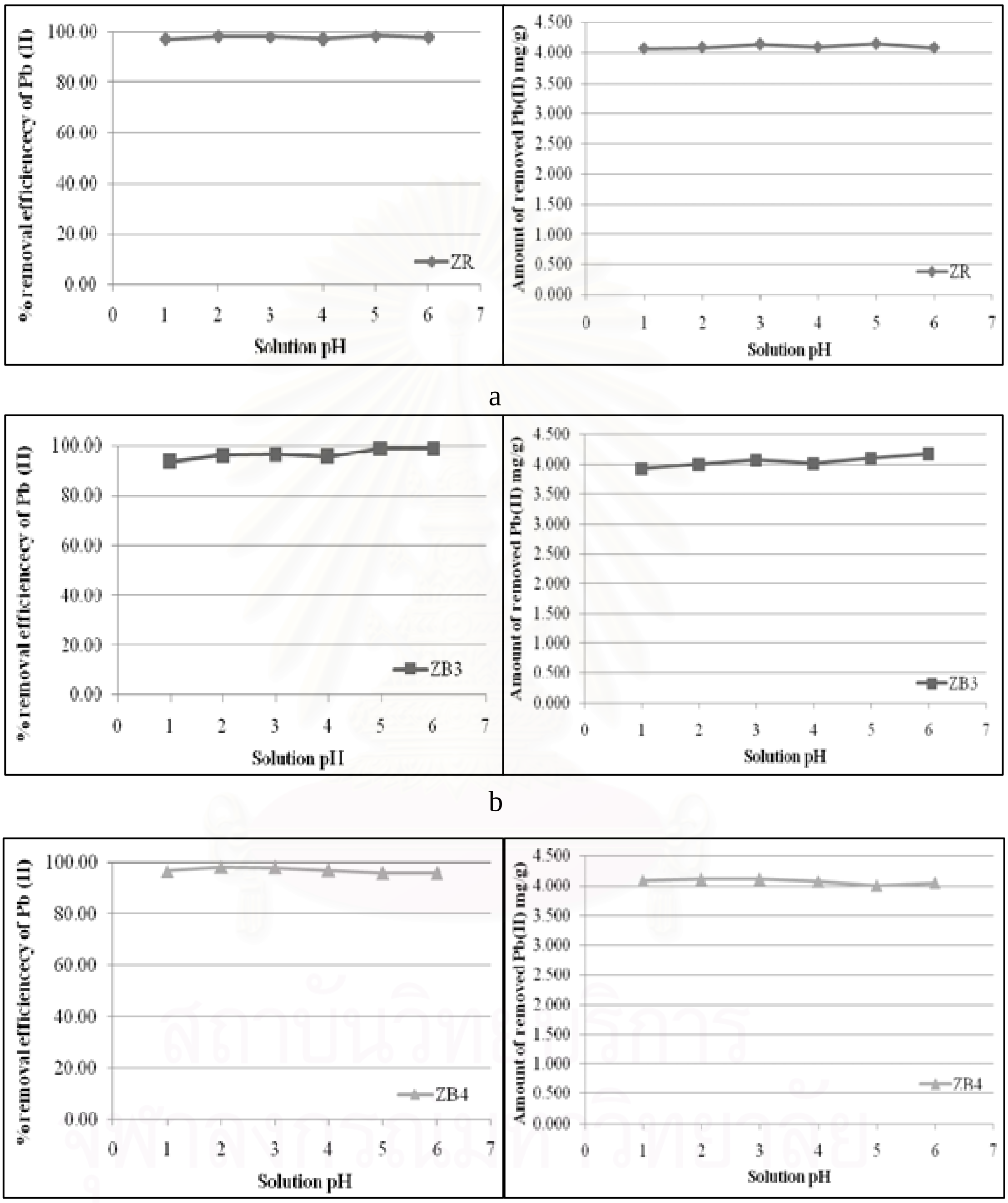
The immobilization of heavy metal ions from aqueous solution on zeolite is complex process consisting of ion exchange and adsorption, likely to be accompanies by precipitation of metal ion hydroxide complexes on active sites of particle surface. Efficiency of metal sorption depends on the pH level of aqueous solution. Metal adsorption decreases with the pH decrease due to competition of hydrogen ions. As the pH level increases the concentration of the hydrogen ions as competitor decreases and this leads to an increase of the amounts of adsorption. This is likely to be via an ion exchange mechanism where the Pb^{2+} cations replace cations in the zeolite structure:

$$\text{Z-Na} + \text{Pb}^{2+} \longrightarrow \text{Z-Pb}^{+} + \text{Na}^{+}$$

Where Z- represents an exchange site in the zeolite framework

As pH increases this exchange equilibrium is pushed to the right in accordance with Le Chatelier’s principle as competition from Na^+ for exchange sites decreases. Thus it is possible to manage metal uptake from aqueous solutions by changing the pH value (Myroslav S., Buszewski B., Artur P.T., Jacek N**.,** 2006)

A general increase in adsorption with increasing pH of solution was observed for the metal ions up to a pH value of 6.0. Beyond this pH the determination could not be performed due to the low solubility of the metal ions. A similar behavior has been reported by many authors (Christensen, 1984; Farrah & Pickering, 1976 a,b, 1979; Netzer & Wilkinson, 1976; Benjamin & Leckie, 1980) for the uptake of metal ions on various adsorbents. It is evident from the results that the pH for maximum uptake of lead is 6.0. But, for this study the initial pH of solution is 5.0 and 6.0 that gave the same results (Figure 4.11). Therefore, the pH value of 5.0 is the equilibrium pH for next experiment. The adsorption efficiency of synthetic zeolite from rice husk, biomass 3 and biomass 4 is 98.45%, 98.85%, and 96.04% and the amount of removed Pb is 4.14, 4.10, and 4.00 mg/g at pH = 5.0, respectively.



a

b

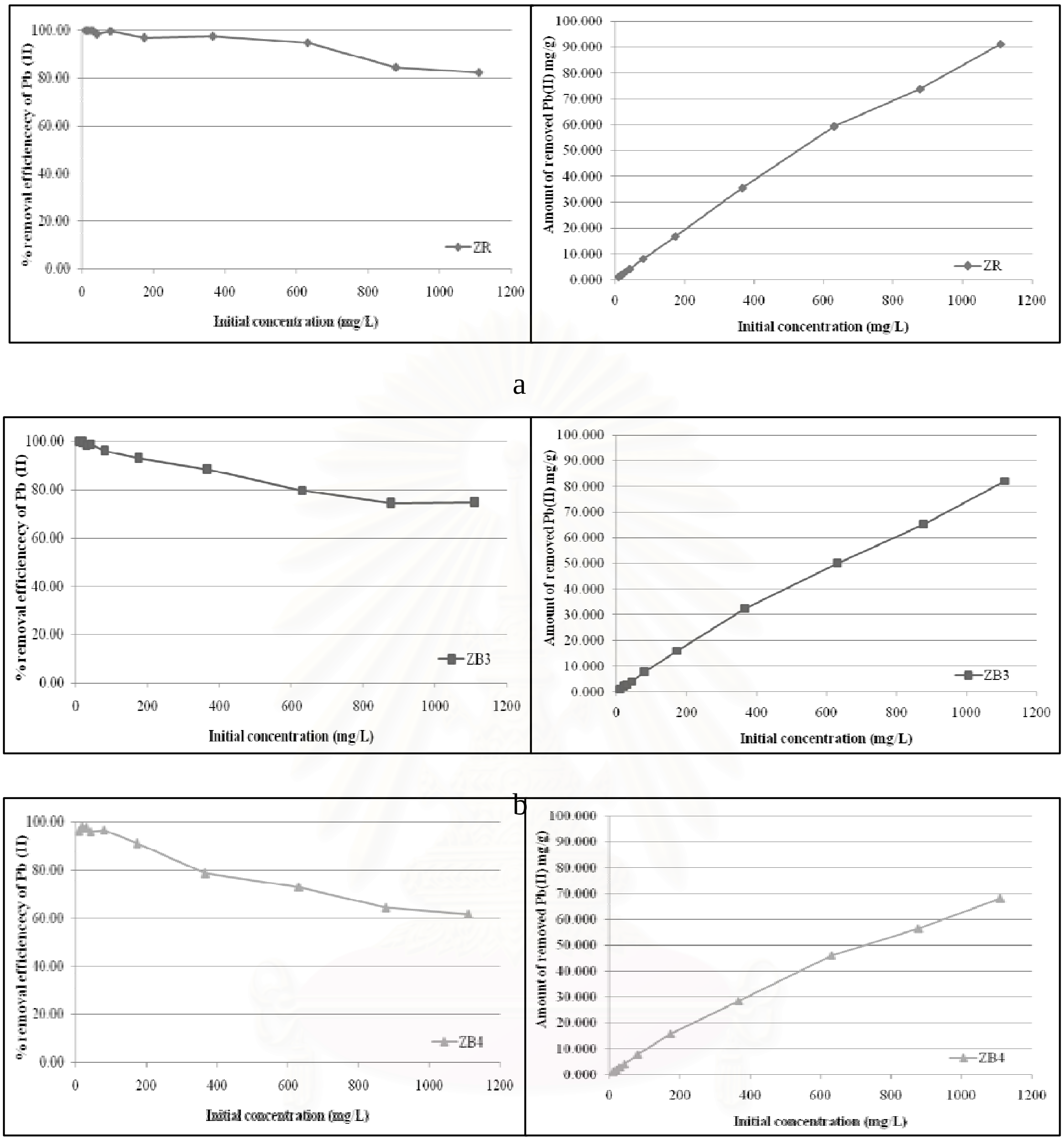
c

Figure 4.11 Effect of pH on removal of Pb(II) and amount removal of Pb(II) (time 15 min, Initial Conc. 10mg/L, dose 10 g/L) for (a) Rice husk (b) biomass 3 (c) biomass 4

4.3.3 Effect of initial concentration

The effect of the initial metal ion concentration (C_0) on the adsorption behavior of lead in this study was conducted with initial metal ion concentrations ranging from 10 to 1000 mg/L with a fixed adsorbent dose of 10 g/L at a pH value of 5.0. Plots were prepared between the metal ions adsorbed versus the equilibrium metal ion concentration (Figure 4.12). It is inferred that for the same equilibrium time. The removal efficiency of Pb ions in solution is from 98.45% (4.14 mg/g) to 82.43% (91.32 mg/g) for ZR with initial concentration of Pb ions varies from 40 to 1000 mg/L, 99.61% (2.00 mg/g) to 74.68% (82.07 mg/g) for ZB3 with initial concentration of Pb ions varies from 30 to 1000 mg/L, and 96.14% (1.08 mg/g) to 61.70% (68.11mg/g) for ZB4 with initial concentration of Pb ions varies from 20 to 1000 mg/L. For ZR, ZB3, ZB4, at initial concentration less than 40, 30, and 20 mg/L, respectively, the equilibrium concentration was less than detection limit of AAS use in the study (0.05 mg/L).

It can be observed that the removal of Pb ions on all of synthetic zeolite showed similar trend; that is, it decrease with increasing initial concentration of Pb ions. Similar observations have also been reported by other researcher who investigated the adsorption Pb ion by using natural zeolite (Peric J., Trgo M., Vukojevic M. N., 2004, Myroslav S., Buszewski B., Artur P.T., Jacek N., 2006). The metal ion adsorbed is higher for greater values of initial metal ion concentration or the percentage adsorption is more for lower concentration of metal ions and decreases with increasing initial metal ion concentration. This is obvious because a more efficient utilization of the adsorptive capacities of the adsorbent is expected due to a greater driving force by a higher concentration gradient pressure (JAIN C. K. and RAM D., 1997)



a

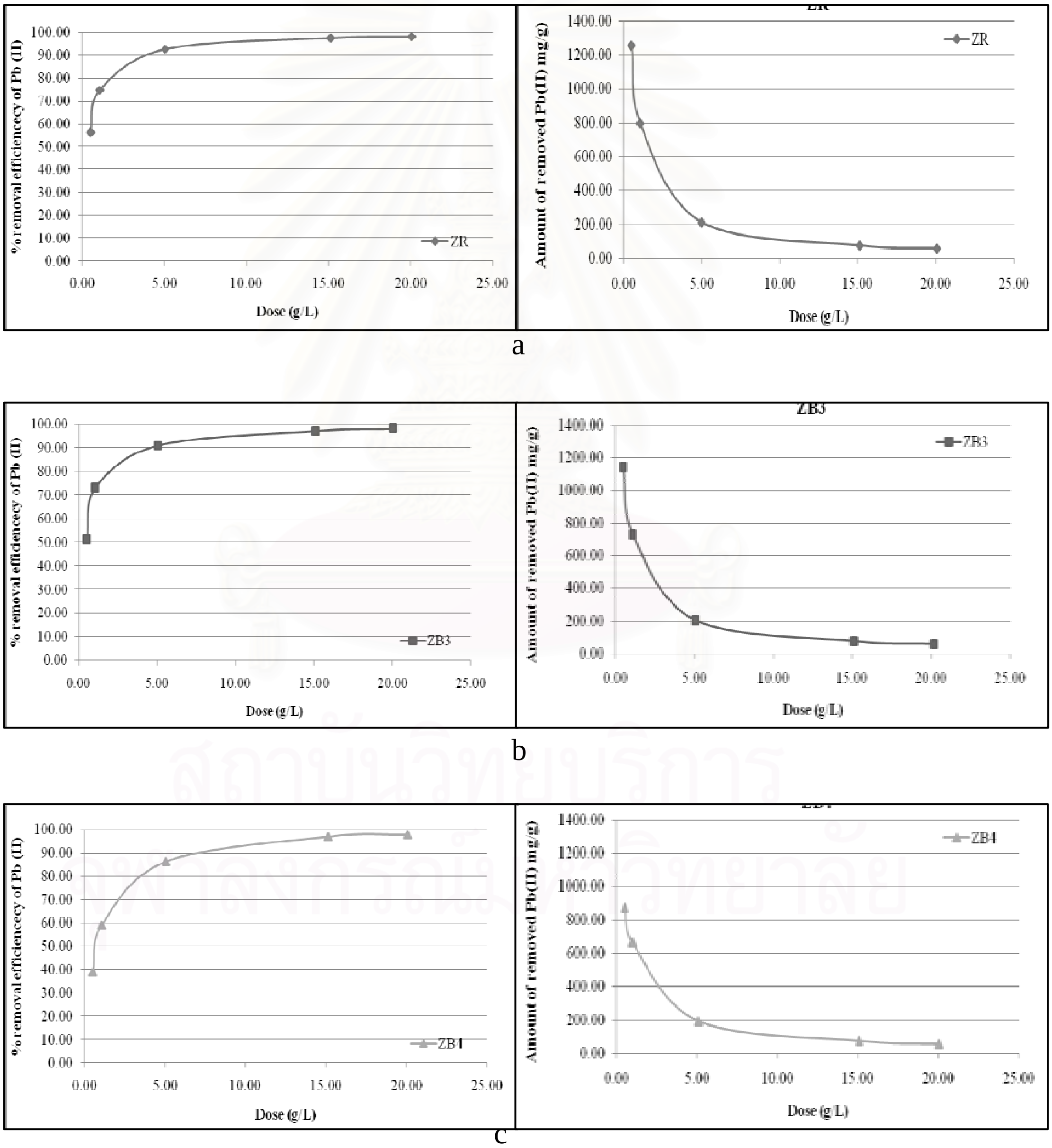
b

c

Figure4.12 Effect of initial conc. on removal of Pb(II) and amount removal of Pb(II) (time 15 min, pH 5, dose 10 g/L) for (a) Rice husk (b) biomass 3 (c) biomass 4

4.3.4 Effect of dose

Figure 4.13 are showed the effect of adsorbent dose on the adsorption properties of synthetic zeolite was studied at contact time 15 min, pH 5,Initial Conc. 1000 mg/L with different adsorbent doses varying from 0.5 to 20 g/L and at a fixed initial metal ion concentration of 1000 mg/L. It may be observed that for a fixed initial metal ion concentration, the adsorption of metal ions per unit weight of adsorbent decreased from 1253.21 to 55.48 mg/g for ZR, 1142.89 to 55.20 mg/g for ZB3 and 874.51 to 55.40 mg/g for ZB4 with increasing adsorbent dose. The adsorption increased from 56.19% to 98.28%, 51.04% to 98.09%, and 39.06% to 97.93% for ZR, ZB3 and ZB4, respectively with an increasing adsorbent dose because of increase in surface area of the adsorbent (Patil K.I., Raut N.B., Shinde G.B., 2007) or the greater availability of the exchangeable sites.



a

b

c

Figure4.13 Effect of dose on removal of Pb(II) and amount removal of Pb(II) for (a) Rice husk (b) biomass 3 (c) biomass 4

4.3.5 Adsorption isotherm

Isotherm for the removal of Pb(II) onto synthetic zeolites are showed in Figure 4.14. The Linear, Langmuir and Freundlich isotherms for the removal lead onto synthetic zeolite are showed in Figure 4.15, 4.16 and 4.17, respectively. Table 4.10 describes the adsorption date; equations and regression coefficient (R^2) for Linear, Langmuir and Freundlich models. The result of data could be concluded that the Freundlich model is appropriate for all of synthetic zeolites. The values for n are very close to unity indicating a strong tendency to linear sorption isotherm and the K_f values are close to K_d values. The high value of correlation indicates that the data conforms well to the Freundlich model.

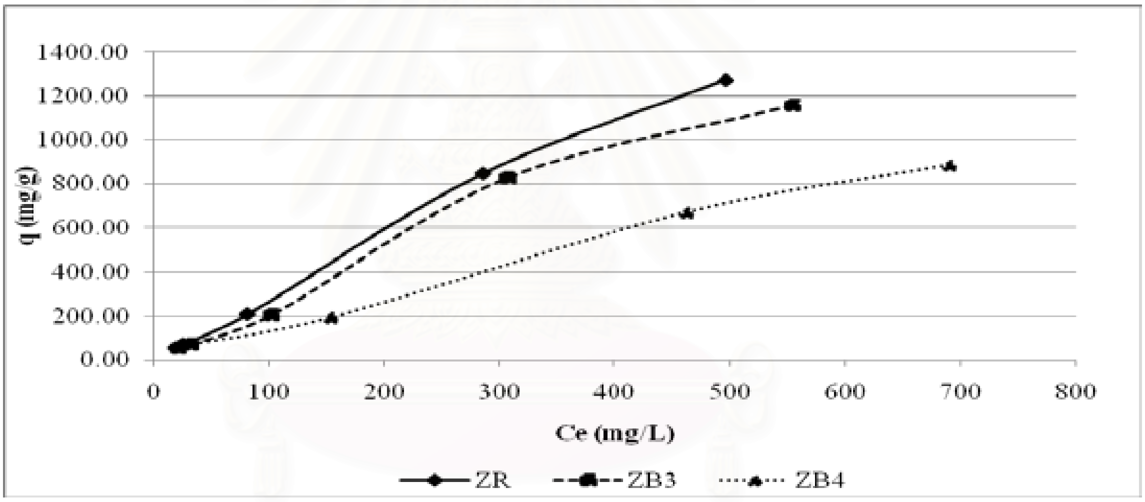


Figure 4.14 Isotherm for the removal of Pb(II) onto synthetic zeolites from rice husk (ZR), biomass 3(ZB3), biomass 4 (ZB4) at contact time 15 min, initial conc. 1000 ppm, pH 5

Adsorption isotherm of Pb(II) onto synthetic zeolite fitted well by Freundlich isotherm, it may be due to characteristic of surface of material. The Freundlich isotherm equations assume that the adsorbent has heterogeneous surface composed of adsorption site with different adsorption potentials. The Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, therefore the surface covering being mathematically unlimited.

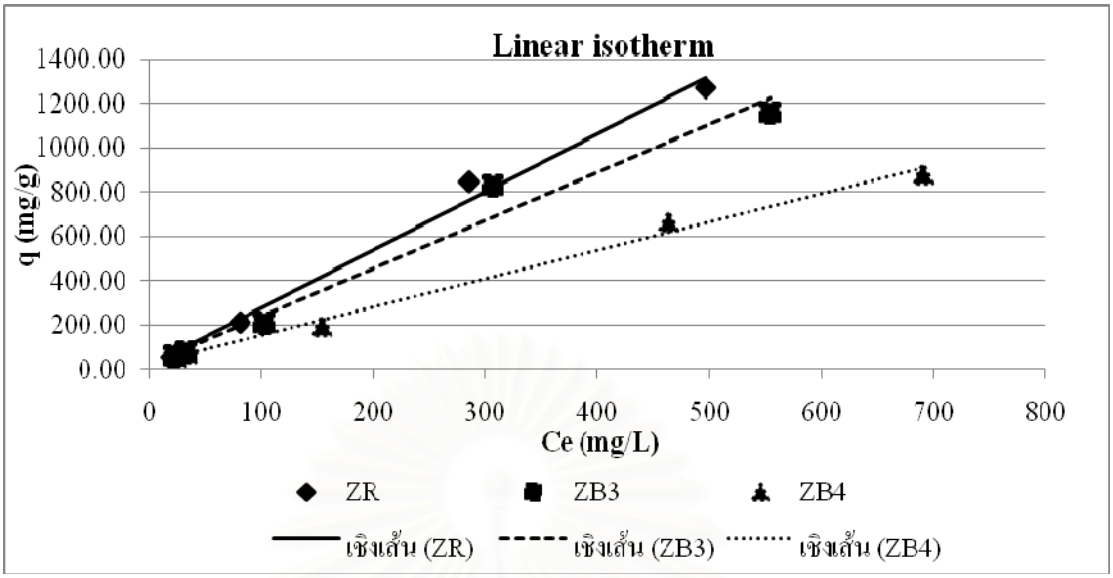


Figure 4.15 Linear isotherms for the removal lead onto synthetic zeolite from rice husk (ZR), biomass 3(ZB3), biomass 4 (ZB4)

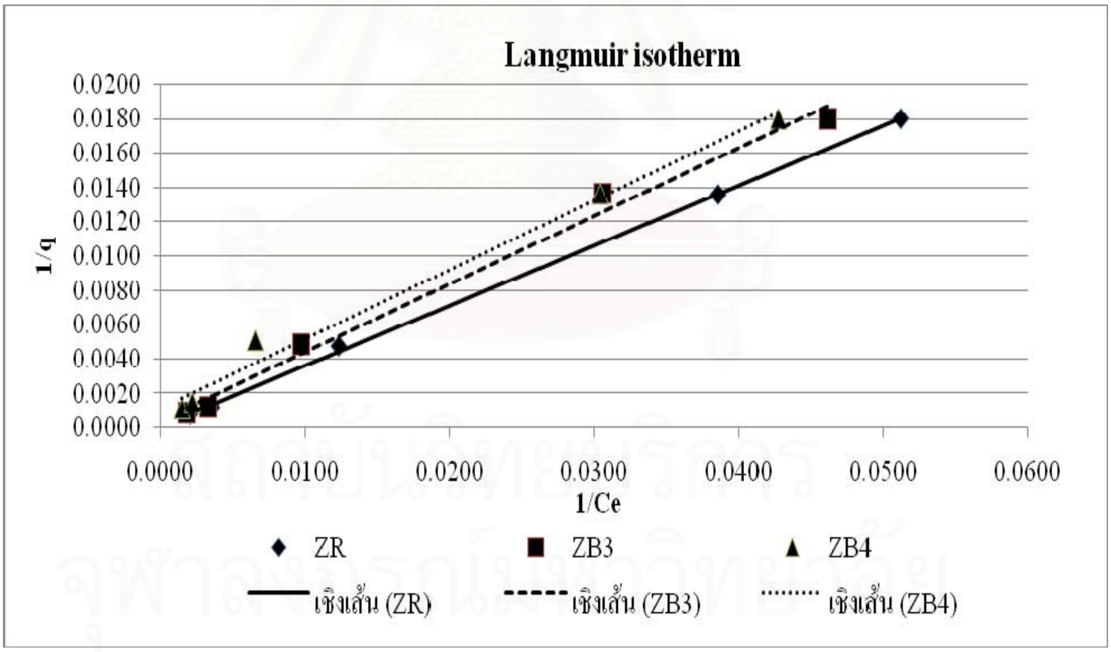


Figure 4.16 Linearized Langmuir isotherms for the removal lead onto synthetic zeolite from rice husk (ZR), biomass 3(ZB3), biomass 4 (ZB4)

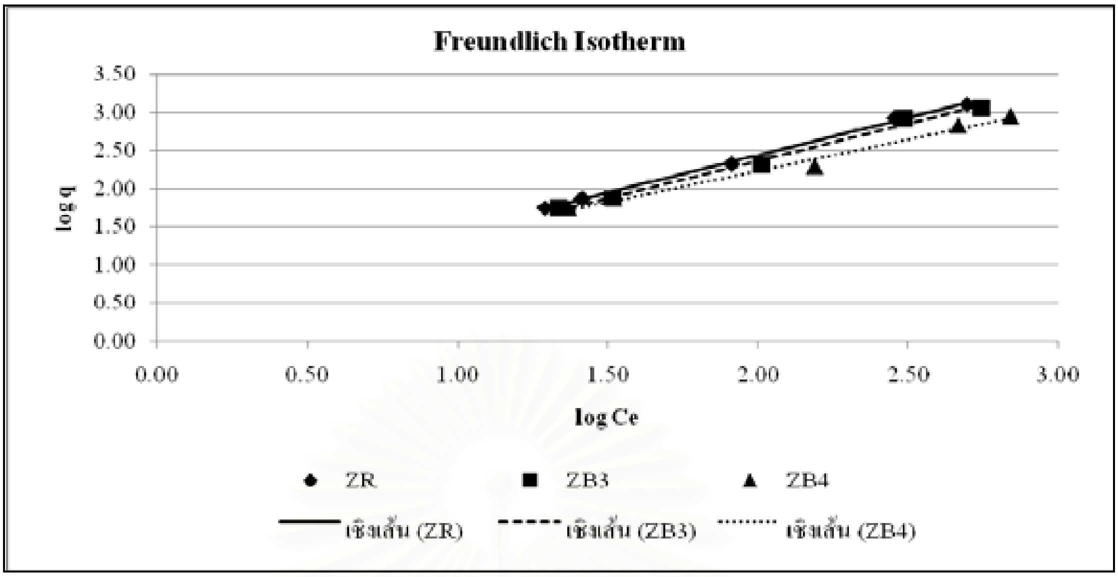


Figure 4.17 Linearized Freundlich isotherms for the removal lead onto synthetic zeolite from rice husk (ZR), biomass 3(ZB3), biomass 4 (ZB4)

From the linearity of Freundlich isotherms, the constant Kf and n could be found to 2.94 and 1.02, respectively for ZR, 2.49 and 1.02, respectively for ZB3 and 1.99 and 1.22, respectively for ZB4 as showed in Table 4.11. As mention above, K_f value which are related to relative adsorption capacity indicated that ZR had more adsorption capacity than ZB3 and ZB4, respectively. n is adsorption intensity. If $n > 1$, the adsorption is favorable. Table 4.12 was showed the recommended isotherm adsorption.

Table 4.10 Equations and regression coefficient (R^2) for Langmuir and Freundlich isotherm

Materials	Langmuir isotherm		Freundlich isotherm		Linear isotherm	
	equation	R^2	equation	R^2	equation	R^2
ZR	y=0.338x + 0.000	0.999	y=0.985x + 0.469	0.998	y= 2.622x + 15.50	0.992
ZB3	y=0.396x + 0.000	0.990	y=0.982x + 0.397	0.991	y=2.168x + 21.78	0.973
ZB4	y=0.401x + 0.001	0.988	y=0.820x + 0.299	0.988	y= 1.284x + 25.60	0.993

Table 4.11 Constant value for Langmuir and Freundlich isotherm

Material	Langmuir isotherm			Freundlich Isotherm		Linear Isotherm
	Q_0	b	r	K_f	n	K_d
ZR	0.00	0.00	1.00	2.94	1.02	2.622
ZB3	0.00	0.00	1.00	2.49	1.02	2.168
ZB4	1000.00	0.00	0.42	1.99	1.22	1.284

Table 4.12 Recommended isotherm equations for ZR, ZB3, and ZB4

Materials	Recommended isotherm equations
ZR	Log (x/m) = 0.985log Ce + 0.469
ZB3	Log (x/m) = 0.982 log Ce + 0.397
ZB4	Log (x/m) = 0.820 log Ce + 0.299

4.3.6 The comparison of adsorption capacity between synthetic zeolites, natural zeolite, and activated carbon

Figure 4.18 was described the adsorption efficiency of synthetic zeolites, natural zeolite, and activated carbon at contact time 15 min, pH 5,Initial Conc. 1000 mg/L, and dose adsorbent 20g/L. The three types of adsorbent is porous material. Synthetic zeolite from three types of ash, zeolite P is highest adsorption efficiency that compare with natural zeolite, and activated carbon. It may be due to the removal lead process of zeolite P is ion exchange and adsorption. While activated carbon use only the adsorption process for remove lead in solution. On the other hand, natural zeolite is least removal efficiency although use ion exchange and adsorption as same as zeolite P. It may be due to the variation of zeolite types and the contaminants.

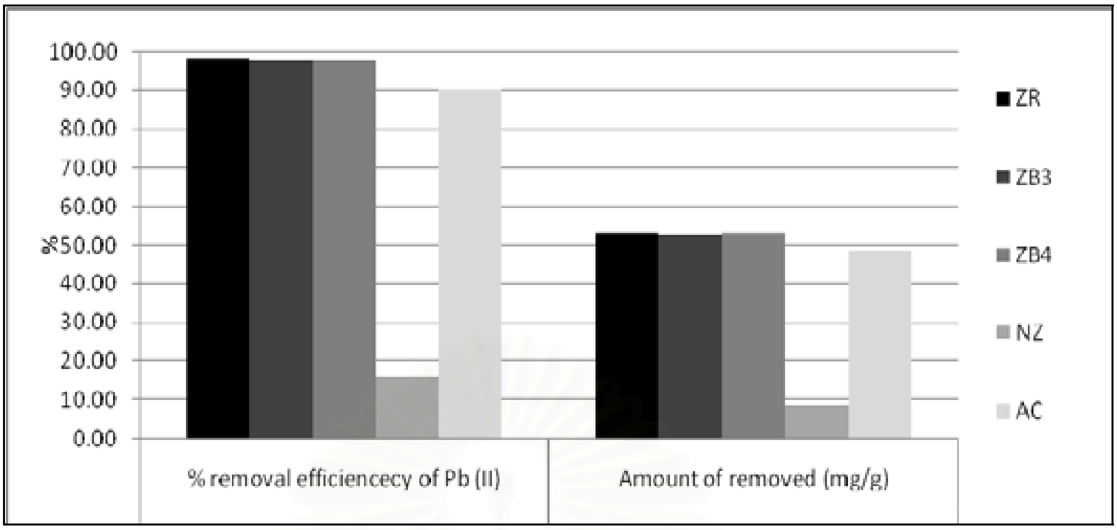


Figure 4.18 The adsorption efficiency of synthetic zeolites, natural zeolite, and activated carbon

4.4 Economic study

Biomass fly ash is converted to synthetic zeolite by using hydrothermal process with alkaline solution. Therefore, they have cost of aluminum powder, cost of alkaline treatment and electrical cost of burning, heat, and dried. For this research is excepted the cost of electricity. Because case study was power plant, it could be use other sources of heat for synthesis of zeolite that they produced such as stream. This research was calculated cost for synthetic zeolite P from biomass ash compared with price of synthetic zeolite for detergent in world market. Synthetic zeolite ranges from US $500 to $600/t for detergent grade (Tony Christie, Bob Brathwaite and Bruce Thompson, 2002) or about 15,790 - 18,942 baht/ton.

4.4.1 Cost of aluminum powder

From the results, the raw materials for synthetic zeolite P are from mixing of biomass ash and aluminum powder. The amount of aluminum powder was added to synthesized zeolite P that showed in Table 4.13. The aluminum powder which this study used is form Al_2O_3. The price of aluminum powder was 3.75 baht per kilogram. Cost of aluminum powder for each raw material that converts to zeolite

P is showed in Table 4.12. The additive aluminum powder cost can then be calculated as follow:

$$\text{Amount of } Al_2O_3 \text{ for 1 ton of zeolite P} = \frac{\text{g of } Al_2O_3 \times 10^{\wedge 6} \text{ g of zeolite P}}{\text{g of sample} \times \text{\% crystal of zeolite P}}$$

$$\text{Cost of } Al_2O_3 = \text{Amount of } Al_2O_3 \times \text{price of aluminum}$$

Table 4.13 Cost of aluminum powder

Content	ZR	ZB3	ZB4
Amount of Al_2O_3 (kg/ Ton of zeolite P)	484.87	630.24	397.27
Cost of Al_2O_3 (baht/ton)	1,818.26	2,363.40	1,489.76

4.4.2 Cost of alkaline treatment

Important factor for synthesis of zeolite P was sodium hydroxide (NaOH) that molecular weight equal 40. These chemical was used 150 ml of 3 M for treated rice husk ash, and 150 ml 0f 2 M for Biomass ash 3 and 4. The price of NaOH is equal 18 baht per kilogram. The cost of alkaline treatment is showed in Table 4.14. The calculation cost of NaOH as followed:

$$\text{Amount of NaOH} = \frac{\text{Molar of NaOH} \times 150 \text{ ml} \times 1 \text{ L} \times \text{MW.} \times 10^{\wedge 6} \text{ g of zeolite P}}{1000 \text{ ml} \times 1\text{mol} \times \text{g of sample} \times \text{\% crystal of zeolite P}}$$

$$\text{Cost of NaOH} = \text{Amount of NaOH} \times \text{price of NaOH}$$

Table 4.14 Cost of alkaline treatment

Content	ZR	ZB3	ZB4
Amount of NaOH (kg/ Ton of zeolite P)	12.22	12.42	12.71
Cost of NaOH (baht/ton)	219.96	223.56	228.78

4.4.3 Cost of synthetic zeolite P from ash

Total cost of synthesis of zeolite P is from cost of aluminum powder and sodium hydroxide. Table 4.15 show total cost of zeolite P and calculation cost as followed:

Total cost of synthesis of zeolite P = Cost of Al_2O_3 + Cost of NaOH

Table 4.15 Total cost of synthesis of zeolite P from ash

Zeolite product	Total cost of zeolite P (prices / ton)
ZR	2,038 baht
ZB3	2,587 baht
ZB4	1,719 baht

From this result of economic study, cost of aluminum powder is high valuable for cost analysis. The zeolite product from biomass 4 is lowest cost synthesis than another one although it has lowest % crystalline. It may be due to the amount of Al_2O_3 in raw material is high thus the additive of Al_2O_3 is less. Then the ratio of crystalline of zeolite P to amount of Al_2O_3 is high. On the other hand, biomass ash 4 has moderate of Al_2O_3. But it gets highest cost of synthesis. Because it gave low crystalline of zeolite P compare with amount of Al_2O_3 that they used.

However, the cost of synthetic zeolite P from three recipes of biomass ash is lowest price when compare with synthetic zeolite on market. Due to the biomass fly ash is by product of electricity power. They saved cost of raw materials for synthetic zeolite; sodium silicate and sodium aluminate. Therefore, the biomass ash is suitable raw material for synthetic zeolite in this study.

4.5 Environmental aspect

Ash from the power boiler is a function of the fuels that are used. It comprises the inorganic content of fuels. It is unlikely that the power boiler would be burning 100% of any of the fuels for any length of time, unless there was an oversupply or shortage of a particular fuel. The biomass fuels produce high ash that require good management for eliminating them. Zeolitization is one way for reducing ash from biomass; it called waste reduction and it increase value of ash. Moreover, zeolite from biomass ash can use as material to reduce some hazardous waste such as removal metal in solution and removal some gaseous (CO, CO_2, NO_x) by adsorption process. Nevertheless, the synthesis of zeolite produced alkaline wastewater. This wastewater requires the appropriate treatment process such as precipitation.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Synthesis of zeolite study

The objective of this study was to synthesize zeolite from ash of biomass power plant by using hydrothermal process in optimum condition. The following conclusions have been drowning from the above investigation:

1. Biomass ash has been converted to zeolite by hydrothermal process. By treating ash with NaOH and adding $Al(OH)_3$ that zeolite P can form.

2. The optimal conditions which treat rice husk ash change to zeolite is 3M NaOH and Biomass 3 and 4 are 2M NaOH at 99˚C for 24 hours. The ion exchange property of product was quantitatively measured by CEC.

3. The CEC values of treating rice husk ash, biomass 3, and biomass 4 are 381.08, 164.43, 216.96 mg $CaCO_3$/g zeolite and specific surface of 99.95, 97.18, 90.40 m^2/g zeolite, respectively.

4. %crystalline of zeolite P was 98.17%, 64.42%, and 62.93% for zeolite from rice husk ash, biomass ash 3, and biomass ash 4, respectively.

5. Fly ash was treated with base solution. They are increasing SSA, CEC but decreased particle size

5.1.2 Removal Study

The removal studies can conclude as follow:

1. The efficiencies of lead adsorption on to zeolite from biomass ash were found to be between 56 to 98 %

2. Contact time, initial concentration, and adsorbent dose affected lead removal efficiency. Lead removal efficiency increased with increasing Contact time, and adsorbent dose but decreased with increasing initial concentration. In addition, they were affected lead adsorption capacity, adsorption capacity increased with increasing Contact time, and initial concentration but decreased with increasing adsorbent dose.

3. Zeolite from rice husk ash was better lead adsorbent comparing to zeolite from biomass ash. It may be due to specific surface area and cation exchange capacity of Zeolite from rice husk.

5.1.3 Economic studies

In this study, these result showed the cost of synthetic zeolite from rice husk ash, biomass ash 3, and biomass ash 4 were 2,038 2,587 1,719 baht per ton of synthesis zeolite, respectively that except electrical cost. Biomass ash 4 was converted to synthetic zeolite P that gave the lowest cost. The zeolite P from biomass ash 3 was gave the highest cost. However, the biomass ash is suitable raw material for synthetic zeolite.

5.2 Recommendations

1. Biomass fly ash can convert to zeolite which in this study, it gave zeolite P. Therefore, it should be developed into the other synthetic zeolites by varies Si to

Al ratio or the speed of mixing or other parameters. This developing brings about new type of synthetic zeolite.

2. For removal studies, they should be change type of heavy metal or use the combination of heavy metal species.

3. Zeolite from biomass ash should be use in environmental field to solve the environment problem such as use to remove CO_2 in air, wastewater treatment, and hazardous waste treatment, especially metal and oil waste.

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APPENDICES

APPENDIX A

Chemical composition of raw biomass ash

Compounds	Rice Husk Ash	Biomass Ash 3	Biomass Ash 4
Moisure	0.0828	1.4964	1.4483
LOI	4.25	5.06	6.11
Na2O	0.07	0.19	0.31
MgO	0.50	1.10	1.60
Al2O3	0.19	0.50	7.89
SiO2	88.09	73.82	59.67
P2O5	1.17	1.43	1.73
SO3	0.25	0.78	1.76
Cl	0.44	2.09	0.87
K2O	3.20	4.84	3.99
CaO	0.78	7.10	9.29
TiO2	0.00	0.03	0.47
MnO	0.24	0.33	0.30
Fe2O3	0.22	0.91	3.92
Co3O4	0.05	0.04	0.04
NiO	0.00	0.00	0.00
CuO	0.02	0.02	0.03
ZnO	0.00	0.00	0.03
As2O3	0.00	0.00	0.00
Br	0.00	0.02	0.00
Rb2O	0.01	0.03	0.02
SrO	0.00	0.00	0.06
Y2O3	0.00	0.01	0.01
ZrO2	0.00	0.04	0.09
Nb2O5	0.00	0.00	0.00
MoO3	0.04	0.04	0.04
BaO	0.03	0.00	0.07
CeO2	0.00	0.00	0.04
Yb2O3	0.00	0.12	0.00
WO3	0.34	0.00	0.18
Re	0.05	0.01	0.00
HgO	0.00	0.00	0.01
PbO	0.00	0.00	0.00
SUM	100.00	100.00	100.00

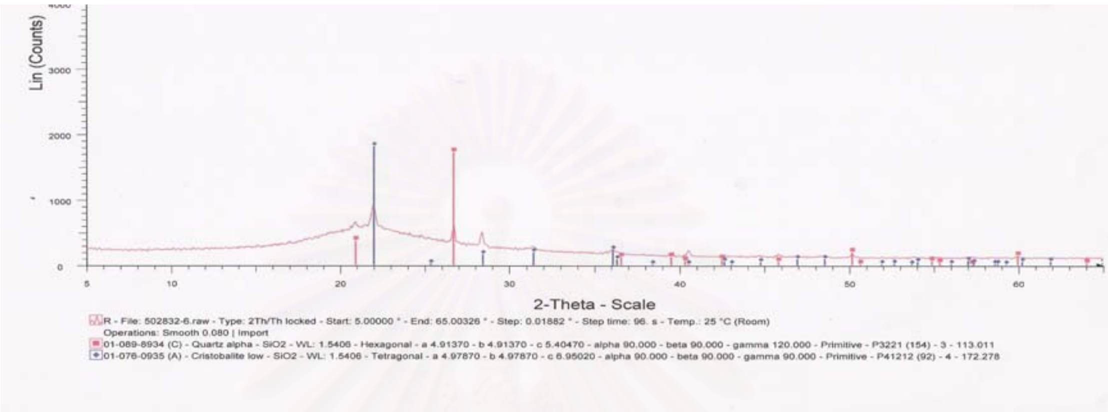
APPENDIX B

Particle size distribution of raw fly ash

Size	% distribution			Size	% distribution		
	Rice Husk Ash	Biomass Ash 3	Biomass Ash 4		Rice Husk Ash	Biomass Ash 3	Biomass Ash 4
0.58	100.00	99.98	99.98	26.20	87.34	88.79	77.67
0.67	100.00	99.95	99.94	30.53	83.51	85.74	71.94
0.78	100.00	99.91	99.89	35.56	78.56	81.79	65.31
0.91	100.00	99.86	99.83	41.43	72.38	76.78	57.86
1.06	100.00	100.00	99.77	48.27	65.02	70.60	49.79
1.24	100.00	99.81	99.71	56.23	56.69	63.29	41.29
1.44	100.00	99.76	99.65	65.51	47.69	54.98	32.51
1.68	100.00	99.70	99.59	76.32	38.40	45.88	24.40
1.95	99.93	99.65	99.53	88.91	29.03	36.16	17.42
2.28	99.87	99.60	99.45	103.58	20.77	27.03	11.84
2.65	99.79	99.55	99.36	120.67	13.99	19.06	7.71
3.09	99.69	99.49	99.24	140.58	8.82	12.60	4.92
3.60	99.55	99.41	99.09	163.77	5.16	7.76	3.20
4.19	99.38	99.30	98.89	190.80	2.75	4.43	2.20
4.88	99.14	99.15	98.62	222.28	1.25	2.30	1.60
5.69	98.84	98.93	98.26	258.95	0.33	1.01	1.16
6.63	98.47	98.64	97.79	301.68	0.00	0.24	0.77
7.72	98.02	98.25	97.16	351.46	0.00	0.00	0.41
9.00	97.48	97.76	96.33	409.45	0.00	0.00	0.13
10.48	96.84	97.32	95.24	477.01	0.00	0.00	0.00
12.21	96.08	96.39	93.80	555.71	0.00	0.00	0.00
14.22	95.14	95.47	91.92	647.41	0.00	0.00	0.00
16.57	93.94	94.34	89.48	754.23	0.00	0.00	0.00
19.31	92.35	92.93	86.36	878.67	0.00	0.00	0.00
22.49	90.22	91.13	82.46				

APPENDIX C

X-ray diffraction graph of raw biomass ash (a) Rice husk (b) Biomass feed recipe #3 (c) Biomass feed recipe #4



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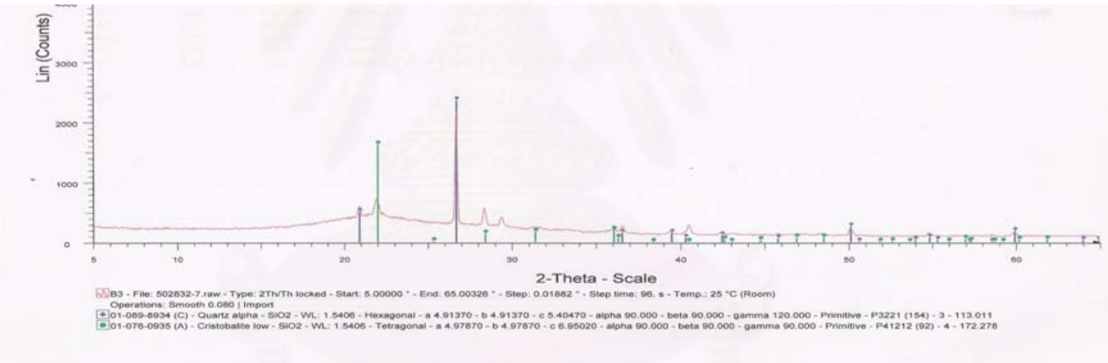

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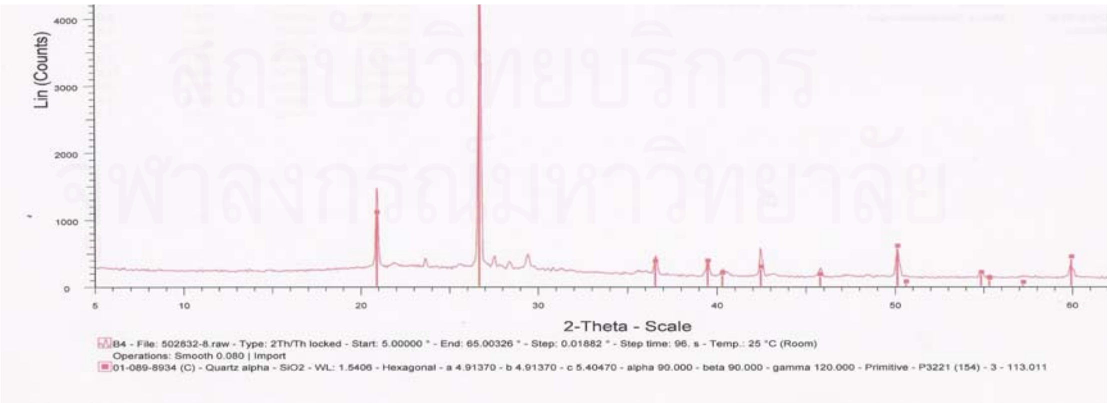

c

APPENDIX D

Effect of alkaline solution for synthesis of zeolite

Type sample	Conditions				CEC (mg CaCO3/g zeolite)
	Base	Conc.(M)	Temp.	Time (hr)	
Rice Husk	NaOH	2	80	24	128.63
Rice Husk	NaOH	2	80	24	135.83
Rice Husk	KOH	2	80	24	107.68
Rice Husk	KOH	2	80	24	107.66
Biomass 3	NaOH	2	80	24	135.15
Biomass 3	NaOH	2	80	24	132.99
Biomass 3	KOH	2	80	24	98.35
Biomass 3	KOH	2	80	24	94.77
Biomass 4	NaOH	2	80	24	160.60
Biomass 4	NaOH	2	80	24	160.19
Biomass 4	KOH	2	80	24	141.67
Biomass 4	KOH	2	80	24	138.79

APPENDIX E

Effect of concentration of alkaline solution for synthesis of zeolite

Type sample	Conditions				CEC (mg CaCO3/g zeolite)
	Base	Conc.(M)	Temp.	Time (hr)	
Rice Husk	NaOH	1	80	24	78.42
Rice Husk	NaOH	1.5	80	24	93.05
Rice Husk	NaOH	2	80	24	135.83
Rice Husk	NaOH	2.5	80	24	118.20
Rice Husk	NaOH	3	80	24	151.86
Rice Husk	NaOH	5	80	24	111.07
Biomass 3	NaOH	1	80	24	62.93
Biomass 3	NaOH	1.5	80	24	94.26
Biomass 3	NaOH	2	80	24	135.15
Biomass 3	NaOH	2.5	80	24	96.40
Biomass 3	NaOH	3	80	24	112.16
Biomass 3	NaOH	5	80	24	103.09

APPENDIX F

Effect of temperature for synthesis of zeolite

Type sample	Conditions				CEC (mg CaCO3/g zeolite)
	Base	Conc.(M)	Temp.	Time (hr)	
Rice Husk	NaOH	3	70	24	100.32
Rice Husk	NaOH	3	75	24	128.48
Rice Husk	NaOH	3	80	24	151.86
Rice Husk	NaOH	3	99	24	381.08
Biomass 3	NaOH	2	70	24	104.38
Biomass 3	NaOH	2	75	24	98.10
Biomass 3	NaOH	2	80	24	135.15
Biomass 3	NaOH	2	99	24	164.43
Biomass 4	NaOH	2	70	24	93.02
Biomass 4	NaOH	2	75	24	117.88
Biomass 4	NaOH	2	80	24	160.60
Biomass 4	NaOH	2	99	24	216.96

APPENDIX G

Effect of reaction time for synthesis of zeolite

Type sample	Conditions				CEC (mg CaCO3/g zeolite)
	Base	Conc.(M)	Temp.	Time (hr)	
Rice Husk	NaOH	3	99	6	119.36
Rice Husk	NaOH	3	99	12	111.79
Rice Husk	NaOH	3	99	24	381.08
Rice Husk	NaOH	3	99	48	107.54
Rice Husk	NaOH	3	99	72	108.01
Biomass 3	NaOH	2	99	6	87.40
Biomass 3	NaOH	2	99	12	73.76
Biomass 3	NaOH	2	99	24	164.43
Biomass 3	NaOH	2	99	48	85.19
Biomass 3	NaOH	2	99	72	115.86
Biomass 4	NaOH	2	99	6	97.39
Biomass 4	NaOH	2	99	12	93.22
Biomass 4	NaOH	2	99	24	216.96
Biomass 4	NaOH	2	99	48	108.05
Biomass 4	NaOH	2	99	72	157.72

APPENDIX H

Particle size distribution of zeolite from biomass ash

Size	% distribution			Size	% distribution		
	ZR	ZB3	ZB4		ZR	ZB3	ZB4
0.58	99.85	99.78	99.84	26.20	58.76	48.25	54.59
0.67	99.56	99.36	99.53	30.53	53.63	43.51	49.31
0.78	99.15	98.77	99.10	35.56	48.23	38.59	43.75
0.91	98.68	98.08	98.59	41.43	42.71	33.63	38.06
1.06	98.15	97.30	98.03	48.27	37.23	28.74	32.40
1.24	97.58	96.45	97.42	56.23	31.96	23.99	26.87
1.44	96.98	95.55	96.77	65.51	26.96	19.74	21.95
1.68	96.36	94.61	96.08	76.32	22.51	16.06	17.74
1.95	95.71	93.60	95.36	88.91	18.59	12.97	14.25
2.28	95.03	92.51	94.57	103.58	15.16	10.41	11.39
2.65	94.28	91.31	93.69	120.67	12.15	8.29	9.04
3.09	93.44	89.94	92.68	140.58	9.51	6.53	7.08
3.60	92.46	88.37	91.50	163.77	7.21	5.04	5.42
4.19	91.34	86.57	90.13	190.80	5.23	3.75	3.97
4.88	90.05	84.54	88.55	222.28	3.55	2.63	2.71
5.69	88.56	82.26	86.76	258.95	2.18	1.66	1.64
6.63	86.89	79.77	84.75	301.68	1.12	0.87	0.81
7.72	85.00	77.08	82.54	351.46	0.41	0.32	0.26
9.00	82.90	74.21	80.13	409.45	0.30	0.00	0.00
10.48	80.55	71.17	77.49	477.01	0.00	0.00	0.00
12.21	77.92	67.95	74.61	555.71	0.00	0.00	0.00
14.22	74.94	64.53	71.42	647.41	0.00	0.00	0.00
16.57	71.58	60.88	67.87	754.23	0.00	0.00	0.00
19.31	67.77	56.96	63.90	878.67	0.00	0.00	0.00
22.49	63.49	52.75	59.47				

APPENDIX I

Yield of zeolite products

Follow this step-by-step;

1. Balance the reaction and determine the stoichiometry or ratios of reactants to products.

$$6NaOH + 10SiO_2 + 3Al_2O_3 + 12H_2O \longrightarrow Na_6[(AlO_2)_6(SiO_2)_{10}]^{\cdot}15H_2O$$

2. Find the number of moles of each starting material used from 15 g sample.

Sample	Moles of starting material		
	NaOH	SiO_2	Al_2O_3
Zeolite from rice husk	3	0.023	0.023
Zeolite from biomass ash 3	2	0.018	0.018
Zeolite from biomass ash 4	2	0.012	0.012

3. Determine which reagent is limiting. SiO_2 is limiting agent for three type of zeolite product.
4. Calculate the moles of product expected if the yield were 100% based on the limiting reagent.
5. Calculate the grams of product corresponding to the number of moles expected.

Sample	Theoretical yield (mol)	Amount of synthetic zeolite (g)	Actual yield(mol)
Zeolite from rice husk	0.023	37.1832	0.027
Zeolite from biomass ash 3	0.018	32.7782	0.024
Zeolite from biomass ash 4	0.012	26.1255	0.019

APPENDIX J

Effect of Contact Time on Removal Efficiency

(at initial concentration 11.73 mg/L and initial pH 4.0)

Sample	sample Dose g / 50 ml	Dose g/L	Contact time min	Equilibrium concentration (mg/L)	%Absorption	Absorption capacity mg/g
No sample	0	0	0	11.73±0.07	0.00	0
ZR	0.5041	10.08	3	0.16±0.04	98.64	1.15
ZR	0.5073	10.15	6	0.15±0.04	98.71	1.14
ZR	0.5014	10.03	9	0.13±0.04	98.87	1.16
ZR	0.5045	10.09	12	0.14±0.02	98.80	1.15
ZR	0.5087	10.17	15	0.13±0.02	98.91	1.14
ZR	0.5027	10.05	30	0.13±0.02	98.93	1.15
ZB3	0.5039	10.08	3	0.20±0.04	98.27	1.14
ZB3	0.5039	10.08	6	0.21±0.04	98.19	1.14
ZB3	0.5011	10.02	9	0.20±0.03	98.34	1.15
ZB3	0.5060	10.12	12	0.19±0.03	98.37	1.14
ZB3	0.5064	10.13	15	0.17±0.02	98.58	1.14
ZB3	0.5048	10.10	30	0.16±0.04	98.60	1.15
ZB4	0.5024	10.05	3	0.29±0.04	97.50	1.14
ZB4	0.5008	10.02	6	0.32±0.02	97.29	1.14
ZB4	0.5022	10.04	9	0.27±0.03	97.71	1.14
ZB4	0.5046	10.09	12	0.26±0.02	97.78	1.14
ZB4	0.5001	10.00	15	0.26±0.02	97.78	1.15
ZB4	0.5035	10.07	30	0.19±0.03	98.36	1.15

APPENDIX K

Effect of pH on Removal Efficiency

(at initial concentration 42.22 mg/L and contact time 15 min)

Sample	sample Dose g / 50 ml	Dose g/L	initial pH	Equilibrium concentration (mg/L)	%Absorption	Absorption capacity mg/g
ZR	0.5036	10.07	1	1.28±0.04	96.97	4.06
ZR	0.5075	10.15	2	0.78±0.01	98.16	4.08
ZR	0.5002	10.00	3	0.87±0.05	97.95	4.13
ZR	0.5021	10.04	4	1.20±0.05	97.17	4.09
ZR	0.5018	10.04	5	0.66±0.03	98.45	4.14
ZR	0.5061	10.12	6	0.96±0.03	97.73	4.08
ZB3	0.5034	10.07	1	2.68±0.03	93.65	3.93
ZB3	0.5086	10.17	2	1.61±0.05	96.19	3.99
ZB3	0.5010	10.02	3	1.46±0.03	96.55	4.07
ZB3	0.5035	10.07	4	1.82±0.04	95.68	4.01
ZB3	0.5090	10.18	5	0.49±0.01	98.85	4.10
ZB3	0.5007	10.01	6	0.49±0.01	98.83	4.17
ZB4	0.5018	10.04	1	1.28±0.03	96.96	4.08
ZB4	0.5046	10.09	2	0.72±0.04	98.29	4.11
ZB4	0.5040	10.08	3	0.80±0.02	98.11	4.11
ZB4	0.5044	10.09	4	1.22±0.02	97.11	4.06
ZB4	0.5074	10.15	5	1.67±0.05	96.04	4.00
ZB4	0.5008	10.02	6	1.70±0.04	95.98	4.05

APPENDIX L

Effect of Initial Concentration on Removal Efficiency

(at initial pH 5.0 and contact time 15 min)

Sample	sample Dose g / 50 ml	Dose g/L	Initial Conc. (mg/L)	Equilibrium concentration (mg/L)	%Absorption	Absorption capacity mg/g
ZR	0.5038	10.08	11.39	0.00±0.04	100.00	1.13
ZR	0.5014	10.03	20.07	0.01±0.04	99.97	2.00
ZR	0.5015	10.03	30.45	0.01±0.04	99.96	3.03
ZR	0.5018	10.04	42.22	0.66±0.03	98.45	4.14
ZR	0.5036	10.07	81.32	0.27±0.01	99.67	8.05
ZR	0.5024	10.05	174.20	5.54±0.19	96.82	16.79
ZR	0.5038	10.08	367.10	8.89±0.35	97.58	35.55
ZR	0.5037	10.07	631.30	32.27±0.51	94.89	59.46
ZR	0.5022	10.04	877.90	136.00±0.43	84.51	73.86
ZR	0.5010	10.02	1110.00	195.00±0.73	82.43	91.32
ZB3	0.5016	10.03	11.39	0.00±0.05	100.00	1.14
ZB3	0.5010	10.02	20.07	0.08±0.02	99.61	2.00
ZB3	0.5053	10.11	30.45	0.46±0.07	98.48	2.97
ZB3	0.5090	10.18	42.22	0.49±0.01	98.85	4.10
ZB3	0.5018	10.04	81.32	3.36±0.04	95.86	7.77
ZB3	0.5028	10.06	174.20	12.45±0.24	92.85	16.08
ZB3	0.5011	10.02	367.10	43.18±0.42	88.24	32.32
ZB3	0.5030	10.06	631.30	128.30±0.24	79.68	50.00
ZB3	0.5011	10.02	877.90	225.80±0.79	74.28	65.07
ZB3	0.5050	10.10	1110.00	281.10±0.45	74.68	82.07
ZB4	0.5060	10.12	11.39	0.44±0.00	96.14	1.08
ZB4	0.5048	10.10	20.07	0.45±0.03	97.74	1.94
ZB4	0.5090	10.18	30.45	0.77±0.05	97.47	2.92
ZB4	0.5074	10.15	42.22	1.67±0.05	96.04	4.00
ZB4	0.5005	10.01	81.32	2.71±0.05	96.67	7.85
ZB4	0.5019	10.04	174.20	15.54±0.30	91.08	15.81
ZB4	0.5064	10.13	367.10	78.89±0.40	78.51	28.46
ZB4	0.5007	10.01	631.30	170.27±0.60	73.03	46.04
ZB4	0.5014	10.03	877.90	312.00±0.08	64.46	56.43
ZB4	0.5028	10.06	1110.00	425.10±0.86	61.70	68.11

APPENDIX M

Effect of Dose of Adsorbent on Removal Efficiency

(at initial concentration 1133 mg/L, initial pH 5.0 and contact time 15 min)

Sample	sample Dose g / 50 ml	Dose g/L	Equilibrium concentration (mg/L)	%Absorption	Absorption capacity mg/g
ZR	0.0254	0.51	496.37±3.17	56.19	1253.21
ZR	0.0533	1.07	285.41±8.40	74.81	795.11
ZR	0.2514	5.03	81.43±4.09	92.81	209.14
ZR	0.7569	15.14	25.94±2.97	97.71	73.13
ZR	1.0035	20.07	19.53±2.79	98.28	55.48
ZB3	0.0253	0.51	554.70±5.61	51.04	1142.89
ZB3	0.0566	1.13	306.80±4.24	72.92	729.86
ZB3	0.2535	5.07	102.66±4.96	90.94	203.22
ZB3	0.7556	15.11	32.72±5.14	97.11	72.81
ZB3	1.0066	20.13	21.65±4.10	98.09	55.20
ZB4	0.0253	0.51	690.50±5.19	39.06	874.51
ZB4	0.0504	1.01	463.10±3.77	59.13	664.58
ZB4	0.2552	5.10	153.90±3.22	86.42	191.83
ZB4	0.7526	15.05	32.93±2.01	97.09	73.08
ZB4	1.0015	20.03	23.42±2.76	97.93	55.40

APPENDIX N

Data for Langmuir adsorption isotherm

Sample	Dose g/L	Co mg/L	Ce mg/L	x mg/L	q mg/g	1/Ce	1/q
ZR	0.5	1133	496.37	636.63	1273.26	0.00	0.00
ZR	1	1133	285.41	847.59	847.59	0.00	0.00
ZR	5	1133	81.43	1051.57	210.31	0.01	0.00
ZR	15	1133	25.94	1107.06	73.80	0.04	0.01
ZR	20	1133	19.53	1113.47	55.67	0.05	0.02
ZB3	0.5	1133	554.70	578.30	1156.60	0.00	0.00
ZB3	1	1133	306.80	826.20	826.20	0.00	0.00
ZB3	5	1133	102.66	1030.34	206.07	0.01	0.00
ZB3	15	1133	32.72	1100.28	73.35	0.03	0.01
ZB3	20	1133	21.65	1111.35	55.57	0.05	0.02
ZB4	0.5	1133	690.50	442.50	885.00	0.00	0.00
ZB4	1	1133	463.10	669.90	669.90	0.00	0.00
ZB4	5	1133	153.90	979.10	195.82	0.01	0.01
ZB4	15	1133	32.93	1100.07	73.34	0.03	0.01
ZB4	20	1133	23.42	1109.58	55.48	0.04	0.02

APPENDIX O

Data for Freundlich adsorption isotherm

Sample	Dose g/L	Co mg/L	Ce mg/L	x mg/L	q mg/g	logCe	log q
ZR	0.5	1133	496.37	636.63	1273.26		
ZR	1	1133	285.41	847.59	847.59	2.70	3.10
ZR	5	1133	81.43	1051.57	210.31	2.46	2.93
ZR	15	1133	25.94	1107.06	73.80	1.91	2.32
ZR	20	1133	19.53	1113.47	55.67	1.41	1.87
ZB3	0.5	1133	554.70	578.30	1156.60	1.29	1.75
ZB3	1	1133	306.80	826.20	826.20	2.74	3.06
ZB3	5	1133	102.66	1030.34	206.07	2.49	2.92
ZB3	15	1133	32.72	1100.28	73.35	2.01	2.31
ZB3	20	1133	21.65	1111.35	55.57	1.51	1.87
ZB4	0.5	1133	690.50	442.50	885.00	1.34	1.74
ZB4	1	1133	463.10	669.90	669.90	2.84	2.95
ZB4	5	1133	153.90	979.10	195.82	2.67	2.83
ZB4	15	1133	32.93	1100.07	73.34	2.19	2.29
ZB4	20	1133	23.42	1109.58	55.48	1.52	1.87

APPENDIX P

Comparison between synthetic zeolite, natural zeolite, and activated carbon

(at initial concentration 1084 mg/L, initial pH 5.0 and contact time 15 min)

Sample	sample Dose g / 50 ml	Dose g/L	Equilibrium concentration (mg/L)	%Absorption	Absorption capacity mg/g
ZR	1.0035	20.07	19.53	98.20	53.04
ZB3	1.0066	20.13	21.65	98.00	52.77
ZB4	1.0015	20.03	23.42	97.84	52.95
NZ	1.0038	20.08	913.6	15.72	8.49
AC	1.0052	20.10	106.5	90.18	48.62

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Peerada Bowornthammatus and Manaskorn Rachakornkij. *Synthesis of Zeolite from Ash of Biomass Power Plant Using Hydrothermal Process.* The Proceedings of 7th National Environmental Conference, March 12 -14, 2008, at Chulabhon Research Institue, Bangkok, Thailand, Organized by the Environmental Engineering Association of Thailand