

# **Zeolites: Synthesis, Characterisation & Practice**

**-Dr Ho Soon Min  
-Dr. Nik Ahmad Nizam  
-Prof. Ahmed Osumanu Haruna  
-Mr. Peter Adeniyi Alaba**

# **Zeolites:**

## **Synthesis, Characterisation & Practice**

### **Dr Ho Soon Min**

Associate Professor, Faculty of Information Technology-Math & Science, INTI International University, Malaysia.

### **Dr Nik Ahmad Nizam**

Senior lecturer and Head of Department, Department of Biotechnology and Medical Engineering, Faculty of Biosciences and Medical Engineering and Research Group Leader of Novel Materials Research Group, Frontier Materials Research Alliance, Universiti Teknologi Malaysia

### **Prof. Ahmed Osumanu Haruna**

Professor, Department of Crop Science, Faculty of Agriculture and Food Sciences  
University Putra Malaysia.

### **Peter Adeniyi Alaba**

Research Officer, Department of Chemical Engineering, University of Malaya, Malaysia.

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427, Palhar Nagar, RAPTC, VIP-Road, Indore-452005 (MP) INDIA  
Phone: +91-731-2616100, Mobile: +91-80570-83382  
E-mail: [contact@isca.co.in](mailto:contact@isca.co.in) , Website: [www.isca.co.in](http://www.isca.co.in)

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<b>Author(s):</b>	<b>Dr Ho Soon Min, Dr Nik Ahmad Nizam, Prof. Ahmed Osumanu Haruna, Peter Adeniyi Alaba</b>
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## Chapter 1 Zeolites and their applications: review

\*HO SOONMIN

Centre of Applied Chemistry and Green Chemistry, Faculty of Information Technology-Math & Science,  
INTI International University, Putra Nilai, 71800, Negeri Sembilan, MALAYSIA.

\* Tel.: +606-7982000; E-mail address: [soonmin.ho@newinti.edu.my](mailto:soonmin.ho@newinti.edu.my)

### Abstract:

A number of studies were carried out on different types of zeolites. Zeolites are used in a variety of applications such as adsorbents, catalysts, solar energy storage, thermal adsorption storage and in medicine industry due to their unique porous properties. Zeolites showed good adsorption capacities for removal of organic pollutants and heavy metals from wastewater.

**Keywords:** zeolite, catalyst, adsorbent, porosity, surface area

### Introduction:

Zeolites are three dimensional, crystalline solids, made from interlinked tetrahedral of alumina and silica. They form with many different crystalline structures and have a unique ability to act as molecular sieves. Generally, zeolites are grouped into two major categories, namely natural and synthetic zeolites. Volcanic rocks containing natural zeolites. Natural zeolites are rarely pure and are contaminated to varying degrees by other minerals. According to observation, there are more than 40 natural zeolites have been successfully identified during the past 200 years. Some of the common natural zeolites such as mordenite, stilbite, clinoptilolite, analcime, chabazite and natrolite have been studied by several researchers [1-4]. On the other hand, synthetic zeolites such as zeolite A, petroleum catalyst ZSM-5, zeolite X and Y are prepared industrially on a large scale. These zeolites are manufactured in a uniform sizes and phase pure state in order to suit a particular application. Nowadays, there are more than 150 zeolites have been synthesized by many scientists [5-7] from around the world in an effort to discover more efficiency catalyst in petroleum industry.

In this review paper, applications of different types of zeolites (consist of natural and synthetic form) were studied.

### Literature survey:

Solar energy is a renewable source, safe and available all over the world. Nowadays, zeolites can keep the stored energy long time [8] because of suitability of adsorbing and desorbing water without damage the structure [9]. Utilization of zeolite for solar energy storage has been reported by many researchers [10-13]. For example, natural zeolites can be used as storing solar energy material

completely instead of the 13X synthetic zeolite below 100°C. However, 13X synthetic zeolite has significant advantages in 100 to 200 °C. On the other hand, beginning in ancient times up to present, zeolite has the potential to be used in thermal adsorption storage due to the large availability and low cost of zeolite. Two natural zeolites of different origin (Greece and Serbia) were studied by Janchen et al, (2015) for thermal adsorption storage application. They found that zeolites should be focused on building materials for environmental control [14].

In recent years, zeolites are widely used in medicine industry (Table 1). Based on experts' assessments, these materials are harmless, bactericidal and antioxidative effects. Zeolites eliminate a number of toxic substances from the organism. Zeolites adhere to pathogenic bacteria and therefore, they play great role as detoxicants. Natural zeolite (clinoptilolite) contains silica and alumina tetrahedra with complex formula, has been shown to display diverse biological activities by many researchers. Researchers conclude that clinoptilolite is safe and non-toxic based on their experimental findings.

Table 1: Medical application of zeolites

Reference	Description
[15]	✓ A new anti-diarrheic drug for humans has been developed according to purified natural clinoptilolite.
[16]	✓ A powder of micronized zeolite (natural clinoptilolite) inhibited the viral proliferation of HSV 1, coxsackievirus B5 and echovirus 7 more efficiently than adenovirus 5.
[17]	✓ Micronized zeolite (natural clinoptilolite) reduced the metabolic rate of cancer cells and increased binding of 4-hydroxynonenal to albumin in vitro.
[18]	✓ Nano-sized clinoptilolite exerted a hypoglycemic effect in streptozocin-induced diabetic rats

Applications of natural zeolites in wastewater treatment and their properties have been studied by many scientists (Table 2). Researchers conclude that there are various natural zeolites around the world have shown good ion-exchange capacities for cations, and could be used as cost effective adsorbent for the removal of organic pollutants. These materials have unique porous behaviors and are environmentally friendly adsorbent. The recovery ability was evaluated by many researchers in order to investigate the reusability of the adsorbent. This process is quite important to reduce the need for extracting materials from the environment to be employed in the industrial processes.

Table 2: Application of zeolites in water treatment

Reference	Description
[19]	✓ Removal of polyaromatic hydrocarbon (anthracene, phenanthrene, and pyrene) and azo dyes from wastewater using natural zeolite incinerator waste

[20]	<ul style="list-style-type: none"> <li>✓ Zeolite has 20-200 mesh size was employed to remove aluminum ion from polluted tap water.</li> <li>✓ The highest removal efficiency was found in different conditions, such as pH 6.5 (85 %), and 30 °C (93 %).</li> </ul>
[21]	<ul style="list-style-type: none"> <li>✓ 1-3 mm of clinoptilolite from Semnan mines was used.</li> <li>✓ The best conditions were 15 minutes, pH 4, adsorbent dosage of 1g per liter and concentration of 2.5 ppm cadmium.</li> </ul>
[22]	<ul style="list-style-type: none"> <li>✓ Zeolite has very high surface area (2762 cm<sup>2</sup>/gm).</li> <li>✓ The maximum biochemical oxygen demand removal about 31 % from the combined waste water of sugar industry (160 gm/L of zeolite)</li> </ul>
[23]	<ul style="list-style-type: none"> <li>✓ Removal of Mn<sup>2+</sup> ions using zeolite consists of clinoptilolite and mordenite.</li> <li>✓ The surface area of adsorbent is 118 m<sup>2</sup>/g. The highest adsorption of Mn<sup>2+</sup> at pH 6-6.8.</li> <li>✓ Modified zeolite (treated with NaCl, NaOH, Na<sub>2</sub>CO<sub>3</sub> &amp; NH<sub>4</sub>Cl) show increased its uptake ability when compared with the natural zeolite.</li> </ul>
[24]	<ul style="list-style-type: none"> <li>✓ The sizes and surface area of natural zeolite are 0.4 to 1.5 mm and 15 m<sup>2</sup>/g, respectively.</li> <li>✓ Removal of phenol (0.21 g phenol/1 g clinoptilolite) and aniline (98 % sorption using clinoptilolite) in motor transportation and auto repair enterprises have been studied.</li> </ul>
[25]	<ul style="list-style-type: none"> <li>✓ Removal of ammonium ions from wastewater using clinoptilolite.</li> <li>✓ Adsorption capacity rises with decrease in particle size of zeolite from 4-10 mm to 1-2 mm.</li> </ul>
[26]	<ul style="list-style-type: none"> <li>✓ Removal of lead ions using clinoptilolite mineral (25-140 mesh size)</li> <li>✓ The highest Pb<sup>2+</sup> ions removal efficiency was under pH 5, 30 °C and 200 rpm shaking speed.</li> </ul>
[27]	<ul style="list-style-type: none"> <li>✓ The highest adsorption capacity of formaldehyde from waste water using 1-2 mm natural zeolite occurs at 8 hours, pH -3.</li> </ul>
[28]	<ul style="list-style-type: none"> <li>✓ Natural zeolite has a limited adsorption capacity for reactive dyes.</li> <li>✓ Modification of Heulandite with hexamethylenediamine can be easily performed.</li> </ul>
[29]	<ul style="list-style-type: none"> <li>✓ Adsorption of basic dye (methylene blue) by zeolites synthesized from fly ash.</li> <li>✓ Research findings show the highest adsorption capacity in zeolite X if compared to zeolite A.</li> </ul>
[30]	<ul style="list-style-type: none"> <li>✓ Zeolite ZX1 was produced from fly ash by alkali fusion and hydrothermal treatment for removal methyl orange.</li> <li>✓ Higher solution pH and lower temperature result in higher adsorption capacity.</li> </ul>
[31]	<ul style="list-style-type: none"> <li>✓ Adsorption of Crystal Violet Dye using zeolite A prepared from coal fly ash.</li> <li>✓ The best adsorption happens at pH 6, 45 minutes and room temperature.</li> </ul>

Zeolite catalysts play an important role in the petroleum refining and chemical manufacturing processes (Table 3) in order to reduce the costs associated with filtration and disposal of chemical

waste. These catalysts are employed in catalytic crackers which turn petroleum (hydrocarbon molecule) into useful products and chemicals. Zeolite synthesis technology offers great promise for petrochemicals include phenol alkylation, oxygenate production, isobutene alkylation, alkane isomerization, alkene interconversion and ethoxylation of glycol. This is due to vigorous trapping of molecules in pores and chemical reactions readily take place.

Table 3: Industrial applications of zeolite catalysts

Reference	Description
[32]	<ul style="list-style-type: none"> <li>✓ Zeolite supported catalysts are the most suitable for the hydrocracking of vegetable oil to produce bio jet fuel.</li> <li>✓ Non sulphide zeolite catalysts such as ZSM-5 and beta zeolite were used to reduce pollution and greenhouse effect.</li> </ul>
[33]	<ul style="list-style-type: none"> <li>✓ The pore structure and acidities of zeolite catalyst were important factors in the isobutylene amination process.</li> <li>✓ Pore diameter with less than 0.5 nm and strong acid strength were not conducive to the process</li> </ul>
[34]	<ul style="list-style-type: none"> <li>✓ The influence of magnesium impregnated NaY zeolite catalysts for the glucose isomerization into fructose has been studied.</li> <li>✓ Glucose conversion improves (6-49 %) with magnesium addition (0-15 %) because of an increase on the number of basic sites.</li> </ul>
[35]	<ul style="list-style-type: none"> <li>✓ Conversion yield of triolein to biodiesel (93 %) using zeolite LTA under optimal conditions such as 146 minutes, 62.9 °C, catalyst loading at 72 % of triolein used.</li> </ul>
[36]	<ul style="list-style-type: none"> <li>✓ FAU-type zeolite was synthesized from hydrothermal of shale rock and served as a catalyst in the liquid phase oleic acid esterification process.</li> <li>✓ These zeolites have a high surface area (571 m<sup>2</sup>/g), reaching a maximum of 78 % conversion after 90 minutes.</li> </ul>
[37]	<ul style="list-style-type: none"> <li>✓ Zeolite based catalysts were treated with HCl and NaOH, then were used for transesterification of waste sunflower vegetable oil in order to produce biodiesel.</li> <li>✓ The maximum biodiesel yield of 97 % could be found in 2 hours reaction time, 800 rpm, 335 catalyst particle size and 50 °C.</li> </ul>
[38]	<ul style="list-style-type: none"> <li>✓ Cycloaddition of dimethylfuran for renewable p-xylene with zeolite beta nanosponge prepared using hydrothermal process.</li> <li>✓ The better catalytic activity of this zeolite than commercial beta zeolite due to mesoporous (4.5 nm) and many external Bronsted acid sites.</li> </ul>
[39]	<ul style="list-style-type: none"> <li>✓ Development of mesoporous ZSM-15 zeolite and its application for methanol to hydrocarbon reactions.</li> <li>✓ The results show that the propene/ethane ratio as high a 9.1 from the methanol to hydrocarbon reaction was reached.</li> </ul>
[40]	<ul style="list-style-type: none"> <li>✓ They reported that the large pore zeolite beta and mesoporous MCM 36/56 exhibited the highest phenol conversions (99-100 %).</li> <li>✓ This process represents transformation of lignocellulose derived compounds to automotive and jet fuels.</li> </ul>
[41]	<ul style="list-style-type: none"> <li>✓ Conversion of methanol to propylene over mesoporous ZSM-15 zeolites produced under hydrothermal conditions.</li> <li>✓ The high yield production (44 %) of propylene could be seen with TPOAC/CTAB =3, in 76 hours.</li> </ul>
[42]	<ul style="list-style-type: none"> <li>✓ Vanadium and molybdenum supported zeolite catalyst produced using solid state ion exchange.</li> </ul>



	✓ These catalysts exhibited good activity and selectivity in the ammoxidation of ethylene to acetonitrile due to the catalytic performances depend on the zeolite structure.
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### Conclusion:

The zeolite materials have been extensively studied by many researchers. The adsorption process for the removal of organic pollutants is favored by the employ of low cost materials that display unique porous structure.

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## Chapter 2 Zeolite as a Potential Alternative Adjuvant Therapy for Cancer

Noor Azhana Ghazi, \*Nik Ahmad Nizam Nik Malek, Salehuddin Hamdan

\*Department of Biotechnology and Medical Engineering, Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor, Malaysia.

Email: [niknizam@fbb.utm.my](mailto:niknizam@fbb.utm.my); Tel: +607-5558440

### Introduction

Cancer refers to the condition of an uncontrolled growth of cells which will invade and destroy the cell functions, particularly the main organs. It has been one of the major causes of deaths in the world. There are many factors that may contribute to the rise of cancer cases such as genetic hereditary, tobacco, unhealthy diet, lack of physical activities, ultraviolet (UV), radiation and prolonged exposures to carcinogens (Vogelstein and Kinzler, 2004; Ezzati *et al.*, 2005; Sankpal *et al.*, 2012). Historically, surgery was the only way to treat cancer but now it is limited to certain cases like primary tumor treatment, metastases resection and staging purposes.

Cancer staging is essential in order to identify the extent of the disease and in selecting the best treatment regime for the patient. The most common staging system is the tumor node metastasis (TNM) system (Edge and Compton, 2010). Cancer diagnosis and staging is normally confirmed by biopsy. The samples obtained will be sent to the laboratory where they will be examined, processed and stained using immunohistochemistry method. A pathologist will generate a cytology and histopathology report before the oncologist can decide and initiate the necessary treatment.

There are many available choices of treatment nowadays besides surgery such as chemotherapy, radiotherapy, targeted therapy, hyperthermia, stem cell transplant and photodynamic therapy. The choice of treatments, however, depends on the type of cancer and its classification (World Health Organization, 2008; Ministry of Health Malaysia, 2002 and 2003). Combined treatments may be arranged through neoadjuvant therapy or adjuvant therapy to ensure the effectiveness of the main treatment. Neoadjuvant therapy is normally given prior to surgery in order to shrink the tumor beforehand. On the other hand, adjuvant therapy is a systemic therapy that is given to the patients after the main treatment particularly for those with a high risk of recurrence. The objective is to prevent tumor cells progression and boost the immune system so the patients will be able to live long and comfortable life despite the disease.

Even with ample choices given, there are restrictions to the available treatments. One example is the possibility of recurrence after surgery (Snyder and Greenberg, 2010), meaning that cancer may come back after treatment at the same site (local) or at a different site (distant). Another major concern is drug resistance in chemotherapy through adaptation of the tumor cells to the given drugs

(Casanovas, 2012). Cancer treatment by radiotherapy is useful for localized cancer but may affect the normal cells nearby, while treatments by hyperthermia and stem cell transplant have yet to prove their effectiveness in clinical studies. With all the limitations at hand and no definite cure as yet, the use of adjuvant therapy is very much relied on, although it means that patients have to suffer the immediate side effects or the delayed late toxicity. Therefore, an effort on new potential anticancer adjuvant that possesses good anticancer activity with fewer side effects or toxicity is very much anticipated.

### Adjuvant Therapy for Cancer

Adjuvant therapy is an additional treatment that helps to improve the benefits of a primary cancer treatment and reduce the probability of a recurrence. It plays an important role in the management of cancer patients and provides an impact on their survival rates. There are many types of adjuvant therapy offered for the time being such as radiation therapy, chemotherapy, hormone therapy, immunotherapy and targeted therapy. An adjuvant radiation therapy is sometimes recommended after surgery to decrease local recurrence (Jabbour and Thomas, 2010). Another type of adjuvant therapy that is normally considered for certain cancer patients is chemotherapy (Verrill, 2009; Gray *et al.*, 2007). It is a systemic treatment in which drugs are delivered into the body by intravenous injection or oral consumption. It often consists of two or three types of drugs combination for a certain period of time with intervals between each cycle. A decision on the treatment regimens generally depends on the cost and the level of toxicity. Besides radiation and chemotherapy, hormone therapy, immunotherapy and targeted therapy are among the usual adjuvant therapies considered for cancer patients (Widmer *et al.*, 2014; Scott *et al.*, 2012; Gonzalez and Lage, 2007). These therapies mainly involved the manipulation of inhibitors in blocking the receptors that are involved in the growth of the cancer cells. Table 1 listed the examples of adjuvant therapy that are administered for various types of cancers.

**Table 1:** Examples of adjuvant therapy for various types of cancer

Types of cancer	Adjuvant therapy	Reference
Breast	Chemotherapy (Paclitaxel, Docetaxel) Hormone therapy (Tamoxifen, Letrozole)	Sparano <i>et al.</i> (2008) Goss <i>et al.</i> (2005)
Cervical	Radiation therapy	Peters <i>et al.</i> (2000)
Pancreatic	Chemotherapy (Cisplatin, 5-fluorouracil) Radiation therapy (chemoradiotherapy, intraoperative radiation therapy (IORT), brachytherapy)	Neoptolemos <i>et al.</i> (2003)
Colon	Chemotherapy (5-fluorouracil, Gemcitabine, Raltitrexed, Irinotecan, Oxaliplatin, Paclitaxel, Doclitaxel) Chemotherapy (5-fluorouracil, Leucovorin, Capecitabine, Tegafur-uracil (UFT), tegafur-gimeracil (S1), Irinotecan, Oxaliplatin)	Andre <i>et al.</i> (2009), Carrato (2008)

	Targeted therapy (Cetuzimab, Bevacizumab)	
Rectal	Radiation therapy Chemotherapy (5-fluorouracil, Leucovorin, Oxaliplatin)	Carrato (2008)
Prostate	Radiotherapy Hormone therapy (Goserelin)	Thompson <i>et al.</i> (2006) Messing <i>et al.</i> (1999)

The use of adjuvant therapy had been proven to benefit many patients with various cancer types. Primary radiation therapy that was followed by adjuvant hormone therapy in appropriately selected prostate cancer patients had increased the overall survival (OS) when compared to treatment using radiation therapy alone (Bossi, 2009). Patients with stage III and stage II colon cancer was proven to obtain benefits after adjuvant chemotherapy (Andre *et al.*, 2009; Carrato, 2008). Similarly, breast cancer patients who were given adjuvant chemotherapy showed improvement for disease-free and overall survival (Sparano *et al.*, 2008). A study made by Neoptolemos *et al.* (2003) agreed that the use of adjuvant therapy after the primary treatment had indeed showed benefits to pancreatic cancer patients. Nonetheless, a combination of adjuvant therapies did not present any significant difference to using a single adjuvant therapy. In order to achieve maximum benefits, the grade or stage of cancer was the most important prognostic and predictive factor when considering adjuvant therapy for a cancer patient (Italiano *et al.*, 2010; Vanderveen *et al.*, 2009). Likewise, the method and timing of administration play a role in determining the safety of the given adjuvant therapy (Chau and Cunningham, 2006).

### Limitations of Current Adjuvant Therapy for Cancer

Even though there are many advantages of adjuvant therapy, it still has some limitations to it. Various side effects that may affect the quality of life (QOL) of the cancer patients are the main limitation for current cancer adjuvant therapy. Some of the common side effects of current adjuvant therapies are listed in Table 2. These side effects may appear immediately, may develop after a few weeks or some may present late toxicity. Most of the side effects are usually mild but they can be severe depending on the response from the individual patient. Based on 5 years follow-up review, many cancer patients would delay the time in seeking for treatment or avoid further treatment totally (Radzniwan *et al.*, 2009). Although further explanations on the reasons were not included in the review, fear and anxiety of chemotherapy, prolonged depression and adjustment disorder were the probable reasons for the trend. Nonetheless, Leong *et al.* (2009) reported that the majority of the cancer patients would rather choose traditional or alternative therapy than receiving hospital treatment.

**Table 2:** Some common side effects of current adjuvant therapies

Types of treatment	Side effects	Reference
Radiation therapy	Mouth and throat changes (dental caries, infection) Mental retardation, learning disorder Pain, nausea and vomiting, anorexia, diarrhea, constipation, mouth sores, fatigue, urinary infection, headache Neuropathy (nerve damage)	Schiff and Ben-Arye (2011) Duffner (2006) Alzabaidey (2012) Backes and Martin (2015)
Chemotherapy	Anxiety, depression Cardiac effects (irregular heartbeat, heart inflammation, heart failure) Oral mucositis, nausea and vomiting  Pain, nausea and vomiting, anorexia, diarrhea, constipation, mouth sores, fatigue, urinary infection, headache Neurotoxicity (sensory problems)	Lua <i>et al.</i> (2011) Monsuez <i>et al.</i> (2010) Schiff and Ben-Arye (2011) Alzabaidey (2012)  Pasetto <i>et al.</i> (2006)
Hormone therapy	Weight gain, sexual dysfunction, hot flashes, anemia, fatigue, diabetes Possible cardiac effects (heart failure)	Nguyen <i>et al.</i> (2015) Edelman <i>et al.</i> (2014)
Targeted therapy	Cardiac effects (heart failure, hypotension) Fatigue, pain, depression, dementia, urinary infection	Monsuez <i>et al.</i> (2010) Storey <i>et al.</i> (2011)

Another limiting factor to the current adjuvant therapy is drug resistance in chemotherapy, targeted therapy and hormone therapy (Mitsuhashi *et al.*, 2015; Groenendijk and Bernards, 2014). According to Whiteside (2010), the resistance is most likely caused by immune editing, where molecular alterations in tumor cells eliminate the malignant cells that are sensitive to therapy and allows for the survival of the resistant variants. Recurrence is also another limitation to the current adjuvant therapy administration. Most of the recurrences happened when the specific genes that mediate the metastasis process were not identified with generic treatment, when serosal invasion was present or when lymph nodes involvement were detected (Teh *et al.*, 2012; Carrato, 2008; Yoo *et al.*, 2000; Peters *et al.*, 2000).

With all the limitations, there is no doubt that research on cancer is still relevant and very much needed. Furthermore, due to the complex interactions between biological and environmental factors such as genetic diversity, socioeconomic disparities and regional preferences that resulted in differences in the outcome of anticancer therapy, all researchers are encouraged to focus on cancer therapy development (Ma *et al.*, 2010).

## Current Research on Adjuvant Therapy for Cancer

Cancer research has been a broad and current interest for scientists. Several success researchers had come out with drugs for prevention and treatment of the diseases. Among those that stood out was the introduction of prophylactic human papillomavirus (HPV) vaccine (Pagliusi and Aguado, 2004). The vaccine with the trade name Gardasil<sup>®</sup> (Merck and Co.) was intended for the prevention of cervical cancer and some other related cancers such as vulvar, anal, vaginal and oropharyngeal cancers (Barr and Sings, 2008). Administration of human papillomavirus (HPV) vaccine (HPV16 L1 VPL) recorded a 94% efficacy in cervical cancer prevention and could last for at least 3.5 years after immunization (Mao *et al.*, 2006).

Other than finding new methods for cancer prevention, researchers have been focusing on improving cancer diagnostics, finding a better combination of available adjuvant therapies and introducing new adjuvants for cancer therapy. Studies on new adjuvants for cancer therapy have been made on various agents, from natural compound to inorganic materials, in order to look for possible anticancer properties and inhibition activities on the proliferation of cancer cells. Table 3 listed some of the recent and ongoing researches on new anticancer adjuvants.

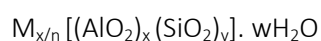
**Table 3:** Recent and ongoing researches on new anticancer adjuvants

Study	Agent	Relevant findings
Youssef <i>et al.</i> (2015)	Zeolite Na-A	Ag-substituted micronized zeolite Na-A (Z-Ag) showed cytotoxic activity against lung carcinoma (A549), breast adenocarcinoma (MCF7), hepatocellular carcinoma (HepG2) and colon carcinoma (HCT116) cell lines
Bojko <i>et al.</i> (2015)	Cucurmin and Tyrphostins (tyrosine-kinase inhibitors)	The mixture showed anticancer effects towards human brain cancer cells (LN229) through viability, cell cycle, apoptosis, ROS and genotoxicity studies
Li <i>et al.</i> (2015)	<i>Hedyotis diffusa</i> Willd (Chinese herb)	Ethanol extracts of HDW (EEHDW) significantly reduced the cell viability of multidrug-resistant colorectal cancer cell line (HCT8/5-FU)
Chu <i>et al.</i> (2014)	<i>Rubus idaeus</i> (raspberry)	Treatment with extract of raspberries by ethyl acetate (RIAE) inhibited the highly metastatic human lung cancer cells (A549) in both <i>in vitro</i> and <i>in vivo</i> studies
Merzouk <i>et al.</i> (2012)	<i>Leech saliva extracts (LSE)</i>	LSE has cytotoxic activity against small cell lung cancer cell line (SW 1271)
Bhattacharya <i>et al.</i> (2012)	<i>MFI-type zeolite nanoparticles</i>	MFI-type zeolite nanoparticles induced oxidative stress and cause genotoxicity towards human lung alveolar cells (A549)



## Zeolites

Zeolites are inorganic materials that consist of hydrated silicates and aluminium, known as aluminosilicates. The three-dimensional frameworks of zeolites are built of  $\text{SiO}_4$  and  $\text{AlO}_4$  in tetrahedral composition, bound by oxygen bridges and formed microporous structures that could accommodate cations such as sodium, calcium, and magnesium (Breck, 1974). The cations are usually present in the pores and voids in order to compensate for the negative framework charge created by aluminium substitution. Water molecules are also present in the pores and voids as solvent or guest molecules. The structural formula for zeolites is represented as:



where:

M = an alkali or alkaline earth cation

n = the valence of the cation

x + y = the total number of tetrahedral per unit cell

w = the number of water molecules per unit cell

[ ] = the framework composition

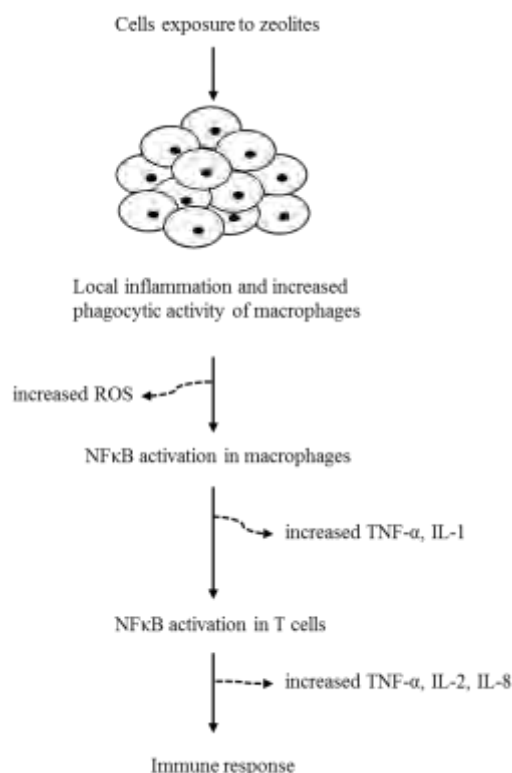
Zeolites can be obtained naturally or by chemical synthesis (Jeannette, 1980). Some examples of common natural zeolites are clinoptilolite, chabazite and mordenite while the examples for synthetic zeolites are zeolite A, zeolite X and zeolite Y. Natural zeolites are obtained from the uncontrolled environment after some natural processes such as from volcanic sediments, whereas synthetic zeolites are produced in a closed environment at the laboratory. Therefore, natural zeolites often have impurities and irregularities in the structures that may limit their application while synthetic zeolites are usually high in purity and regular in crystallinity. Additionally, the structure and properties of a synthetic zeolite can be tailored according to the intended application (Sherman, 1999).

## Zeolites in Cancer Therapy

The application of micronized clinoptilolite as an anticancer adjuvant was first revealed by Pavelic *et al.* in 2001. From the same research group, Zarkovic *et al.* (2003) continued to study on the effect of micronized clinoptilolite at several different concentrations on *in vitro* cell proliferation using a number of human cell lines including HeLa (cervical carcinoma), MiaPaCa-2 (pancreatic carcinoma), Caco-2 (colon carcinoma), MCF-7 (breast carcinoma), Hef522 (diploid fibroblasts), SW620 (colon carcinoma) and Hep-2 (laryngeal carcinoma). The antiproliferative activity of the micronized clinoptilolite against cancer cells was described as the result of the attenuation of survival signals and induction of tumor suppressor genes. Additionally, the micronized clinoptilolite was proven to produce some positive effects in cancer therapeutics through *in vivo* experiments using dogs and mice that were infected with several types of tumor cell line. Their findings supported the work

by Pavelic *et al.* (2001) where overall health status improvement with the prolongation of life span was reported and tumors size were found to decrease in some of the animals tested.

Pavelic *et al.* (2002) suggested that zeolites would activate macrophages that would stimulate the cellular immune response, which was proven by the increase in reactive oxygen species (ROS) production as well as other stimulants of the T cells such as TNF- $\alpha$  and cytokines. It acts as immunoactivator by inducing the translocation of the NF $\kappa$ B p65 subunit to its nucleus (Pavelic *et al.*, 2002). According to Taraphdar *et al.* (2001), the activation of transcription factor NF- $\kappa$ B involving its translocation to the nucleus has been linked to apoptosis. Figure 1 summarized the stimulation of cellular immune response induced by zeolites.



**Figure 1:** Stimulation of cellular immune response induced by zeolites (Pavelic and Hadzija, 2003)

Meanwhile, Katic *et al.* (2006) reported on the changes in the ion concentration of the cellular microenvironment after treatment with clinoptilolite. It was found that the clinoptilolite could affect the activity of signaling pathways as the silicates and aluminosilicates could interact directly with particular cells, leading to the regulation of critical genes. The most significant changes reported in the analysis of signaling pathways was in the activities of key proteins involved in regulating the cell survival or apoptosis (PKB/Akt) and cell division (ERK1/2). DNA synthesis was found to decrease in parallel with the increase in apoptosis thus, the cell viability was reduced. Further investigation by Katic *et al.* (2006) showed that antitumor effect on cells *in vitro* was partly due to the adsorption of growth factors from serum in the cell culture medium that was added with clinoptilolite. Inhibition of

protein kinase B/Akt by clinoptilolite treatment was shown only in the presence of serum indicating that the mechanisms of zeolite action may relate to the adsorption of serum components.

The use of zeolite as anticancer adjuvant has been debated by the experts in the Memorial Sloan Kettering Cancer Centre (2016). They discussed profoundly on the efficacy of using zeolite as an alternative adjuvant in cancer therapy and listed several precautions that should be acknowledged by patients, caregivers and healthcare professionals regarding the usage of zeolite for cancer treatment. Many companies marketed zeolite as a product that can treat or cure cancer without providing any published scientific reports to support their claim. This raised a lot of concern among medical practitioners and health regulators. Thus, the Food and Drug Association (FDA) issued warning letters to several distributors for the misleading information in their marketing claims and false advertisement. Other than the published studies by Pavelic and his research group, there had been no other clinical data or human trials reported on the efficacy of zeolites as anticancer drugs. The implications of consuming zeolite for cancer treatment are still unclear.

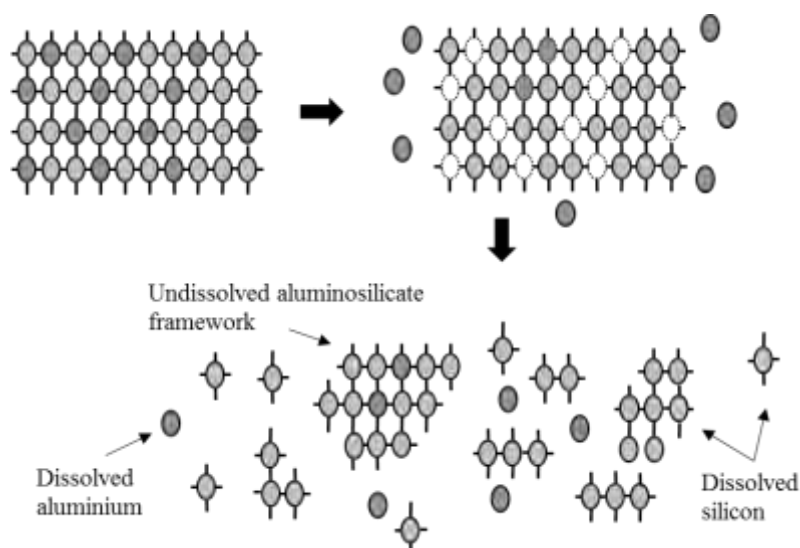
Currently, there are many dietary supplements derived from zeolites such as Natural Cellular Defense (Waiora), ZETOX (Global Health Products) and Destroxin (ZEO Health). Therefore, the review by Memorial Sloan Kettering Cancer Centre (2016) included several guides on the use of zeolite as a supplement as well as some warnings of the possible effects upon its consumption. Among the emphasized effects were the possibilities of zeolites interference with other medications upon overexposure such as premature disintegration of enteric coated drugs, decreased bioavailability of antibiotics, decreased effectiveness in chemotherapy drugs and rejection in transplant patients. Nonetheless, zeolite has not been regarded as a toxic substance with the FDA categorized zeolite as Generally Recognized as Safe (GRAS). Furthermore, several types of zeolites have been reported for other biomedical application such as in hemodialysis, antidiarrhea, antacid and drug support system. These zeolite products have been patented (Cerri *et al.*, 2004), studied *in vitro* (Pellegrino *et al.*, 2011), underwent clinical trials (Kee *et al.*, 2015; Rodriguez-Fuentes *et al.*, 1997 and 2006) and approved by the health regulators for use as new drugs in the pharmaceutical industry (Rodriguez-Fuentes *et al.*, 1997 and 2006). Hence, it was substantially proven that zeolite can be consumed with proper guidance and under safety precautions.

### Effects of Zeolites in Gastric and Intestinal Fluid

Most anticancer adjuvants are administered through intravenous (i.v.) either by bolus injection or continuous intravenous infusion. The direct route ensures immediate and complete bioavailability of the treatment as well as overcomes the variable absorption patterns of the gastrointestinal tract (Mazzaferro *et al.*, 2013). However, a study performed by Borner *et al.*, (2002) on colorectal cancer patients on the preferred type of treatments revealed a clear preference towards oral treatment than intravenous treatment. Convenience and toxicity consideration are among the main reasons stated.

Nevertheless, the bioavailability of oral anticancer drug depends on the sensitivity of the drug towards the condition of the gastrointestinal tract (Mazzaferro *et al.*, 2013). The stomach and the intestine are the two main organs of the gastrointestinal tract. Thus, the bio-relevant simulated media involved for developing predictive *in vitro* models for orally administered drugs are the simulated gastric fluid (SGF) and the simulated intestinal fluid (SIF) (Jantratid and Dressman, 2009). These simulated media can be used in the studies for the assessment of a drug product development.

The pH in normal stomach condition is between 1 and 3. This is because the gastric acid that is produced as digestive fluid in the stomach is mainly composed of the hydrochloric acid (HCl). The acidic environment of the stomach may have some effects on zeolites. Hartman and Fogler (2007) studied the dissolution and precipitation of zeolite A (LTA), analcime (ANA) and zeolite Y (FAU) in hydrochloric acid. It was reported that zeolite A dissolved rapidly in the HCl solution, analcime was partially dissolved while zeolite Y did not appear to dissolve with the silicate framework remain intact. Previously, Hartman and Fogler (2006) had demonstrated the influence of Si/Al ratio in the mechanism for dissolution of zeolites. Based on their study, dissolution of zeolite by hydrogen ion attack was found to be highly dependent on the number and arrangement of Al atoms within the crystal structure. The removal of Al was selective and subsequently resulted in the release of Si atoms. As a result, the crystal structure disintegrated and collapsed. Figure 2 illustrates the mechanism of a zeolite dissolution in hydrochloric acid as described by Hartman and Fogler (2006).



**Figure 2:** Mechanism of a zeolite dissolution in hydrochloric acid (Hartman and Fogler, 2006)

According to the results from the experiment performed by Kavak and Ulku (2013), the presence of zeolites in the gastrointestinal fluid did not show substantial interaction such as in the chemical composition of the zeolites and in the amount of enzyme levels in the fluid. A change in the

pH and ionic strength could be due to the protonation of the negative and neutral surface hydroxyl groups of the active sites on the zeolites (Kavak and Ulku, 2013).

### Cytotoxicity of Zeolites

Several cytotoxicity studies of the zeolites or nanozeolites had been performed by other researchers. Adamis *et al.* (2000) had studied the cytotoxicity for clinoptilolite and mordenite against peritoneal macrophages by the LDH (Lactate dehydrogenase) assay method. The LDH released after the incubation were found to be statistically insignificant to the negative control, indicating that both clinoptilolite and mordenite were not cytotoxic. Then, Petushkov *et al.* (2009) investigated the cytotoxicity of silicalite-1 nanoparticles using human embryonic kidney cells (HEK-293) and macrophage cell lines (RAW264.7) with different concentrations of silicalite-1 (0.25 mg/ml, 0.5 mg/ml and 1 mg/ml). From the investigation, it was found that the cytotoxicity of silicalite-1 depends on the dose, particle size, surface functional group and type of cell line. However, at lower concentrations of between 0.05 mg/ml and 0.2 mg/ml, silicalite-1 showed no toxicity towards the human cervical carcinoma (HeLa) cells (Kihara *et al.*, 2011). In the study by Kihara *et al.* (2011), the cytotoxicity of zeolite Soconil Mobil-5 (ZSM-5), zeolite A (LTA) and zeolite L (LTL) against HeLa cells was found to be dose and size dependent.

Meanwhile, Laurent *et al.* (2013) studied the cytotoxicity of LTL- and EMT-type zeolites against the HeLa cell lines. Various concentrations of the zeolites were used ranging from 0.05 to 0.4 mg/ml. The results showed negligible cytotoxicity as the viability of HeLa cells was not significantly affected by both types of zeolites. Earlier, Thomassen *et al.* (2012) investigated the cytotoxicity of nanozeolite A and Y by the LDH and MTT (tetrazolium dye) assay methods. Three types of human cell lines (alveolar epithelial (A549), umbilical vein (EA.hy926) and monocytic leukemia (THP-1) cells) were exposed to various doses of the nanozeolites (0.025, 0.05, 0.1, 0.25, 0.5, 1.0 and 2.0 mg/ml). There was no LDH leakage observed after 24-hour exposure to both nanozeolite A and Y at all concentrations while a significant decrease in the mitochondrial activity was only observed at 2 mg/ml for both nanozeolites. Table 4 summarized the cytotoxicity studies of the zeolites and nanozeolites that had been performed by other researchers.

**Table 4:** Previous cytotoxicity studies of the zeolites and nanozeolites

Study	Agent	Cells	Relevant Findings
Laurent <i>et al.</i> (2013)	LTL-type and EMT-type zeolites	Cervical cancer cells (HeLa)	No significant cytotoxicity
Thomassen <i>et al.</i> (2012)	Nanozeolites A and Y	Alveolar epithelial cells (A549), umbilical vein cells	Cytotoxicity was dose dependent

		(EA.hy926) and monocytic leukemia cells (THP-1)	
Kihara <i>et al.</i> (2015)	Silicalite-1, ZSM-5, Zeolite A, Zeolite L	Cervical cancer cells (HeLa)	Cytotoxicity was dose and size dependent
Petushkov <i>et al.</i> (2009)	Silicalite-1	Human embryonic kidney cells (HEK-293), macrophage (RAW 264.7)	Cytotoxicity was dependent on dose, particle size, surface functionalization group and type of cell lines
Adamis <i>et al.</i> (2002)	Clinoptilolite, Mordenite	Peritoneal macrophage	No cytotoxicity observed

### Selection of Zeolite: Overview

Zeolite was first discovered by Cronstedt in 1756 with the discovery of stilbite (Breck, 1974). The term zeolite comes from two Greek words, “*zeo*” (to boil) and “*lithos*” (stone). Zeolite is an aluminosilicate with a relatively open framework due to its porous structure. The zeolite framework consists of Si-O tetrahedral complex and at some places in the framework Si<sup>4+</sup> is replaced by Al<sup>3+</sup>. This results in a negative framework charge which is due to the deficiency of an electron at the Al-O tetrahedral (Maesen and Marcus, 2001). Charge-compensating cation from the alkali or alkaline earth metals, enters the pore as extraframework to maintain the electroneutrality of the overall zeolite framework. However, the molecules entering the pore would be selectively sieved by the size of each molecule. These unique properties contribute to the major function of zeolites as catalysts, ion exchangers and adsorbents with vast application in many industries.

The revelation of natural zeolite, clinoptilolite, as an anticancer adjuvant that is able to inhibit the growth of cancer cells and promotes longer lifespan with low side effects is appreciated (Pavelic *et al.*, 2001). However, natural zeolites contain impurities from the open environment. Variation in the mineral composition of the natural zeolite may result in diverse levels of anticancer activity which will make dosage determination difficult. Therefore, a purification process of natural zeolites is necessary before any biomedical application. Unfortunately, it does not ensure complete extraction of the unwanted minerals (Tomasevic-Canovic, 2005). Unless a complete preliminary characterization is made and the zeolite material is standardized, the use of natural zeolites in biomedical application should be reconsidered as natural zeolites are poor materials to begin with (Colella, 2011). A possible alternative to natural zeolites is the synthetic zeolites. Synthetic zeolites will ensure standardization in the matter of purity, size distribution, cationic composition and the production procedures. Synthesis of zeolite generates zeolites that are engineered to the desired form and provides rooms for modification in order to enhance the capability of the zeolites for the intended application. For example, decreasing the size of the zeolites to nanoscale will create larger surface area, expose more active sites and reduce diffusion path lengths and thus, will increase the activity of the zeolites

(Mintova *et al.*, 2013). Napierska *et al.* (2009) had proven the inverse relationship between particle size and cytotoxicity of monodisperse silica nanoparticles. Most methods for the preparation of synthetic nanozeolites, however, require the use of huge quantity of organic templates which is not environmentally friendly and costly. Modification through green methods by fine controlling the nucleation and adjusting the growth steps through chemical or physical conditions may help to reduce the use of environmental hazards in the synthesis process (Mintova *et al.*, 2013; Ng *et al.*, 2012a).

Each type of zeolites has different Si/Al ratio. Zeolite with a low Si/Al ratio would have a high negative charge due to the high number of aluminium, and thus a high number of exchangeable cations in the extraframework (Meinander, 2014). It was hypothesized that the mechanism for zeolite antiproliferation activity against the cancer cells might be related to the adsorption of serum components since the activity was detected only in the presence of serum (Katic *et al.*, 2006). As an adsorbent, the mechanism for the adsorption of cations by zeolites is through ion exchange (Meinander, 2014). Therefore, zeolites with low ratio of Si/Al were selected as they have higher cation exchange capacity compared to zeolites with high Si/Al ratio (Breck, 1974). Besides that, the pore size of the zeolites was also considered. Zeolites with large pores such as zeolites X and Y (0.6-0.8 nm) would allow large molecules to be adsorbed into their pores while zeolite with small pore size such as zeolite A (0.35-0.45 nm) might prevent large molecules from entering its pore (Flanigen, 2001; Breck, 1974). Zeolites in the sodium form would give an advantage due to the low electronegativity of the sodium ion, which means it could be easily replaced by other cations (Meinander, 2014).

The efficacy of the application through oral consumption is of the main concern once the selected nanozeolite is synthesized. The nanozeolite is expected to be unstable in the acidic environment of the stomach due to the alkaline nature of the nanozeolite. The structure of the nanozeolite may collapse as the extraframework cations of the nanozeolite would be replaced by the hydronium ions and followed by dealumination (Colella, 2011). On the other hand, the basic condition of the intestinal tract would favor the dissolution of nanozeolite releasing the silicate and aluminate from the nanozeolite framework (Colella, 2011). It is also important to ensure that the application of zeolite will not interfere with the biological environment that will affect the physiological aspect. Thus, the challenge is to attain the concentration that is structurally stable, tolerable to the gastrointestinal condition and capable of inhibiting the proliferation of cancer cells. In order to ensure the stability of the zeolite structure, zeolite NaY could be used instead of zeolite NaX or zeolite NaA, due to its higher Si/Al ratio. Dissolution or disintegration of the framework is highly dependent on the Si/Al ratio of the zeolite, where zeolites with higher Si/Al ratio such as zeolite Y were found to be more stable in acidic solution when compared to zeolites with low Si/Al such as zeolite A (Hartman and Fogler, 2007).

The antiproliferative activity of nanozeolites is normally cell type-dependent and dose-dependent (Petushkov *et al.*, 2009). They were found to be non-toxic to the cells at low concentrations (Laurent *et al.*, 2013), but cytotoxicity at concentrations above 0.5 mg/ml had been reported

(Thomassen *et al.*, 2012). Therefore, the question whether the antiproliferative activity of the synthesized nanozeolite will remain after passing through the gastrointestinal tract is an additional concern. A study by Kavak and Ulku (2013) showed an insignificant decrease in the antiproliferative activity of digested zeolite. Thus, a slight decrease in the antiproliferation activity would be expected, but most importantly the synthesized nanozeolite must have low toxicity against the normal cells for it to function as an anticancer adjuvant alternative to the clinoptilolite.

The efficiency of the zeolites either synthetically produced or naturally occurring zeolites as anticancer adjuvant could be assessed by studying its stability in simulated gastrointestinal fluid and measuring its cytotoxicity via *in vitro* tests. Figure 3 shows the possible contribution of the zeolite in the vicinity of all the research for cancer treatments.

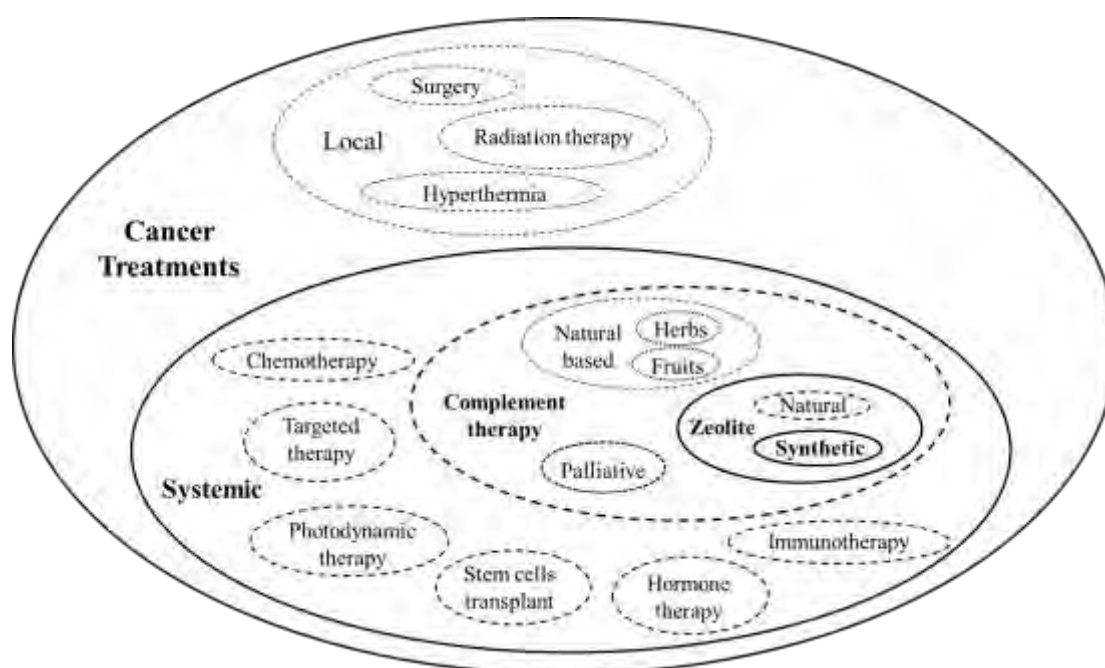


Figure 3: Contribution of zeolite in cancer treatment

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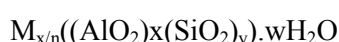
### Chapter 3 Overview of the Synthesis of Nanozeolite from Agro-Waste

Mashitah Mad Salim, Noor Azhana Ghazi, \*Nik Ahmad Nizam Nik Malek,  
Salehuddin Hamdan

\*Department of Biotechnology and Medical Engineering, Faculty of Biosciences and Medical  
Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor, Malaysia.  
Email: [niknizam@fbb.utm.my](mailto:niknizam@fbb.utm.my); Tel: +607-5558440

## Introduction

Zeolite is an inorganic crystal material with three dimensional structure of hydrated aluminosilicate which consists of cations and water molecules in its framework structure. The cations are presented in zeolite to compensate the negative charges of the zeolite framework which are obtained from aluminium. The cations are from group I and/or group II in the periodic table (e.g. sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca)). The water molecules in the zeolite are reversible where it can enter or left the zeolite framework without affecting the zeolite framework structure (Breck, 1974). Zeolite consists of SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> as its backbone which functions as the main building unit of the framework and attributed to the framework charge, respectively. The alkaline cations present in the zeolite are counter ions of the framework charge. Water is the solvent of the zeolite, while is the mineralizer present in the zeolite. The AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra of the zeolite framework are linked together with oxygen, forming an infinitely extended three-dimensional framework structure of the zeolite. Zeolites have high cation exchange capacity (CEC) and high specific surface area (Khalil, 2013) mainly due to its structures which have high porosity (Breck, 1974). The crystalline unit cell of the zeolite can be described as follows:



Where, M is the cation, n is the valence of cation, w is the ratio of the tetrahedral silica to alumina and portion ( ) is the framework composition.

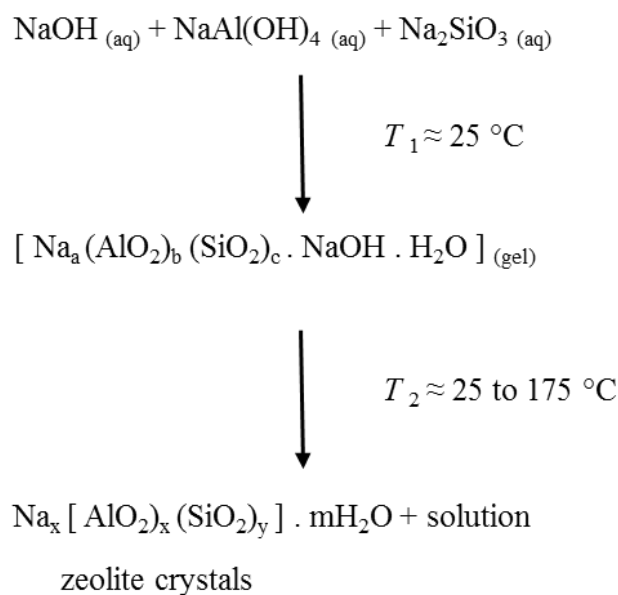
Zeolite is known as molecular sieves due to the microscopically small size of the zeolite pores which are in the molecular size dimensions. The different sizes of the guest molecules and cations are discriminated by the zeolite through its windows and channels (Chen *et al.*, 1994). Zeolites are applied as catalyst, ion exchanger and adsorbent material. In the zeolite structure, Si exists in 4+ linked with two molecules of oxygen, forming Si-O tetrahedral which is electrically neutral. Meanwhile, Al exists in 3+ oxidation state linked with two molecules of the oxygen, forming Al-O tetrahedral left deficient of one electron. This condition causes zeolite framework to have negative

charge which can be compensated by the cations to maintain the zeolite framework to be in neutral charge (Breck, 1974).

Synthetic zeolite is pure and uniform in composition and it is suitable to be used in many purposes, mainly for research and industrial applications (Breck, 1974). However, the usage of synthetic zeolite such as NaY zeolite is expensive due to the expensive chemical reagents as reported by Matti and Surchi (2014), and a longer production period is needed as it is synthesized in the laboratory in a small amount at one time. The production of nanosized zeolites for the commercialization purpose is generally new due to the limited machines and expensive chemical reagents (Willis and Benin, 2007). Besides, the cost for characterization of the materials is expensive as zeolite has to be characterized in every batch. Thus, it limits the tendency to produce nanosized zeolites for commercialization purposes. Thus, the nanosized zeolite could be synthesized with minimal production cost using agro-waste such as rice husk ash as the silica source in large-scale production at one time.

### Synthesis of Zeolites

Zeolites can be synthesized under hydrothermal conditions from gel containing silica, alumina, source of cations and water. According to Breck (1974), general requirement for the synthesis of zeolites includes reactive starting materials such as a freshly prepared gel or amorphous solids, a relatively high pH that is introduced in the form of an alkali metal hydroxide, low temperature hydrothermal conditions with concurrent low autogenous pressure at saturated water vapor pressure and a high degree of supersaturation of the components that will lead to the nucleation of the desired crystals. Most zeolites are synthesized by dissolving a source of alumina and a source of silica in a strongly basic aqueous solution (Maesen and Marcus, 2001). Figure 1 illustrates general procedure required for the synthesis of a zeolite using the example of  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system.



**Figure 1:** Gel preparation and crystallization step in the synthesis of zeolites (Breck, 1974)

### Synthesis of Nanozeolites

Modern researches are focusing on nanozeolite synthesis as nanosized zeolites provide important and improved characteristics such as larger surface areas, controlled pore size and easier functionalization for advance application (Tosheva and Valtchev, 2005). Among key factors that would influence the synthesis of nanozeolites are the use of organic templates or structure-directing agents (OSDA), type of precursor of synthesis gel or suspension, initial silicon and aluminum sources, synthesis conditions such as temperature, pressure and time and heating methods for examples conventional, microwave and sonication (Mintova *et al.*, 2013). The abundant use of organic templates in order to obtain a homogeneous precursor solution system makes the method cost-ineffective (Wong *et al.*, 2012). Further needs for the removal of the organic templates at the end of the process makes the procedure more unfavorable. Therefore, a method for the preparation of nanozeolite without the use of organic templates is highly desirable as to avoid any problem related to the excess waste of organic solvent.

The use of rice husk ash as an alternative silica source has been acknowledged by many previous researchers. Hamdan *et al.* (1997) reported more than 98% silica powder production whereas Della *et al.* (2002) reported a 95% silica powder production after thermal treatment of the rice husk ash. Several types of zeolites have been successfully synthesized using rice husk ash as the silica source such as zeolite beta (Prasetyoko *et al.*, 2006; Loiha *et al.*, 2009), zeolite A (Bhavornthanayod and Rungrojchaipon, 2009; Katsuki and Komarneni, 2009; Yusof *et al.*, 2010; Azizi and Yousefpour, 2010; Tan *et al.*, 2011), zeolite X (Dalai *et al.*, 1985; Katsuki and Komarneni, 2009; Yusof *et al.*, 2010) and zeolite Y (Rahman *et al.*, 2009; Yusof *et al.*, 2010; Saceda and Leon, 2011; Tan *et al.*, 2011). A few reports have been made on the synthesis of nanosodalite, nanozeolite NaA, nanozeolite



NaX, nanocrystalline zeolite L and EMT-type zeolite nanocrystals from rice husk ash without the use of organic templates, but none was reported on the synthesis of nanozeolite NaY from rice husk ash. Table 1 summarizes some of the previous researches on the synthesis of nanozeolites.

**Table 1** : Previous researches on the synthesis of nanozeolites

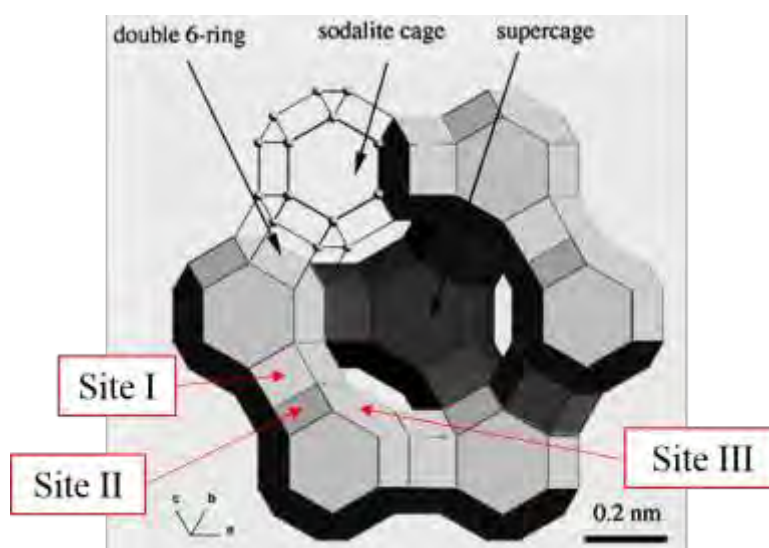
Product	Size	Procedures	Reference
Nanosodalite	30 - 60 nm	Low temperature, without organic templates, rice husk ash as silica source, 5 hours of crystallization time	Ghasemi <i>et al.</i> (2011)
	50 - 100 nm	Low temperature, without organic templates, rice husk ash as silica source, 3 hours of crystallization time	Rusmili <i>et al.</i> (2012)
Nanozeolite A	40 - 80 nm	Reverse microemulsion-microwave, without organic template	Chen <i>et al.</i> (2005)
	50 - 120 nm	Room temperature, without organic templates, rice husk ash as silica source, crystallization under shaking condition	Ghasemi and Younesi (2011)
Nanozeolite X	40 - 150 nm	Hydrothermal crystallization in temperature-controlled shaker, without organic template	Fathizadeh and Aroujalian (2011)
	40 - 120 nm	Without organic template, rice husk ash as silica source, crystallization under shaking condition	Ghasemi and Younesi (2012)
Nanozeolite Y	20 - 31 nm	Periodically removing the synthesis products and recycling the unused reagents, using organic templates	Song <i>et al.</i> (2005)
	59 nm	Bentonite as the starting material, without organic templates, 20 hours of aging time, crystallization at 97°C	Faghihian and Godazandeha (2009)
	50 nm	Using organic templates	Taufiqurrahmi <i>et al.</i> (2011)
	10 - 15 nm	Without organic templates, low temperature at 4°C	Awala <i>et al.</i> (2015)
EMT-type nanozeolite	15 nm	Ambient temperature, without organic templates, rice husk ash as silica source	Ng <i>et al.</i> (2015)

## NaY Zeolite

X and Y zeolites are synthetic zeolites in the group of FAU-type zeolite which has similar structure as the framework structure of the naturally occurring faujasite type zeolite, but with differences silica and alumina ratio (Bhatia, 1990). The Y zeolite has Si/Al ratio almost similar to the Si/Al ratio of the faujasite type zeolite, while the Si/Al ratio of X zeolite is lower than Y and faujasite

zeolites (Bhatia, 1990). Hence, both of the zeolites (X and Y) have different physicochemical properties (Bhatia, 1990). The FAU-type zeolite is a group of zeolite, which has the most open framework among the zeolites and has 51% of void volume (Szostak, 1992). The unit cell of the faujasite structure of zeolite has a cubic form structure with a large cell dimension which possess 192 (Si/Al) $O_4$  tetrahedra (Szostak, 1992). The information regarding the Si/Al ratio of the zeolite and the zeolite framework structure is crucial in order to evaluate the zeolite materials that are suitable to be used as adsorbent material. As the negative charge of the zeolite exchange sites are obtained from the aluminium in the zeolite framework, the zeolite which has more aluminium (low Si/Al ratio) would have more exchange sites which reflect high cation exchange capacity of the zeolite, and thus able to adsorb high amount of any compound on its surface and in its framework. NaY zeolite is a good carrier system since it possesses relatively high ion exchange capacity and lattice stability (Cheng *et al.*, 2012). According to Hagiwara *et al.* (1990), zeolite which has a specific surface area at least 150 m<sup>2</sup>/g and the Si/Al ratio below 14 is suitable to be applied as an adsorbent.

The Y zeolite consists of secondary building units of 4, 6 and 6-6 with a three-dimensional pore structure which perpendicular to each other and located in the x, y and z planes similar to LTA (Linde Type-A). The pore diameter of the Y zeolite is about 7.4 Å (0.74 nm) exists from a 12-member oxygen ring continues to the large cavity with a diameter of 12 Å. The large cavity is surrounded by ten truncated octahedral of the sodalite cages connected with each other by hexagonal faces. The unit cell of the Y zeolite is in cubic form ( $a=24.7$  Å), Fd-3m symmetry, 0.48 void volume fraction (Bhatia, 1990) and 0.53 cm<sup>3</sup> pore volumes (Barrer, 1982). The Y zeolite has Si/Al ratio about 2.43 and thermally decomposed at 793°C (Rahman *et al.*, 2009). The framework structure of Y zeolite is shown in Figure 2.



**Figure 2:** The framework structure of Y zeolite (Gu *et al.*, 2000) with three types of cation sites.

The secondary building unit (SBU) is the smallest unit of the zeolite framework with three-dimensional structure which is formed from the tetrahedron  $TO_4$  ( $T=Si$  or  $Al$ ) (Breck, 1974). The SBU is one of the important characteristics used to differentiate the zeolites. The cations are located at three different sites in the zeolite framework, namely at the centre of the hexagonal prism (site I), at the six membered rings (site II) and at the walls of the channels (site III). The amount of sodium ions occupies the sites in a unit cell of Y zeolite is about 56 (16 cations in site I, 32 cations in site II and 8 cations in site III), while 86 sodium ions occupy the X zeolite (16 cations in site I, 32 cations in site II and 38 cations in site III) (Breck, 1974). Zeolites are divided into six groups based on the number of the oxygen atoms in the largest ring of each zeolite. The Y zeolite is grouped into 12-membered ring systems (Chen *et al.*, 1994), which is known to have large pores. The Y zeolite was discovered by Breck and his co-workers in 1961 when they tried to synthesize X zeolite with Si/Al ratio of 4.7. However, the synthesized zeolite showed different physicochemical properties from the X zeolite when the Si/Al ratio of the zeolite was above 3.0. The synthesized zeolite was eventually defined as Y zeolite. According to Robson and Occeli (1988), the X zeolite is a zeolite with Si/Al ratio between 2.0 to 3.0, while Y zeolite is a zeolite with Si/Al ratio of 3.0 to 6.0. The chemical formula of Y zeolite in moles of oxides is as follows (Breck, 1974):



In the chemical formula, the value of  $w$  is in the range of more than 3 and up to 6, whereas the value of  $x$  may be up to 9. Among the synthetic zeolites, the Y zeolite has been used in various applications, for example as the cracking catalysts in the petroleum cracking industry in the 1960s to replace the X zeolite because Y zeolite has extra thermal stability which was contributed by its higher Si/Al ratio compared to X zeolite (Smart and Moore, 1993).

### Nanosized NaY Zeolites

In order to reduce the cost and facilitate the synthesis of the zeolites, natural sources from industrial by-products and certain agro-wastes could be used as the silica source. Zeolites have been synthesized from various natural silicate sources such as fly ash (Tosheva *et al.*, 2012), rice husk ash (Yusof *et al.*, 2010) and clay minerals (Ngoc *et al.*, 2013; Matti and Surchi, 2014). In Malaysia, there are abundant of rice husk ash which can be obtained from paddy fields after harvesting season (Hamdan and Keat, 1993). The decomposed rice husk ash generates environmental problems such as haze, as most decomposition procedure is normally carried out by open burning on the fields (Yusof *et al.*, 2010). In order to solve the problem, rice husk ash has been used as a source of silica in the synthesis of NaY zeolite (Hamdan and Keat, 1993).

Based on previous works on the synthesis of nanosized NaY zeolite, the synthesis conditions such as crystallization temperature is one of the important parameters that need to be controlled (Sang *et al.*, 2006; Ghasemi *et al.*, 2011). At low temperature, it will prolong the aging condition and form enormous amount of viable nuclei; considering that low concentration of silica and aluminium gel mixture are left and thus, limiting the size of the zeolite formed. For other types of nanozeolites such as sodalite (Zhan *et al.*, 2002; Rusmili *et al.*, 2012), the crystallization time was found to affect the nanosized zeolite. Zhan *et al.* (2002) synthesized NaX zeolite (size of 20-800 nm) by changing the crystallization temperature and include the agitation process. Shorter crystallization time and low crystallization temperature have resulted in the formation of zeolite with small crystal size, whereas the agitation would induce the formation of large amounts of viable nuclei, and thus producing zeolite with small crystal.

According to Tago and Masuda (2010), high concentrations of Si and Al source in the gel mixture would increase nucleation rate and result in decreasing the zeolite crystal size. The gel mixture of Si and Al was prepared with high amount of synthesis reagents at one time with the remaining ratio of Na<sub>2</sub>O/SiO<sub>2</sub>. The homogeneous distribution of the reactive species during the gel preparation will influence uniform nucleation in the system and hence, producing narrow particle size distributions of zeolite crystals (Awala *et al.*, 2015). On the other hand, the non-homogeneous gel mixture during gel preparation results in the formation of zeolite with impurities (Masih *et al.*, 2007).

The nanosized NaY zeolite can be synthesized using chemical reagents aided by organic template as the structure directing agent (Charkhi *et al.*, 2012; Sharma *et al.*, 2015). However, the organic-template approach has several disadvantages such as non-environmentally friendly, non-recyclable and costly. In addition, the thermal method of removing the template from the nanosized zeolite contributes to the irreversible aggregation forming larger particles. After the zeolite has been synthesized using the structure directing agent, the structure directing agent need to be removed from the zeolite by calcination leaving zeolite with porous structure. However, calcination of the zeolite with structure directing agent at high temperature resulted in the formation of irreversible aggregation between the nanosized zeolite particles caused by the formation of Si-O-Si bridges (Tosheva and Valtchev, 2005) and eventually lost the advantages of small particles properties. Besides, it was reported that the highest yield of the FAU nanocrystals was approximately 6-10 wt.% which is still below the amount of commercially obtained micrometre-sized zeolite (80 wt.%). Ultimately, the synthesized nanosized zeolite showed a microporosity and specific surface area lower than the microsized zeolites (the highest micropore volume of nanosized FAU zeolite synthesized in the presence of tetramethyl ammonium cations is about 0.12 cm<sup>3</sup>/g and Brunauer-Emmett-Teller (BET) specific surface area is about 448 m<sup>2</sup>/g) (Awala *et al.*, 2015). Thus, the synthesis of nanosized NaY zeolite with low synthesis cost, but able to produce high yield of high zeolite purity and crystallinity is greatly desirable.

The synthesized nanosized NaY zeolite is not as pure as commercial NaY zeolite because the silica source used in synthesizing the zeolite is from the agro-waste of rice husk ash that contained a small amount of impurities such as  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and others (Yusof *et al.*, 2010). However, a small amount of the impurities present in the rice husk ash is expected not to give much effect to the zeolite structure as these impurities only act as inert materials in the zeolite synthesis (Juan *et al.*, 2007).

### Rice Husk Ash as the Silica Source

There are many methods could be used to extract silica from the rice husk, for example chemical treatment, biological treatment, hydro thermo-baric and thermal treatment at 400-700°C (Soltani *et al.*, 2015). Most previous works using thermal treatment (400-700°C) as well as chemical treatment with alkaline treatment and acid leaching to produce an amorphous form of rice husk ash from the rice husk residues. The amorphous rice husk ash is a reactive form of silica that is used to synthesis pure zeolites (Paya *et al.*, 2001). Using thermal treatment at 600°C for one hour can yield rice husk ash (Yusof *et al.*, 2010). Based on previous study, the synthesized zeolites (NaA, NaX and NaY) were calcined to remove the impurities from the zeolites (Malek, 2011). If the rice husk ash pre-treatments have no effect to the purity and crystallinity of the synthesized zeolites, the pre-treatment steps can be avoided to simplify the procedure of zeolite synthesis.

The purpose of treating rice husk ash with acid or alkali is to remove the metallic impurities (Rahman *et al.*, 2009) that could influence the purity and crystallinity of the synthesized zeolite (Zi *et al.*, 1988). According to the research performed by Rahman *et al.* (2009), treating rice husk ash with 10%  $\text{H}_2\text{SO}_4$  could produce amorphous form of silica which contained 95.85%  $\text{SiO}_2$ , while the untreated rice husk ash (without acid wash) only produced 90%  $\text{SiO}_2$ . Moreover, according to Ali *et al.* (2016), the acid treated rice husk ash needs a short time to be decomposed by calcination compared to the untreated rice husk ash. Although the acid treated rice husk ash produces amorphous form with a better yield of  $\text{SiO}_2$ , the acid treated rice husk ash contains amorphous form of silica with SiOH on its surface which is unreactive in the synthesis of zeolites (Hamdan *et al.*, 1997). Thermal treatment of rice husk at temperature <800°C produces amorphous form of silica in the form of  $\text{Si}(\text{OSi})_4$  tetrahedral units which is more reactive silica source in the synthesis of Y zeolite (Hamdan *et al.*, 1997). Thermal treatment of rice husk at 1000°C produces crystalline form of silica (e.g. cristobalite and tridymite phases) which is unreactive in zeolite synthesis (Hamdan *et al.*, 1997).

### Summary

The NaY nanozeolite could be synthesized using rice husk ash as the silica source. Rice husk ash contain more than 90% silica (Yusof *et al.*, 2010) and is only agriculture waste that has

high silica content in dry form (Jain *et al.*, 1994). According to the statistic compiled by the Malaysian Ministry of Agriculture, in Malaysia, it was more than 400,000 metric tons of rice husk generated annually after every paddy harvesting season (Wong *et al.*, 2003). This rice husk material is decomposed by burning them on the field (Yalcin and Serinc, 2001) and by rotting (Rahman *et al.*, 2009) which could affect the environment and human health. Thus, by using rice husk ash as the silica source in zeolite synthesis, beneficial products (e.g. zeolites) can be produced from the agricultural waste and also, it can solve the problems occur due to the deposited of rice husk on the field (Rahman *et al.*, 2009).

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**Chapter 4****Synthesis of hierarchical mesoporous zeolite**

Peter Adeniyi Alaba<sup>1\*</sup>, Olumide Bolarinwa Ayodele<sup>2</sup>, Wan Mohd Ashri Wan Daud<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.

<sup>2</sup>Department of Chemical Engineering, Universiti Teknologi Petronas, 32610, Bandar Seri Iskanda, Perak, Malaysia.

\*Corresponding author. Tel.: +2348186628769, E-mail: [adeniyipee@live.com](mailto:adeniyipee@live.com)

**SUMMARY**

This paper provides an updated review on synthesis of hierarchical mesoporous Zeolite. The hierarchical structure enhances the zeolite's structure based on pore volume and size without severe penalization of the micropore volume, making it more efficient. Hierarchical mesoporous zeolites allow diffusion of bulky molecules compared to microporous zeolites. They are more stable hydrothermally than conventional mesoporous zeolites. They are widely used in fast pyrolysis of biomass and product upgrading such as zeolite cracking and hydrodeoxygenation as well as catalysis in general. We discussed synthesis routes including template and template free methods, factors influencing mesophase formation and zeolite crystallization, metal modification, hierarchy factor etc. Moreover, future developments such as scale-up, cheaper synthesis catalyst design as well as eco-friendly processes were also discussed.

**Key words:** Hierarchical, Zeolite, Catalyst, Mesoporous, Hierarchy factor

**1. Introduction**

Modern industrial processes make use of zeolites being a crystalline molecular sieve. These processes include adsorption and catalysis, especially in petrochemical and biodiesel industry (Alaba *et al.*, 2016b). This is simply because zeolites materials possess high thermal and chemical stability, high surface area and adjustable pore size (Alaba *et al.*, 2016). However, the major limitation of zeolites is their micropore size between ~0.5 and 1.5 nm (Alaba *et al.*, 2016). This pore size limitation prevents large molecules from reacting effectively over these microporous materials. To proffer solution to the diffusion problem of reactants in zeolites matrix, synthesis of aluminosilicate materials with flexible mesopore size, such as SBA-15 (Zhao *et al.*, 1998) and MCM-41 (Kresge *et al.*, 1992) have been successful since around 1990s. Mesoporous zeolites allow diffusion of bulk molecules because of their large pore size there by overcoming the drawback of microporous zeolites (Zheng *et*

*al.*, 2013). Nevertheless, they exhibited lower hydrothermal stability and acid sites than conventional zeolites, which restricts their usage in several of industrial applications and reactions. Some scientists later made immense effort at improving the framework crystallinity of these mesoporous materials for industrial applications. However, but all the efforts at improving the hydrothermal strength and the acid sites of the structural framework proved abortive (Liu, 2012).

Some scientists yet made efforts to incorporate the outstanding qualities of microporous and mesoporous zeolites to synthesize mesoporous zeolite materials with improved crystalline structure. These includes carbon materials (Kim *et al.*, 2003; Tao *et al.*, 2003); zeolite products hydrolysis or zeolite seeds assemblage to an ordered mesoporous phase (Liu *et al.*, 2000, 2001; Ooi *et al.*, 2004; Wang *et al.*, 2006; Zhang *et al.*, 2001); simultaneous treatment of the mixture of microporous and mesoporous (Prokešová *et al.*, 2003a, 2003b); acid and alkaline leaching (Corma *et al.*, 1999; J. Groen *et al.*, 2004; Groen *et al.*, 2006; Groen, Peffer, *et al.*, 2005; Groen *et al.*, 2007); partial recrystallization of pre-assembled mesoporous walls of the materials into zeolite structure (Campos *et al.*, 2006); zeolites primal building units coating on the wall of the pores of pre-synthesized mesoporous aluminosilicate (Trong On & Kaliaguine, 2001, 2003). However, some of the synthesized materials were far from the expected, morphology-wise (Na *et al.*, 2010).

Recently, incorporation of the outstanding qualities of microporous and mesoporous zeolites to synthesize mesoporous zeolite has been tremendously improved. The recently successful routes include post synthesis and direct synthesis (Zhao *et al.*, 2011). This could be achieved be with or without the use of organic template which serves as a structural directing agent (SDA). The post synthesis method used are hydrothermal and alkali treatment. The hydrothermal treatment is made successful by introduction of zeolite seed (such as silicalite-1 or ZSM-5) in small amount in a template free synthesis (Liu *et al.*, 2012). Alkali treatment could be via template or template free route (Li *et al.*, 2014; Rahimi & Karimzadeh, 2011; Zhao *et al.*, 2011). However, a better mesoporous zeolite could be achieved by combination of alkali and hydrothermal treatment (Shi *et al.*, 2013). Dual template method is commonly used for direct synthesis route to achieve meso and micro pore simultaneously (Choi *et al.*, 2006; Coriolano *et al.*, 2013). Dual functional template can also be used in a direct synthesis route. This template can direct both micro and meso pore simultaneously (Na *et al.*, 2013; Jo *et al.*, 2011a). The synthesized materials from this route can exhibit dual merit of micro and meso pore structure. The micropore takes care of shape or size selectivity while the mesopore takes care of facile diffusion pathway inside the pore wall.

Hence, in this chapter, we deeply look into post-synthesis modification routes for synthesis of hierarchical mesoporous zeolites and dual templating and dual functional surfactant mechanism. Moreover, we look into metal modification, hierarchy factor, hydrogen adsorption capacity of mesoporous zeolites.

## 2. Zeolites with hierarchical mesopores

Hierarchical mesoporous zeolites are synthetic zeolites that possess more than one level of porosity. They are carefully synthesized in such a way that increase in the mesoporosity does not severely penalize the micropore volume (Alaba *et al.*, 2015). They show better catalytic performance than microporous zeolites. This is attributed to the fact that they are less affected with diffusion limitation, making them a better alternative for reactions that involve large substrates, thereby increasing selectivity towards bulky molecules (Alaba 2016a; Alaba *et al.*, 2016). In fact, diffusion through hierarchical zeolite crystals are faster in a manner that is closely related to Knudsen regime, since the diffusion through mesoporous materials proceeds by molecule to molecule interaction as well as molecule to pore interaction (Serrano & Pizarro, 2013; Solsvik & Jakobsen, 2012). Therefore, they prevent secondary reaction because of the short residence time that they offer. This is capable of reducing deactivation rate especially in thermal cracking since no intermediate is formed (Hartmann, 2004; Perez-Ramirez *et al.*, 2008; Serrano & Pizarro, 2013).

(Liu *et al.*, 2012) investigated hierarchical mesoporous zeolite. They show that most reported mesoporous zeolites exhibit unsatisfactory thermal stability, low strong acid sites and inability to retain acid centers because of their amorphous walls, although they possess regular and periodic pores. While conventional zeolites are strong acids and have good structural stability, there limitation is low molecular diffusion, which so much affects their catalytic activity and selectivity. However, hierarchical mesoporous zeolites combined the strengths of microporous zeolites with efficient diffusion property of mesoporous materials. Recently, scientists synthesized hierarchical porous zeolites with the aid of templates. The templates used are amphiphilic organosilane (Liu *et al.*, 2012), carbon nanotubes (Schmidt *et al.*, 2001), starch, nanosized CaCO<sub>3</sub>, polymers such as Polyvinyl butyral (PVB) and Polydiallyldimethylammonium chloride (PDDA), carbon black (Christensen *et al.*, 2003). After hydrothermal crystallization of the aluminosilica-templates composite, the product is zeolite with blocked pore. Calcination is used to open the composite zeolite pores by removing the template inside. Another route to synthesis of hierarchical mesoporous zeolites crystal is re-crystallization of the wall of mesoporous zeolites such as MCM-41 and SBA-15 zeolites in the present of molecular templates (Fan *et al.*, 2008).

Hierarchical porous zeolites offer better catalytic performance in transalkylation of heavy aromatics (Liu *et al.*, 2012); alkylation of benzene with ethylene (Christensen *et al.*, 2003); superficial toluene disproportion (Liu, 2009); 1,3,5-tri-isopropylbenzene catalytic cracking (Wang *et al.*, 2009); cracking of vacuum gas oil (VGO) (Ishihara *et al.*, 2012); fast pyrolysis of biomass (Li *et al.*, 2014); etc. Therefore, hierarchical mesoporous zeolites are essential in bulky molecule catalysis or in catalytic reaction in aqueous medium in the future.

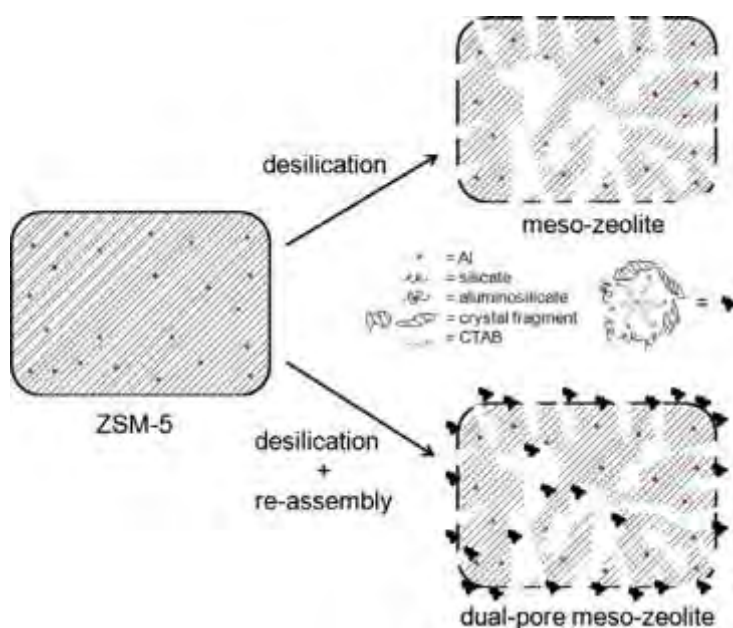
### 3. Synthesis Strategies

#### 3.1. Desilication and re-assembly strategy

Desilication has recently gained significant attention because it is straightforward. This method has been applied to various zeolites such as FER, MFI, BEA and MOR (Groen *et al.*, 2004; Groen *et al.*, 2005; Groen *et al.*, 2004; Groen *et al.*, 2006; Yoo *et al.*, 2012). In an aqueous alkali solution, the less reactive aluminol sites help to maintain the zeolite structure, while the alkali leached some parts of the silica layer increase the pore size of the materials. Recently, (Li *et al.*, 2014) developed a hierarchical mesoporous ZSM-5 zeolites by desilication with NaOH solutions for fast pyrolysis of biomass. They reported that carefully controlled desilication of zeolite can increase conversion of lignocelluloses to valuable aromatic hydrocarbons with low coke formation, thus improving the product distribution in the CPF of lignocellulose.

Desilication offers more adjustable pores and conserves the Brønsted acid sites, while dealumination which is a well-known post-synthesis method for increasing the pore size zeolite framework (Alaba *et al.*, 2016). A well-tailored mesoporosity is obtained by changing the Si/AL ratio of the main zeolites, reaction time, the reaction temperature, and concentration of the alkali via desilication. However, this method reduces the crystallinity of the materials by ~30% as estimated by X-ray diffraction (XRD) and nitrogen sorption measurement. The external surface area enhancement is because of pores size larger than 10 nm (Alaba *et al.*, 2016; Yoo *et al.*, 2012).

However, according to (Yoo *et al.*, 2012), strategic re-assembly method could be used to improve crystallinity. This method is adopted from pseudomorphic transformation concept. Hydrothermal treatment with the aid of surfactant was used to reunite the extracted species of silicates, aluminol and ZSM-5 zeolite crystals fragments to the main zeolite structure (Fig. 1). Scanning and transmission electron microscopy (TEM and SEM), solid state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  magic-angle-spinning (MAS) NMR, nitrogen sorption measurements, elemental analysis by inductively coupled plasma spectroscopy (ICP), temperature programmed ammonia desorption (TPD) and XRD are used to characterize the physicochemical characteristics of the synthesized mesoporous zeolites. The synthesized product exhibits a dual-mesopore size distribution of ~3 nm and ~10-30 nm. The external surface area increases with ~ 83% of the original zeolite matrix based on the calculated micropore pore volumes from nitrogen sorption measurements, and ~ 77% computed from XRD measurements. The XRD and TEM of the products indicate that desilication and re-assembly took place simultaneously to synthesize a dual-pore material. Re-assembling the extracted Si atom and other fragments by micellization of a surfactant leads to formation of smaller pore size of ~ 3nm, whereas desilication leads to formation of larger pore size of ~10-30 nm in the zeolite matrix.



**Fig. 1.** A schematic diagram illustrating mesoporous zeolite formation through desilication (upper right) and desilication and re-assembling process (bottom right) (Yoo *et al.*, 2012).

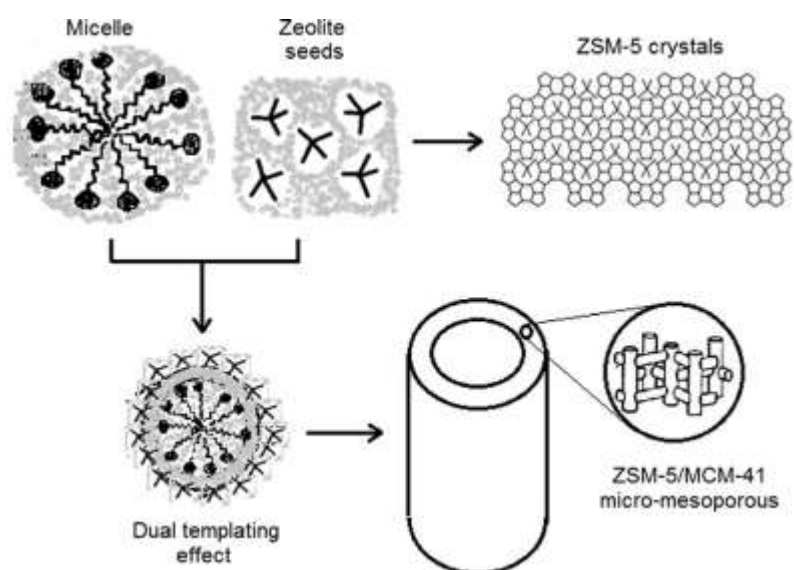
### 3.2. Dual template mechanism

The dual template mechanism is the synthesis method that employs two different templates to generate micro and meso pore in the zeolite materials. One of the templates is to generate mesopore and the other to generate micropore simultaneously (Choi *et al.*, 2006; Yang *et al.*, 2004). Fig. 2 below shows a typical dual mechanism, where both  $\text{CTMA}^+$  (cetyltrimethylammonium) and  $\text{TPA}^+$  (tetrapropylammonium) ion act as templates for the mesoporous MCM-41 and microporous ZSM-5 structure, respectively. The hybrid MCM-41/ZSM-5 formation is because of the charge compensation caused by the  $\text{TPA}^+$  ions on the MCM-41 structure (Coriolano *et al.*, 2013).

In a study of (Coriolano *et al.*, 2013), they prepared a reactive hydrogel of ZSM5, aged for 40 h at  $\sim 25^\circ\text{C}$ , and crystallized at  $90^\circ\text{C}$  for the zeolite seed generation before synthesis using dual template. The mesopore was formed by adding cetyltrimethylammonium bromide (CTMABr) and water solution to the seeds, leading to formation of new micelles. They heated the mixture in an autoclave at  $125^\circ\text{C}$ , between 6 - 12 days, and obtained the highest order of hybrid ZSM-5/MCM-41 on day 7 of the synthesis. The hybrid materials obtained at day 8 and 9 of the synthesis are not hierarchical mesoporous zeolite crystal, while the product of day 12 is predominantly ZSM-5 zeolite. Therefore, the synthesis of ZSM-5 zeolite combined with MCM-41 must not exceed seven days to preventing the second step of crystallization. By increasing the synthesis time, we can synthesize ZSM-5 crystal and further impregnate it into MCM-41 already synthesized. Therefore, we can

synthesize a blend of ZSM-5 and MCM-41 zeolite in the hybrid system fixing microporous ZSM-5 zeolite particles on the cylindrical wall of the MCM-41 mesopore (Fig. 2).

In the hybrid ZSM-5/MCM-41 material obtained on the day 7, a little micropores volume emerged; the ZSM-5 framework structure formation in the mesoporous MCM-41 framework core. The amorphous silica has been deposited on the obtained ZSM-5 crystals, which blocked nitrogen molecules from accessing their micropores. (Frunz *et al.*, 2006), also discovered deposition of amorphous silica during the mesoporous ZSM-5 zeolite formation.



**Fig. 2.** Proposed dual templating mechanism for hybrid micro-mesoporous ZSM-5/MCM-41 material synthesis (Coriolano *et al.*, 2013).

### 3.3. Direct synthesis by dual-functional surfactant approach

Dual-functional surfactants are single surfactants that can simultaneously generate micro and mesopores. Example of dual functional surfactant is a Gemini surfactant, which functionally played a dual role as both microporous zeolite SDA and mesopore template simultaneously (Liu *et al.*, 2012). Gemini surfactants, also known as dimeric surfactants, they possess two hydrophobic head units and two hydrophilic units in the molecules. This is in contrast to conventional surfactants that possess a single hydrophobic head unit and a single hydrophilic unit (Na *et al.*, 2011a). Gemini surfactants can be about ten to a thousand times more active on the surface than commercial surfactants with similar but single hydrophilic and hydrophobic units in the molecules. Their design is to support both formation of nanocrystalline and liquid crystal-like meso-structural order of the zeolite structure (Na *et al.*, 2011). In the studies of (Choi *et al.*, 2009; Jung *et al.*, 2012; Na *et al.*, 2011a; Na *et al.*, 2011) the

dual role of the Gemini dual-porogenic are illustrated by nuclear magnetic resonance spectroscopy and 2D heteronuclear correlation (Vega, 1988). This simplifies the molecular proximity of the surfactant to specific structural moieties. The 2D  $^{29}\text{Si}(^1\text{H})$  HETCOR NMR spectrum shows the important role of the  $\text{Al}^{\text{IV}}$  units in directing the zeolite structures crystallization. A separately acquired 1D  $^{29}\text{Si}$  cross polarization (Polderman *et al.*) magic-angle-spinning (MAS) spectrum (horizontal axis) exhibit broad signal attributed to Qn  $^{29}\text{Si}$  aluminosilicate structure (Barrett *et al.*, 1951; Janicke *et al.*, 1998; Jin *et al.*, 2012; Saito & Foley, 1995) with increasing condensation rate. A single-pulse  $^1\text{H}$  MAS spectrum (vertical axis) indicated partial resolution of  $^1\text{H}$  signal from the porogen molecules with its proton chemical shift assignments shown in 2d  $^{13}\text{C}(^1\text{H})$  HETCOR NMR spectrum.

In dual-porogenic driven synthesis scheme, the porogen aggregates generated the mesopores, while, microporous zeolite crystal structure is formed by multiple  $\text{Al}^{\text{IV}}$  units. We can use surfactants with different gemini-like head units to control wall size and structural topology. The pore size is designed according to addition of hydrophobic growth increase agents or by the tail end of the surfactant (Na *et al.*, 2011a). The porous structure and strong zeolite framework acid sites leads to substantial enhancement of the catalytic performance of several organic reactions that involves large molecules unlike conventional zeolite or amorphous MMSs (Choi *et al.*, 2006; Kruk & Jaroniec, 2001; Lee *et al.*, 2005; Na *et al.*, 2011a).

### 3.4. Hydrothermal synthesis

This is a conveniently meso-scale template free route for hierarchical structured ZSM-5 zeolite synthesis. It could be done by steaming with or without zeolite or silicalite-1 seed. Introduction of seed to hydrothermal synthesis helps to reduce crystallization time. It also helps to increase purity and yield to obtain crystalline zeolite products enriched with large surface area as well as large pores (Wang, Li, *et al.*, 2010). There is a special intersecting channel system in the framework of ZSM-5 zeolite with a straight 10-member ring (10MR) channel parallel to the b-axis and a zig-zag 10MR channel protruding towards the a-axis (Anthony, 1996; Krishna & Paschek, 2001; Wang, Li, *et al.*, 2010; Yu *et al.*, 2006). Therefore, the prepared hierarchical ZSM-5 zeolites with c-axis-oriented nano-rods is of vital importance because of their enriched and large pore opening as well as shortened channels. Hierarchical ZSM-5 zeolites with enhanced surface area as well as enriched mesopores are produced through this method. The improvement on the catalytic properties of the product because of its ease of access to the active sites. This is caused by the few microporous channels and openings of intra-crystal mesopore which remarkably widened zeolite field of application (Wang, Li, *et al.*, 2010).

The pre-added seeds in the synthesis solution play a vital role of inducing formation of hierarchical porous ZSM-5 zeolite structure. The added seeds function as the initial crystal core to initiate secondary nucleation and growth of the nano-sized ZSM-5 zeolite crystal along their preferred plane using 1,6-hexylenediamine (Bell *et al.*, 2008; Cundy & Cox, 2005; Davis *et al.*, 2006; Kumar *et al.*, 2007; Na, Jo, *et al.*, 2011b; D. Wang, Liu, *et al.*, 2010). This leads to formation of a new

hierarchical porous zeolite through partial intergrowth of ZSM-5 nano-rod in similar direction. Such oriented aggregation had been reported as mechanism for crystal growth, producing mono-crystalline frameworks (Niederberger & Cölfen, 2006; D. Wang, Li, *et al.*, 2010; Yuwono *et al.*, 2010; Zhongping Zhang *et al.*, 2005). (D. Wang, Li, *et al.*, 2010) confirmed that because of c-axis oriented ZSM-5 zeolite nano-crystal bundle of arrays, a novel mesoporous material was synthesized as inter-crystal pores. The improved surface area and mesopore volume in the hierarchical mesoporous ZSM-5 zeolite will improve the reactivity and diffusivity of the reacting molecules (Wang *et al.*, 2010).

### 3.5. Combined hydrothermal and alkaline leaching synthesis strategy

This is another template free route for hierarchical structured zeolite synthesis, which involves combined effort of hydrothermal and alkaline treatment. This could be achieved by steaming of the zeolite material followed by alkaline leaching of the zeolite material followed by steaming. (Shi *et al.*, 2013) reported that alkaline treatment after heat treatment exhibits triple effects on the synthesized ZSM-5 zeolite, which involves silicate extraction, re-deposition of aluminum atom and aluminum extra-framework removal; while the heat treatment after alkali modification has binary effect, which involves aluminum atom extraction and stabilization. However, heat treatment after alkali modification is more effective in adjusting the zeolites acidity and mesopores creation. The catalyst derived from ZSM-5 zeolite modified through incorporation of steam and alkali treatment, which exhibits enhanced isomerization activity, better aromatization activity and high stability in the hydro upgrading of gasoline via fluid catalytic cracking. Fig. 3 & Fig. 4 shows the details of this scheme.

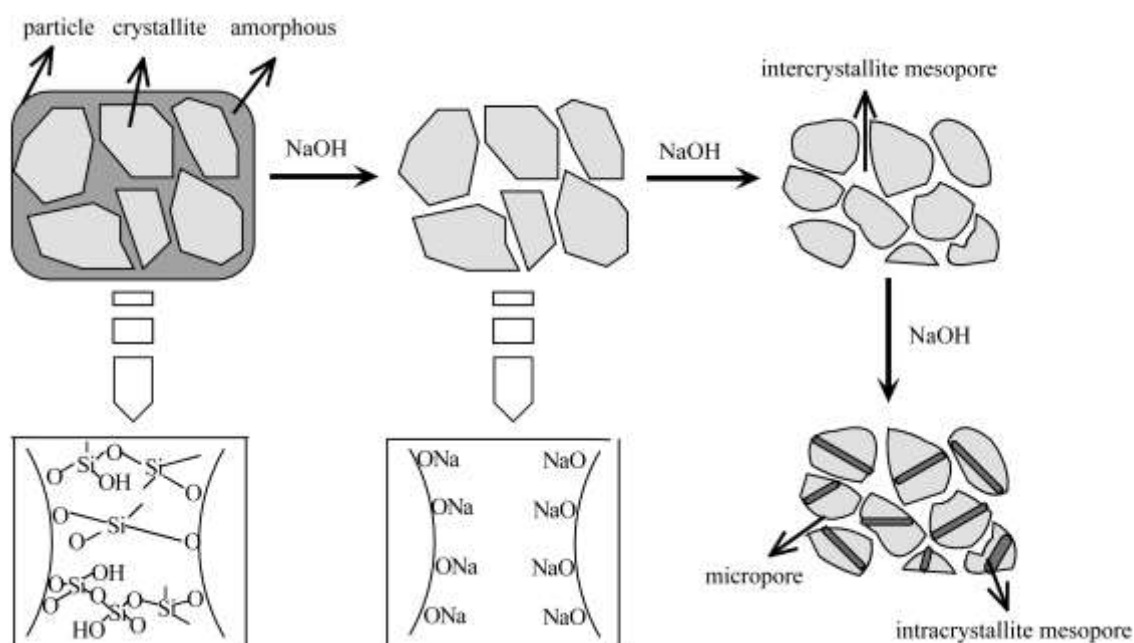


Fig. 3. Mesopores creation in the HZSM-5 zeolite upon alkali treatment (Shi *et al.*, 2013).



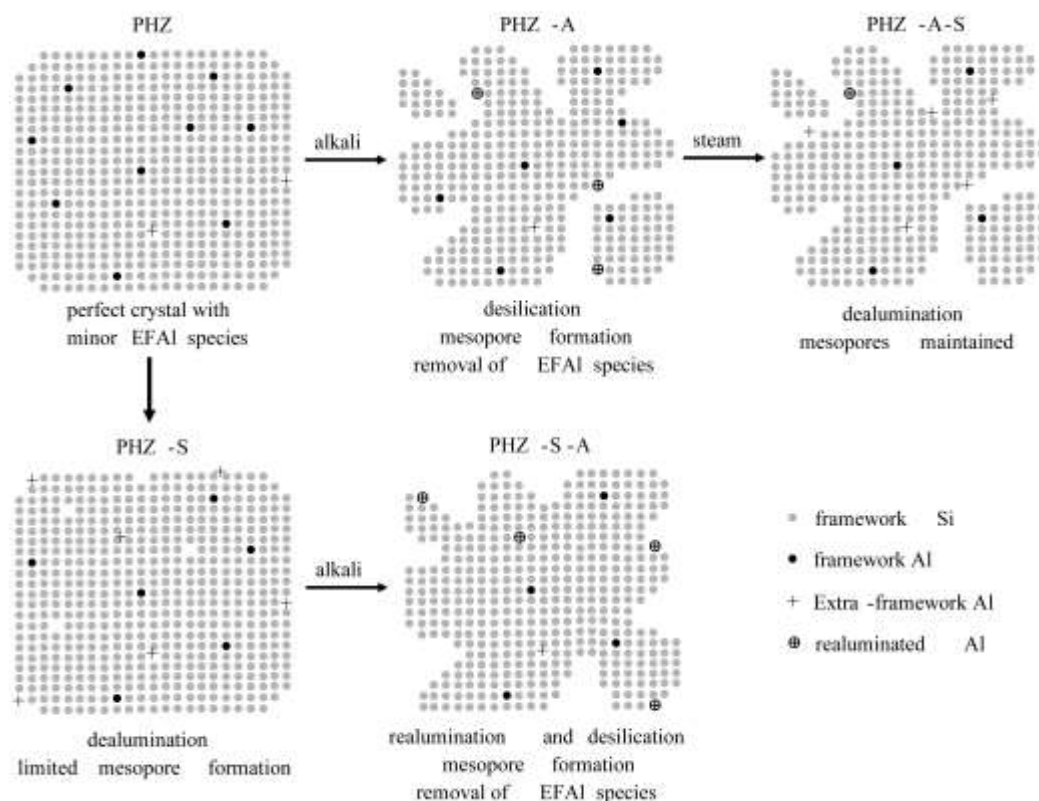


Fig. 4. Evolution of the porosity and composition of the HZSM-5 zeolite upon the various post-treatments (Shi *et al.*, 2013).

#### 4. Factors affecting mesophase formation and zeolite crystallization

(Li *et al.*, 2012) studied the pH value effect and ethanol quantity on the mesophase formation. In reacting solution with addition of ethanol, the solubility of CTAB template increases with decrease in dielectric constant. This change leads to enhancement in the electrostatic repulsion between the template ions within micelles to decrease micelle size as well as boosting the value of critical micelle concentration (CMC) (Zheng, 1997). Excess ethanol prevents formation of micelles in the mixture of Hp-E(X) (synthesized mesoporous zeolite with ethanol additives and X being the ethanol volume).

Essentially, the pH effect on meso porosity can be associated with the concentration of OH<sup>-</sup> ions of the micelles. The OH<sup>-</sup> compressed the double layer of micelles. This leads to reduction in the electrostatic repulsion between the template ions of the micelle by recompensing for the CTAB positive charges while accessing the core of the micelle, making the micelle more stable (Li *et al.*, 2012). Therefore, addition of NaOH in the reacting medium helps to produce hierarchical mesoporous structure even with excess ethanol {Hp-Na(17) (synthesized mesoporous zeolite with ethanol additives of 17 ml and pH controlled by NaOH)}. This is due to the improvement in the micelle

stability. Beside this, the  $V_{\text{micro}}/V_{\text{total}}$  ratio decreases while the pore size increase with the increase in ethanol quantity (Li *et al.*, 2012).

## 5. Hierarchy factor

Hierarchy factor is a viable tool that we can use to measure the degree of structural order of materials. It also helps to correlate and to make quantitative comparison of various zeolite materials produced from different synthesis methods (Alaba *et al.*, 2015; Alaba *et al.*, 2017b).

(Pérez-Ramírez *et al.*, 2009) proposed a model as a tool for classification of hierarchy mesoporous zeolites as derived from the conventional  $N_2$  adsorption analysis. From the effect of the micropore volume on the total pore volume and the effect of the mesopore specific surface area on the total specific surface area of the weighed sample, they defined hierarchy factor (HF) as follows:

$$HF = \frac{V_{\text{micro}}S_{\text{meso}}}{V_{\text{Total}}S_{\text{BET}}} \quad (1)$$

To maximize the value of HF, the mesopore surface area must be enhanced without penalizing the micropore volume severely. This shows that rather than playing a competition role, both porosity levels must complement each other. While the micropores play the active sites, the auxiliary mesopores solved the problem of mass transfer limitation. It is also important to note that two or more different zeolite catalysts prepared through different synthesis routes but with the same value of hierarchical factor may not necessarily exhibit the same catalytic performance in the same reaction because of varying acid strength and distribution. For instance, the one with highest number of Brönsted-acid sites will surely exhibit the best performance (Alaba *et al.*, 2017a).

However, (Zheng *et al.*, 2013) reported that HF seldom show linear relationship with catalytic performance as expected when they tested it with catalytic cracking of isopropylbenzene. For instance, sample MFZ-8 with high mesopore volume but low total specific surface area and micropore volume, possesses a high value of HF (0.13) because HF is defined as a function of total pore volume. To make more reasonable quantitative comparison of the degree of structural order of composite materials, (Zheng *et al.*, 2013), therefore revised hierarchy factor as  $F'$  and

$$HF' = \frac{V_{\text{micro}}*S_{\text{meso}}}{V_{\text{meso}}*S_{\text{BET}}} \quad (2)$$

$$\text{Because } \frac{HF'}{HF} = \frac{V_{\text{total}}}{V_{\text{meso}}} = \frac{V_{\text{meso}}+V_{\text{micro}}}{V_{\text{meso}}} = 1 + \frac{V_{\text{micro}}}{V_{\text{meso}}} \quad (3)$$

Therefore,

$$HF' = HF * \left(1 + \frac{V_{\text{micro}}}{V_{\text{meso}}}\right) \quad (4)$$

Table 1 show several samples of hierarchical mesoporous zeolites and their corresponding HF, F' Brönsted-acid sites and catalytic cracking performance. It is therefore, clearly seen that F' is more reasonable in determining degree of hierarchy of composite zeolites that have similar compositions and acidities in reactions with bulky reactants. It is also important to know that crystallization parameters of the synthesized mesoporous materials have effect on the hierarchy factor. (Koekkoek *et al.*, 2011) synthesized mesoporous zeolites MesoZSM-5(T, y) where T, is the crystallization temperature and y, is the crystallization time (Table 1). From their report, we could see on Table 1 that hierarchy factor increase with increase in crystallization temperature and y is the crystallization time.

## 6. Conclusions and outlook

Synthesis of hierarchical mesoporous zeolite has been successful by various methods including template and template free method. It has proved a better alternative to microporous zeolite in that it takes care of the shortcomings of microporous and mesoporous zeolite. The hierarchical mesoporous zeolites synthesized exhibit high catalytic activities in cracking of large molecule, high hydrogen adsorption and high hydrothermal stability. As a solid acid catalyst, the pore walls of the porous materials synthesized could facilitate molecular transfer through the catalyst matrix, resulting in significant increase in catalyst lifetime. In addition, the improved surface acidity favors large molecules catalytic conversion that was constrained in the conventional zeolites micropores. The synthesized mesoporous zeolites can be used as catalyst support or co-catalyst with metal nano particles. These attributes of hierarchical mesoporous zeolite enabled it as an important absorbent and catalyst used in several fields such as catalytic cracking, deoxygenation and hydrodeoxygenation.

Economic and environmental advantages give the hydrothermal synthesis routes with the aid of zeolite/silicalite1 seed as well as combined hydrothermal and alkaline leaching synthesis route more chances for scale-up. Synthesis method using starch-derived bread as template is also a promising green synthesis method. Moreover, by investigating the early stages of zeolite synthesis, hierarchical mesoporous zeolite can be synthesized in a greener way to neglect the commonly used organic reagents to stabilize the desired phases or to recycle the organic template. In these cases, it is possible to remove and extract organic templates from the zeolite pores under mild conditions. Therefore, in the quest for solid acid catalysts that exhibits little or no mass transfer limitation, strong acidity, pore volume and high specific surface area, hierarchical mesoporous ZSM-5 zeolites can replace commercial microporous zeolites. The synthesis technologies allow a great control of the crystal size, pore size, morphology, acidity, and porosity.

**Table 1** Effect of hierarchical factor, Bronsted acidity on mesoporous zeolites catalytic performance.

Zeolites sample	$V_{\text{meso}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{total}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$S_{\text{meso}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$S_{\text{BET}}$ m ( $\text{cm}^3 \text{g}^{-1}$ )	HF	HF'	B site <sup>a</sup> (mmol/g)	Reaction				Ref.
								Type	Time (h)	T (°C)	Conv. wt.%	
ZRP-1	0.131	0.22	128.7	305.2	0.1706	0.2865	1093	n-Heptane cracking	-	650	100.00	(Chen <i>et al.</i> , 2012)
HZSM-5	0.034	0.186	52.2	368	0.1159	0.6341	197	n-Heptane cracking	-	650	99.79	(Chen <i>et al.</i> , 2012)
HZ (10.0) <sup>b</sup>	0.063	0.185	102.1	338.1	0.1991	0.5848	177	n-Heptane cracking	-	650	99.41	(Chen <i>et al.</i> , 2012)
HZ (25.0) <sup>b</sup>	0.077	0.19	111.7	333.5	0.1992	0.4915	696	n-Heptane cracking	-	650	98.68	(Chen <i>et al.</i> , 2012)
HZ (40.0) <sup>b</sup>	0.133	0.245	109.4	328.4	0.1523	0.2805	836	n-Heptane cracking	-	650	97.91	(Chen <i>et al.</i> , 2012)
HZ (50.0) <sup>b</sup>	0.243	0.344	104.9	305.2	0.1009	0.1429	984	n-Heptane cracking	-	650	97.50	(Chen <i>et al.</i> , 2012)
Hp-Na(0) <sup>c</sup>	0.13	0.22	242	418	0.2368	0.4008		Esterification of lauric acid	23.5 <sup>d</sup>	78	77.00	(H. Li <i>et al.</i> , 2012)
MFZ-17 <sup>e</sup>	0.11	0.36	91	515	0.1227	0.4016		isopropylbenzene cracking	0.1	300	100.00	(Zheng <i>et al.</i> , 2013)
MFZ-16 <sup>e</sup>	0.16	0.42	128	576	0.1376	0.3611		isopropylbenzene cracking	0.1	300	98.79	(Zheng <i>et al.</i> , 2013)
MFZ-14	0.1	0.36	86	546	0.1138	0.4095		isopropylbenzene cracking	0.1	300	99.31	(Zheng <i>et al.</i> , 2013)
MFZ-12 <sup>e</sup>	0.07	0.32	45	497	0.0707	0.3234		isopropylbenzene cracking	0.1	300	99.00	(Zheng <i>et al.</i> , 2013)
MFZ-8 <sup>e</sup>	0.13	0.23	74	242	0.1330	0.2352		isopropylbenzene cracking	0.1	300	98.00	(Zheng <i>et al.</i> , 2013)
Y+M <sup>f</sup>	0.02	0.27	6	524	0.0106	0.1431		isopropylbenzene cracking	0.1	300	99.00	(Zheng <i>et al.</i> , 2013)
MFZ-17 <sup>e</sup>	0.11	0.36	91	515	0.1227	0.4016		isopropylbenzene cracking	8	300	98.10	(Zheng <i>et al.</i> , 2013)
MFZ-16 <sup>e</sup>	0.16	0.42	128	576	0.1376	0.3611		isopropylbenzene cracking	8	300	82.07	(Zheng <i>et al.</i> , 2013)
MFZ-14 <sup>e</sup>	0.1	0.36	86	546	0.1138	0.4095		isopropylbenzene cracking	8	300	93.28	(Zheng <i>et al.</i> , 2013)

MFZ-12 <sup>e</sup>	0.07	0.32	45	497	0.0707	0.3234		isopropylbenzene cracking	8	300	74.66	(Zheng <i>et al.</i> , 2013)
MFZ-8 <sup>e</sup>	0.13	0.23	74	242	0.1330	0.2352		isopropylbenzene cracking	8	300	43.28	(Zheng <i>et al.</i> , 2013)
Y+M <sup>f</sup>	0.02	0.27	6	524	0.0106	0.1431		isopropylbenzene cracking	8	300	43.28	(Zheng <i>et al.</i> , 2013)
BFZ-1.30 <sup>g</sup>	0.21	0.4	80	486	0.0782	0.1489		Methanol cracking	2	250	77.20	(Zheng <i>et al.</i> , 2011)
BFZ-1.35 <sup>g</sup>	0.22	0.37	112	432	0.1051	0.1768		Methanol cracking	2	250	89.70	(Zheng <i>et al.</i> , 2011)
BFZ-1.40 <sup>g</sup>	0.22	0.4	130	454	0.1289	0.2343		Methanol cracking	2	250	91.30	(Zheng <i>et al.</i> , 2011)
BFZ-1.45 <sup>g</sup>	0.24	0.43	172	520	0.1462	0.2619		Methanol cracking	2	250	97.20	(Zheng <i>et al.</i> , 2011)
BFZ-1.45 <sup>g</sup>	0.24	0.43	172	520	0.1462	0.2619		Methanol cracking	72	250	72.00	(Zheng <i>et al.</i> , 2011)
BFZ-1.50 <sup>g</sup>	0.27	0.46	130	514	0.1045	0.1780		Methanol cracking	2	250	88.10	(Zheng <i>et al.</i> , 2011)
BFZ-s <sup>h</sup>	0.08	0.33	45	495	0.0689	0.2841		Methanol cracking	2	250	17.40	(Zheng <i>et al.</i> , 2011)
FAU-BEA <sup>i</sup>	0.13	0.32	64	530	0.0717	0.1765		Methanol cracking	2	250	71.10	(Zheng <i>et al.</i> , 2011)
FBZ <sup>j</sup>	0.11	0.34	72	578	0.0843	0.2605		Methanol cracking	2	250	82.10	(Zheng <i>et al.</i> , 2011)
BEA	0.04	0.22	29	517	0.0459	0.2524		Methanol cracking	2	250	84.70	(Zheng <i>et al.</i> , 2011)
FAU	0.02	0.38	9	738	0.0116	0.2195		Methanol cracking	2	250	53.60	(Zheng <i>et al.</i> , 2011)
MesoZSM-5(150, 0) <sup>k</sup>	0.18	0.189	93	435	0.0102	0.0107	3	n-Heptane cracking	2	353	40.00	(Koekkoek <i>et al.</i> , 2011)
MesoZSM-5(150, 6) <sup>k</sup>	0.41	0.444	555	684	0.0621	0.0673	9	n-Heptane cracking	2	350	40.00	(Koekkoek <i>et al.</i> , 2011)
MesoZSM-5(150, 72) <sup>k</sup>	0.3	0.36	387	569	0.1134	0.1360	51	n-Heptane cracking	2	267	40.00	(Koekkoek <i>et al.</i> , 2011)
MesoZSM-5(150, 120) <sup>k</sup>	0.28	0.355	266	519	0.1083	0.1373	80	n-Heptane cracking	2	255	40.00	(Koekkoek <i>et al.</i> , 2011)

MesoZSM-5(170, 6) <sup>k</sup>	0.25	0.25	360	360	0.0000	0.0000	6	n-Heptane cracking	2	350	40.00	(Koekkoek <i>et al.</i> , 2011)
MesoZSM-5(170,120) <sup>k</sup>	0.11	0.22	90	388	0.1160	0.2320	71	n-Heptane cracking	2	252	40.00	(Koekkoek <i>et al.</i> , 2011)
BFZ-28 <sup>l</sup>	0.245	0.475	130	604	0.1042	0.2021		Hydrogenation of benzene	2.964	400	98.46	(Zheng <i>et al.</i> , 2010)
BFZ-24 <sup>l</sup>	0.21	0.43	101	580	0.0891	0.1824		Hydrogenation of benzene				(Zheng <i>et al.</i> , 2010)
BFZ-18 <sup>l</sup>	0.19	0.39	102	507	0.1032	0.2118		Hydrogenation of benzene	2.964	400	98.46	(Zheng <i>et al.</i> , 2010)

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## Chapter 5

### Effect of amending phosphate fertilizers with Clinoptilolite zeolite on phosphorus availability and selected soil chemical properties of an acid soil

Hasbullah Nur Aainaa<sup>1</sup>, \*Osumanu Haruna Ahmed,<sup>1,2</sup> Nik Muhamad Ab Majid,<sup>3</sup>  
Mohamadu Boyie Jalloh<sup>4</sup>

<sup>1</sup>Department of Crop Science, <sup>2</sup>Agriculture and Environment, Borneo Eco-Science Research Center, Faculty of Agriculture and Food Sciences, Universiti Putra Malaysia Bintulu Sarawak Campus, 97008 Bintulu, Sarawak, Malaysia

<sup>3</sup>Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>4</sup>Crop Production Programme, <sup>5</sup>Sustainable Palm Oil Research Unit (SPOR), Faculty of Sustainable Agriculture, Universiti Malaysia Sabah, Locked Bag No. 3, 90509 Sandakan, Sabah, Malaysia

\*Email: [osman60@hotmail.com](mailto:osman60@hotmail.com)

#### Abstract

Inefficient use of chemical fertilizers such as phosphatic fertilizer which are usually applied to sustain crop production can also cause environmental pollution. Clinoptilolite zeolite with its characteristically large surface area, high CEC and alkalinity can be exploited to increase the retention of basic cations, reduce soil acidity and metal ions solubility (Fe and Al) leading to reduced P fixation in acid soils. An incubation study was conducted to determine the effects of reducing the amount of N, P and K fertilizers amendment with three rates of clinoptilolite zeolite on phosphorus availability and selected soil chemical properties of an acid soil. The treatments were incubated for 30 days, 60 days, and 90 days. Standard procedures were used to determine soil pH, exchangeable cations, soil acidity, total P, available P and inorganic P. Reduced rate of fertilizers with increasing rate of clinoptilolite zeolite significantly increased soil pH. This resulted in a reduction of exchangeable Al which caused a reduction in soil titratable acidity. The results were comparable to that of the recommended fertilizer rates. Retention of Ca and Mg in the treatments with 85% clinoptilolite zeolite and 25% fertilizer reduction (T2, E2 and C2) was comparable to the standard fertilizer recommendation. However, treatments with clinoptilolite zeolite neither significantly reduced exchangeable Fe, P fixation (Al-P, Fe-P, Ca-P, Red-P, and Occl-P) nor increased soil total P and availability of P. Clinoptilolite zeolite effect was not significant because of the reduction in fertilizer rate in the treatments used.

**Keywords:** Inorganic phosphorus, phosphorus availability, clinoptilolite zeolite, nutrients retention, environmental sustainability

## Introduction

Phosphorus (P) is one of the essential nutrients required by crops. Adequate supply of P from early crop growth stage is vital for optimum crop production. However, P availability in acid soils is often limited due to the soil's inherent characteristics. In tropical acid soils, P reacts with predominant Al and Fe ions to form insoluble complexes (precipitated) which are not readily available for plant uptake (Elser *et al.*, 2000; Wardle *et al.*, 2004; Vitousek and Howarth, 1991). The application of large amounts of P fertilizers to saturate the soil sorption sites of P is uneconomical and environmentally unfriendly. The over application of P could pollute water bodies if surface runoff occurs (Grant *et al.*, 2005; Schindler, 1977). Moreover, finite world reserves of P need to be properly utilized (Cordell *et al.*, 2009) as scarcity may increase cost of producing agricultural products. Due to the aforementioned, an effective management of P fertilizers is important to attain optimum crops yield, reduce cost of production, conserve finite resources, and at the same time ensure that the environment is not degraded.

Many efforts have been made to sustain soil quality and resources as well as improving agricultural productivity under intensive production systems. Each approach is different in terms of cost, efficiency, and practicality. The use of soil amendments in agriculture is not new. According to David and Wilson (2005), a soil amendment is any material which is not necessarily a fertilizer that is added to soils to improve their physical and chemical properties such as moisture and nutrients retention, permeability, water infiltration, drainage, aeration, structure, cation exchange capacity and pH. It can be either natural or synthetic, and can contribute significantly to providing a reservoir of soil water to crops on demand in the upper layers of soils where their root systems normally develop by reducing evaporation through restricting movement of water from the sub-surface to the surface layers of the soil (Yangyuoru *et al.*, 2006).

Liming acid soils is one of the most common practice used to improve soil pH, reduce soil acidity, and thus increase P availability in soils. Liming acid soils helps to alleviate soil pH and decreases Al toxicity for optimal crop growth. However, higher pH attributed to increase of exchangeable Ca in soils is conflicting as it had been reported that exchangeable Ca in soils sometimes increase, decrease, or had no effect on P availability (Curtin and Syers, 2001; Anjos and Rowell, 1987; Mahler and McDole, 1985). Thus, this study attempted to exploit the alkaline nature of the zeolites which could be beneficial to reduce P fixation and improve P availability by increasing soil pH and thus reducing soil acidity and solubility of metal ions (Fe and Al).

Zeolites are natural aluminosilicates with an infinite three-dimensional crystal structure, a polyedric shape, with a great open cavity (Ajirloo *et al.*, 2013; Ramesh and Raddy, 2011; Daković *et al.*, 2007). It was first identified by Alex Fredrik Cronsted (a Swedish mineralogist) in 1756. To date, about 50 species of these natural volcanogenic sedimentary mineral has been recognized. The one

used in this study is clinoptilolite zeolite, the most abundant in soils and sediments (Ramesh *et al.*, 2010; Mumpton 1999). The structure of zeolites has been characterized based on its tetrahedron framework, the center of which is occupied by a silicon atom with four oxygen atoms at the vertices. Substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  provides the negative charge of the framework, which is balanced by monovalent or divalent cations located at the surface (Geiger, 2012; Khomami, 2011; Polat *et al.*, 2004). These abundant and cheap minerals are extensively used in agriculture as soil conditioners, slow-release fertilizers, and cleansing agents for contaminated soils (Ming and Allen, 2001). Zeolites are not easily degraded over time which causes them to remain in soils to improve retention of nutrients and control nutrient release for crop use (Ramesh *et al.*, 2010; Eberl, 1993; Zelazny and Calhoun, 1977).

The inclusion of zeolites in fertilization programmes induces dissolution of rock phosphate (RP) and also producing  $\text{NH}_4^+$  as by-product by exchange-induced dissolution system (Pickering *et al.*, 2002; Allen *et al.*, 1993; Barbarick *et al.*, 1990; Lai and Eberl, 1986). Studies have shown that clinoptilolite zeolite can reduced ammonia loss by inhibiting microbial nitrification (Rabai *et al.*, 2012; Lija *et al.*, 2012) and can improve nutrients uptake and use efficiency of *Zea mays* cultivated on acid soils (Omar *et al.*, 2016; Omar *et al.*, 2011; Ahmed *et al.*, 2010). The use of zeolites also improved rice grain yield, N recovery, and use efficiency (Palanivell *et al.*, 2015; Kavooosi, 2007). Zeolites have also been shown to effectively reduce salinity stress and improve nutrient balance in a sandy soil (Al-Busaidi *et al.*, 2008). Mixing zeolites with urea and TSP also enhances phosphorus uptake in plants (Pickering *et al.*, 2002). Bernardi *et al.* (2013) reported that concentrated zeolite enriched with N, P, and K enables slow-release of nutrients for crop use. The application of zeolite with urea improved N use efficiency and when applied with phosphate rock it increased the P availability to crops and also increased water retention and available water capacity of a sandy soil (Omar *et al.*, 2015; Bernardi *et al.*, 2013; Pickering *et al.*, 2002; Barbarick *et al.*, 1990).

Although zeolites have been extensively used in agriculture, there is a dearth of information on the use of zeolites such as clinoptilolite zeolite on P sorption and fixation in highly weathered tropical soils as well as reduction of N, P, and K fertilizers use in agriculture. Thus, the use of reduced amounts of fertilizers amended with clinoptilolite zeolite was investigated to evaluate the effects of this approach on phosphorus dissolution and selected soil chemical properties of an acid soil in a controlled environment, without crop interference (i.e incubation study).

## Materials and methods

### *Characterization of the mineral acidic soil*

The mineral acidic soil used was Bekenu series (Typic Paleudults) and it was sampled from an uncultivated area at Universiti Putra Malaysia, Bintulu Campus Sarawak, Malaysia at 0-15 cm

depth. The coordinates of the soil sampling site are latitude 03° 12.241' N and longitude 113° 04.270' E. The soil was air-dried, ground, and sieved to pass a 2.0 mm sieve for initial characterization and the incubation experiment. Soil texture was determined by measuring the amount of each particle group (sand, silt, and clay) using the hydrometer method (Soil Survey Staff, 2014). The pH of the soil and clinoptilolite zeolite was determined in a 1:25 ratio (soil: distilled water) using a digital pH meter (Seven Easy pH, Mettler-Toledo GmbH, Switzerland) (Peech, 1965). Soil organic matter and total carbon were determined using the loss-on-ignition method (Piccolo, 1996), and soil bulk density was determined using the method described by Soil Survey Staff (2014). The inorganic P associated with Al, Fe and Ca in soil were fractionated and determined following the method described by Kuo (1996). Soil total P (extracted using aqua regia) and available P (extracted using Mehlich No.1) (Tan, 2005) were determined using a spectrophotometer (Lambda 25, Perkin Elmer) after blue color development (Murphy and Riley, 1962). Soil cation exchange capacity (CEC) was determined using the ammonium acetate method (Cottenie, 1980) whereas exchangeable cations (K, Ca, Mg, and Fe) were extracted using double acid as extractant following the method of Mehlich No.1 (Mehlich, 1953). Cations concentrations were determined using atomic absorption spectrometry (Perkin Elmer AAnalyst 800). Exchangeable soil acidity and Al were extracted using 1 M KCl (1:10 soil/solution) and determined using colorimetric method (Rowell, 1994).

The selected physico-chemical properties of Bekenu series are shown in Table 1. The soil used was acidic (pH=4.32), low in CEC (5.33 cmol(+) kg<sup>-1</sup>) and total N (0.06%). Soil total carbon, exchangeable K, Ca, and Mg were slightly higher than the standard range for this soil type (Paramanathan, 2000) because of litter decomposition with time at the soil surface as the soil used in this study was taken from an uncultivated area.

Inorganic P fractions have remarkable differences in mobility, bioavailability, and chemical behavior in soils. Inorganic P distribution in the soil used in this study is in the following order: Fe-P > Al-P > Red-P > Occl-P > Ca-P > Sol-P (Figure 1). Approximately 70% of the inorganic P recovered were associated with Fe and Al. The higher content of Fe-P among the active inorganic P fractions suggests high content of Fe-oxides, low pH, and advanced stage of weathering (Table 1). This finding is consistent with a study by Bidin (1986) who reported that Fe-P was dominant and constituted 79% of inorganic P fractions of Malaysian mineral soils.

Reductant P in the soil constituted the third largest portion (14%) and this is related to various forms of P occluded in poorly crystalline Fe and Al oxides (Delgado and Torrent, 2000; Ruiz *et al.*, 1997). The lower content of Ca-P is consistent with the acidity and advanced pedogenesis of the soil used in this study, which suggests that native apatite is being weathered. Soil Occl-P and Soi-P were only 7% and 1%, respectively. Lower availability of Sol-P indicates the need for P fertilization.

Table 1: Selected physico-chemical properties of Bekenu soil series (Typic Paleudults) before the incubation study

Soil properties	Soil		Clinoptilolite zeolite
	Value obtained	Standard range*	
pH (water)	4.32	4.6-4.9	8.54
Bulk density (g cm <sup>-3</sup> )	1.01	Nd	Nd
CEC (cmol(+)kg <sup>-1</sup> )	5.33	3.86-8.46	75.4
Total N (%)	0.06	0.04-0.17	0.22
Total P (%)	0.005	Nd	0.01
Available P (mg kg <sup>-1</sup> )	2.48	Nd	Nd
Organic matter (%)	5.60	Nd	Nd
Total carbon (%)	3.25	0.57-2.51	Nd
Total Fe	7.51	Nd	0.11
Total acidity	1.38	Nd	Nd
Exchangeable Al	0.9	Nd	Nd
Exchangeable H	0.48	Nd	Nd
Exchangeable K	0.24	0.05-0.19	6.16
Exchangeable Ca	0.76	0.01	22.30
Exchangeable Mg	0.45	0.07-0.21	2.36
Exchangeable Na	3.60	0.01	18.99
Texture	SL	SL	Nd

Note: Nd= not determine, SL= sandy loam, asterisk (\*) subjected to the soil development, standard data range by Paramanathan (2000)

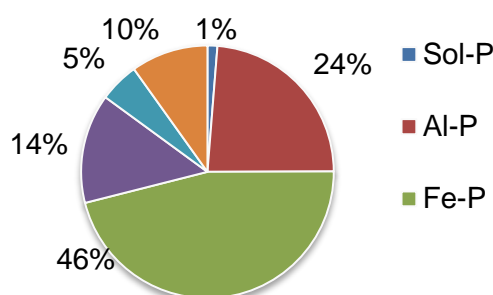


Figure 1: Percentage of inorganic phosphorus fractions distribution in an acid soil. Note: Sol = solution and Occl = occluded

### Characterization of clinoptilolite zeolite

The clinoptilolite zeolite used in this study was imported from Indonesia by MB Plus Sdn Bhd, Johore, Malaysia, in granular form (2-5 mm). Standard procedures as mention in characterization of soil were used to analyse pH, total N, total P, and cations content of clinoptilolite zeolite. However, the cation exchange capacity of the clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986) followed by steam distillation (Bremner, 1965). This method



was used to avoid under-estimation of CEC of the zeolites as it does not lead to entrapment of ammonium ions in its channels. Based on the clinoptilolite zeolite's basic characterization (Table 1), the pH of the clinoptilolite zeolite was indeed high as expected (pH 8.54). However, compared to the attested (by MB Plus Sdn Bhd, Johore, Malaysia), the CEC and total N content of the clinoptilolite zeolite were lower than  $160 \text{ cmol (+) kg}^{-1}$  and 1.37%, respectively.

### Characterization of phosphorus fertilizers

The pH, total P, and total cation content of P fertilizers were determined using standard procedures aforementioned for the soil characterization. The total  $\text{P}_2\text{O}_5$  in triple superphosphate (TSP), Christmas Island rock phosphate (CIRP), and Egypt rock phosphate (ERP) were 41%, 24%, and 27% respectively (Table 2). Calcium in TSP, ERP, and CIRP were 4%, 47%, and 51%, respectively. The higher amount of Ca in ERP and CIRP were due to inherent contents of Ca in the parent materials of the fertilizers. High Ca in the apatite of the rock phosphates contributes to alkalinity of these phosphate fertilizers compared to the acidulated TSP.

Table 2: Selected chemical properties of phosphorus fertilizers

Property	TSP	ERP	CIRP
pH (water)	2.46	7.42	7.93
Total P (%)	18.09	11.96	10.62
Total $\text{P}_2\text{O}_5$ (%)	41.12	27.19	24.15
Total K (%)	0.42	0.25	0.31
Total Ca (%)	4.88	47.55	51.73
Total Mg (%)	0.35	0.17	0.24
Total Fe (%)	0.38	0.61	0.52

### Incubation study

A laboratory incubation study was conducted at Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia. An amount of 250 g of soil was weighed into a polypropylene container and moistened to 60% of moisture content. The caps of the polypropylene containers were perforated to allow good aeration. The soil moisture content was maintained using distilled water when necessary throughout the incubation experiment. The experimental design was a factorial completely randomized design.

The treatments evaluated for 30, 60, and 90 days are summarized in Table 3. The treatments were surface applied and incubated at room temperature ( $26^\circ\text{C}$ ) for 90 days. At 30, 60 and 90 days of incubation, soil samples were mixed and air-dried for pH, exchangeable cation (K, Ca, Mg, Fe, and Al), total P, available P, and inorganic P fractionation determination. The recommended rates of N, P, and K fertilizers used were  $60 \text{ kg N ha}^{-1}$  ( $130 \text{ kg ha}^{-1}$  urea),  $60 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  ( $130 \text{ kg ha}^{-1}$  TSP:  $214 \text{ kg}$

ha<sup>-1</sup> ERP: 200 kg ha<sup>-1</sup> CIRP), and 40 kg K<sub>2</sub>O ha<sup>-1</sup> (67 kg ha<sup>-1</sup> MOP). The rates of the fertilizers applied in this study were scaled down to per plant basis which were equivalent urea (4.85 g plant<sup>-1</sup>), ERP (7.95 g plant<sup>-1</sup>), CIRP (7.42 g plant<sup>-1</sup>), TSP (4.84 g plant<sup>-1</sup>), and MOP (2.47 g plant<sup>-1</sup>) from the standard fertilizer recommendation (Malaysian Agricultural Research and Development Institute, 1990).

Table 3: Treatment evaluated in laboratory incubation study

Treatments		P fertilizer		Urea		MOP		Clinoptilolite zeolite	
		----- (g pot <sup>-1</sup> ) -----							
	T0	250 g soil							
	T1	250 g soil	+	4.85	+	4.85	+	2.47	
TSP	T2	250 g soil	+	3.64	+	3.64	+	1.85	+
	T3	250 g soil	+	2.43	+	2.43	+	1.24	+
	T4	250 g soil	+	1.21	+	1.21	+	0.62	+
ERP	E1	250 g soil	+	7.95	+	4.85	+	2.47	
	E2	250 g soil	+	5.96	+	3.64	+	1.85	+
	E3	250 g soil	+	3.98	+	2.43	+	1.24	+
	E4	250 g soil	+	1.99	+	1.21	+	0.62	+
CIRP	C1	250 g soil	+	7.42	+	4.85	+	2.47	
	C2	250 g soil	+	5.57	+	3.64	+	1.85	+
	C3	250 g soil	+	3.71	+	2.43	+	1.24	+
	C4	250 g soil	+	1.86	+	1.21	+	0.62	+

Inclusion of urea and MOP in the study was to mimic planting inputs which include these fertilizers to sustain plant growth. Clinoptilolite zeolite as amendment was added to the treatments with reduced amount of fertilization. The treatment with 50% fertilizer reduction received 100% clinoptilolite zeolite (the amount of clinoptilolite zeolite used was based on the weight of the recommended fertilization rate). As the fertilizer rate increased by 25% (treatments with 75% fertilization), clinoptilolite zeolite rate was reduced to 85% of the recommended fertilizer weight. The amount of clinoptilolite zeolite added in 75% fertilizer reduction (treatments with 25% fertilization) was 115% of the fertilizer weight. This study was conducted in a closed system without plant interaction and leaching effect to evaluate the reaction of the treatments with soil only.

### Statistical analysis

Analysis of variance (ANOVA) was used to test significant effect of treatments whereas means of treatments were compared using Tukey's test. Statistical analysis System (SAS) version 9.2 was used for all the statistical analysis (SAS, 2008).

## Results and discussion

### *Effects of amending fertilizers with clinoptilolite zeolite on selected soil chemical properties*

Incubation time and interaction between incubation time and treatments significantly affected soil acidity, exchangeable cations (Al, Fe, K, Ca, and Mg), and soil P fractions (Tables 4 and 5). The significant interaction obtained could be due to various chemical and biological processes occurring in the soil including mineralization, immobilization, adsorption, and desorption throughout the study as the soil reacted due to undergone repeated protonation and deprotonation.

Effects of treatments on soil pH at 30, 60 and 90 days after incubation (DAI) are presented in Figure 2. The pH of soil alone (T0) was acidic. Application of fertilizers amended with clinoptilolite zeolite significantly improved soil pH. Treatments with higher amount of clinoptilolite zeolite significantly increased soil pH because of the catalytic effect of the clinoptilolite zeolite and parent material structure (Table 1). The liming effect of the clinoptilolite zeolite does not only raise soil pH, it also reduces soil acidity by minimizing Al hydrolysis in highly weathered soils such as Bekenu series. A recent study has revealed that zeolites are more effective in increasing soil pH compared to organic amendments (Basri *et al.*, 2013) and clinoptilolite zeolite improves soil CEC (Ramesh and Reddy, 2011; Nibou *et al.*, 2009).

The effects of treatments on soil titratable acidity (sum of total  $H^+$  and exchangeable Al) are shown in Figure 2. Soil titratable acidity was higher in the treatments with TSP compared to those of the rock phosphates. For example, T1 which is the treatment with highest amount of TSP showed higher titratable acidity. However, the opposite was true where  $H^+$  and titratable acidity decreased with decreasing amount of TSP and increasing amount of clinoptilolite zeolite. The results for RP treatments were however different. The insignificant differences could be due to inactive displacement of  $H^+$  and the retention of basic cations by clinoptilolite zeolite. Also, there were no plants to contribute  $H^+$  removal through uptake of nutrients in this study. This is also evident in soil exchangeable Ca as the effects of the treatments with 25% fertilizer reduction and recommended fertilizer rates on this cation was similar (Figure 4).

With the exception of soil only, soil exchangeable Al was negligible regardless of incubation time, rates of clinoptilolite zeolite, and P fertilizers. The increase in soil pH reduced exchangeable Al by reducing solubility of Al species to less soluble form during the course of undergoing repeated deprotonation to precipitate (Krstic *et al.*, 2012; Azura *et al.*, 2011).

Soil exchangeable Fe was significantly higher in soil alone (T0) compared with other treatments because the latter showed higher soil acidity than the former (Figure 2). Increase in soil pH

reduces solubility Al and Fe to sorb P. However, among the treatments with P fertilizers and clinoptilolite zeolite, the treatments with lower amount of P fertilizers and higher rates of clinoptilolite zeolite showed higher soil exchangeable Fe because of the inherent content of Fe in the clinoptilolite zeolite and P fertilizers (Tables 1 and 2).

Potassium availability (Figure 3) was highest in the normal rate of P fertilization regardless of the type of P fertilizer and incubation time because of reduction of the amount of fertilizers in the other treatments. Exchangeable Ca (Figure 3) content in soil was similar although fertilizer application was reduced by 25% regardless of the type of P fertilizer used. Soil exchangeable Mg (Figure 3) varied with the treatments with 25% fertilizer reduction and recommended fertilization rates. Soil exchangeable Mg following different amounts of CIRP application was similar (C1=C2). In the case of TSP application, T1 showed significantly higher effect compared with T2 whereas the effect of ERP application on soil exchangeable Mg was the opposite of TSP treatments where E2 showed higher effect than E1. Inherent contents of Mg (Table 2) in the respective P fertilizers could partly explain these observations. The reducing trend of K contents is consistent with reduction of fertilizer with increasing rate of clinoptilolite zeolite. Although clinoptilolite zeolite provides extra vacant sites for bases retention, the affinity of the sorption depends on valence and hydration of the bases. This partly explains the retention of Ca and Mg over K despite 25% reduction of fertilizers. The relatively higher Ca contents in the P fertilizers and clinoptilolite zeolite might have also contributed to this observation (Tables 1 and 2).

Table 4: Mean square values of analysis of variance (ANOVA) to evaluate effects of treatments and incubation time on soil pH, titratable acidity, exchangeable Al, Fe, K, Ca, and Mg

Source of variations	Degree of freedom	Mean square						
		pH	Exchangeable					
			Acidity	Al	Fe	K	Ca	Mg
TSP								
Time	2	0.07*	0.18*	0.014*	154498.9*	309775.5*	174512.9*	920.7*
Treatments	4	5.84*	0.27*	0.180*	72909.5*	44124756.1*	2255759.6*	24021.8*
Treatments*Time	8	0.04*	0.02	0.009*	10355.2*	63857.2*	89966.9*	31.9
Error	30							
ERP								
Time	2	0.19*	0.380*	0.014*	56911.4*	250544*	268093.2*	32.5*
Treatments	4	7.14*	0.055*	0.178*	111109*	48112498.2*	12468482*	376.3*
Treatments*Time	8	0.03*	0.031*	0.009*	18358.3*	51179.2*	284140.1*	154.7*
Error	30							
CIRP								
Time	2	0.15*	0.56*	0.014*	52240.3*	734092.4*	292254.9*	389.4*
Treatments	4	6.41*	0.15*	0.179*	99059.6*	51944144.5*	3921445.8*	3983.7*
Treatments*Time	8	0.05*	0.08*	0.009*	17918.3*	137845	73679.8*	186.9*
Error	30							

Note: Asterisk (\*) indicates significant at  $p \leq 0.05$

Table 5: Mean square values of analysis of variance (ANOVA) to evaluate effects of treatments and incubation time on soil total P, available P, and inorganic P (loosely soluble-P, Al-P, Fe-P, reductant-P, Ca-P, and occluded-P)

Source of variations	Degree of freedom	Mean square							
		Total P	Available P	Sol-P	Al-P	Fe-P	Red-P	Ca-P	Occl-P
TSP									
Time	2	141570.3*	1863895.0*	10932.2*	83234.2*	15793.6*	24.75*	64123.1*	1612.6*
Treatments	4	11997853.0*	8123606.0*	141977.2*	2625319*	74561.1*	2.34*	100898.8*	1327.7*
Treatments*Time	8	152724.2*	512452.3*	2517.6*	67424.7*	4537.8*	3.48*	17763.2*	825.8*
Error	30								
ERP									
Time	2	7593379.8*	1086219.0*	0.003*	216.2*	8.69*	12.98*	972584.7*	605.6*
Treatments	4	35738349.1*	3436152.0*	0.004*	854.8*	274.42*	0.98*	6209968.0*	6892.1*
Treatments*Time	8	3904456.9*	165146.1*	0.002*	78.4*	2.93*	2.75*	498917.5*	353.8*
Error	30								
CIRP									
Time	2	2625341.3*	87580.7*	0.076*	82.17*	365.42*	43.20*	140557.9*	17309.1*
Treatments	4	12470362.3*	669439.5*	0.004*	1805.90*	52561.08*	2.47*	2363812*	72135.5*
Treatments*Time	8	986563.2*	127051.1*	0.022*	291.90*	357.65*	0.80*	187633.5*	3230.3*
Error	30								

Note: Asterisk (\*) indicates significant at  $p \leq 0.05$

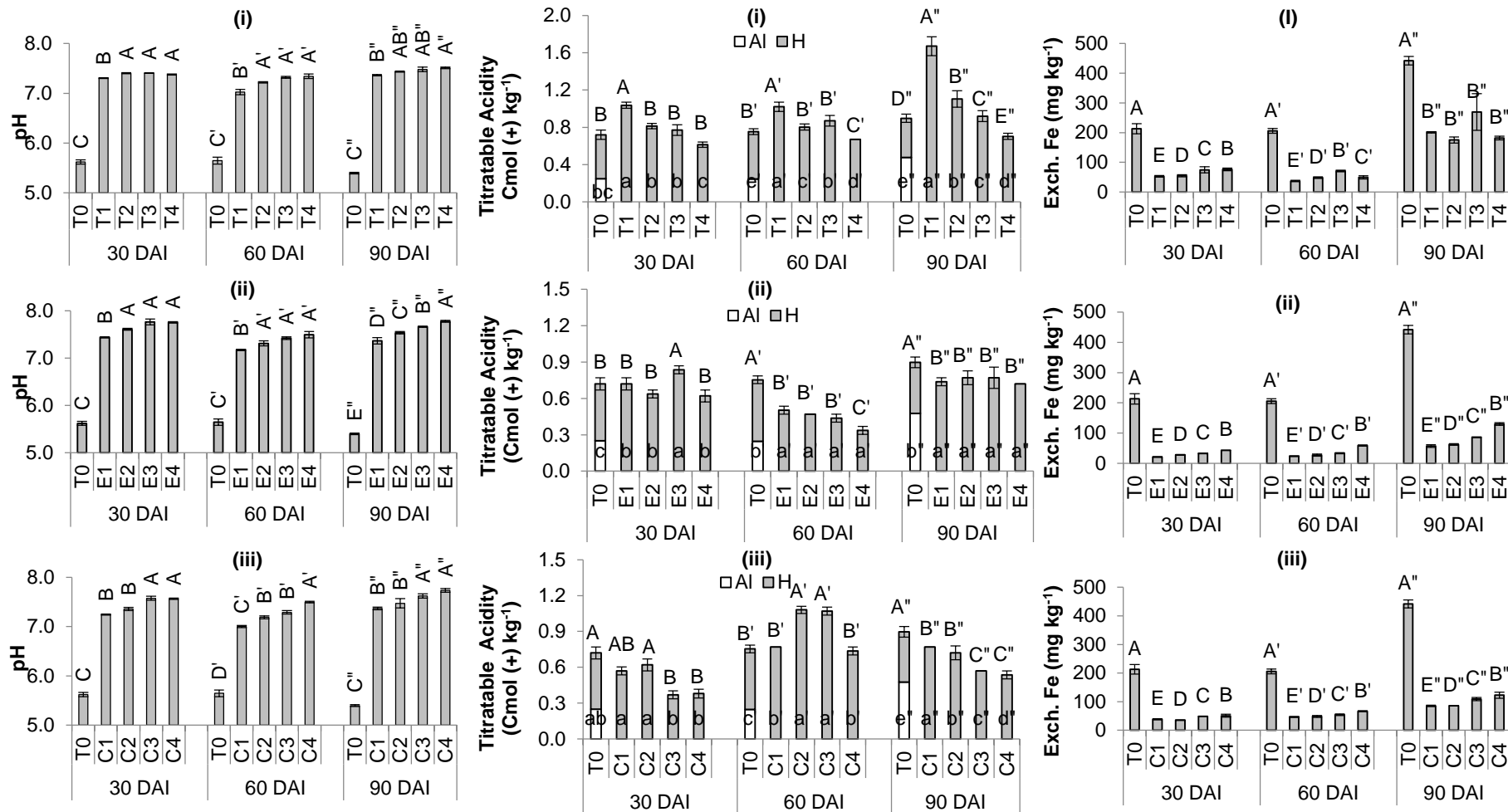
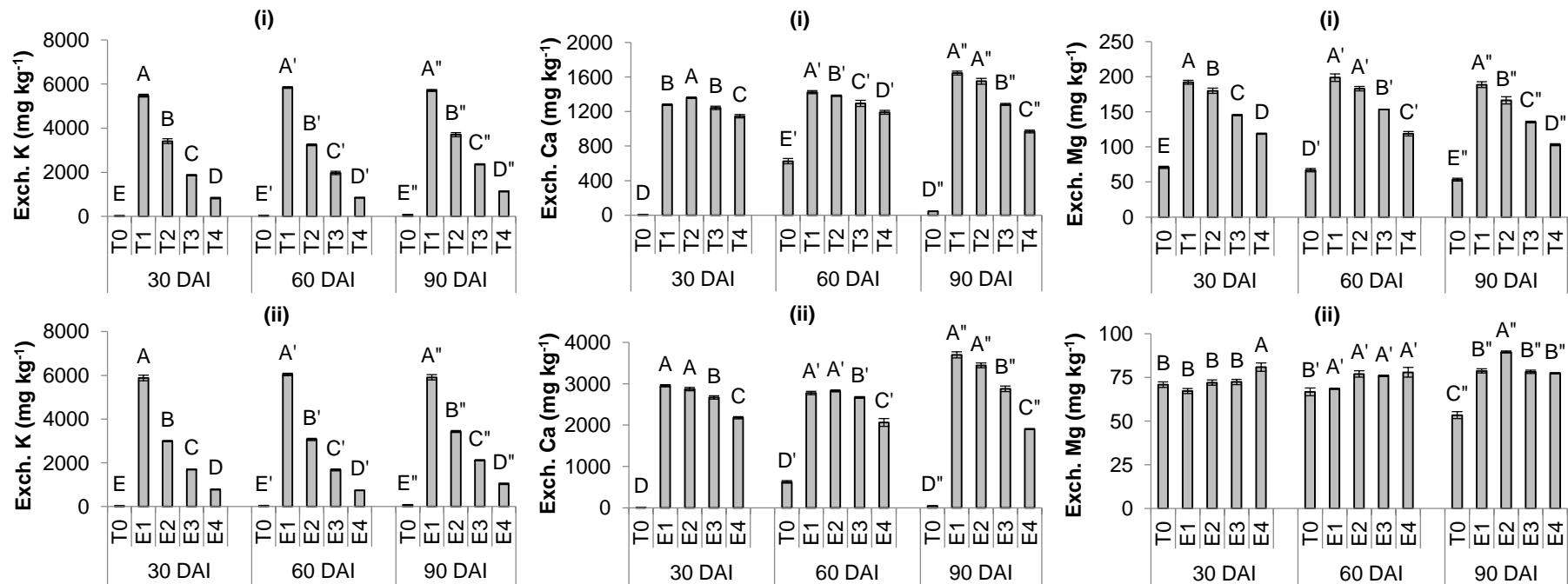


Figure 2: Effects of treatments on soil pH, titratable acidity, and exchangeable Fe at 30, 60, and 90 DAI. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$ . (i), (ii), and (iii) represent treatments with TSP, ERP, and clinoptililite zeolite, respectively. Capital letters indicate titratable acidity whereas small letters indicate  $H^+$ . Note: Letters without prime represent 30 DAI, single prime superscript represents 60 DAI, and double prime superscript represents 90 DAI





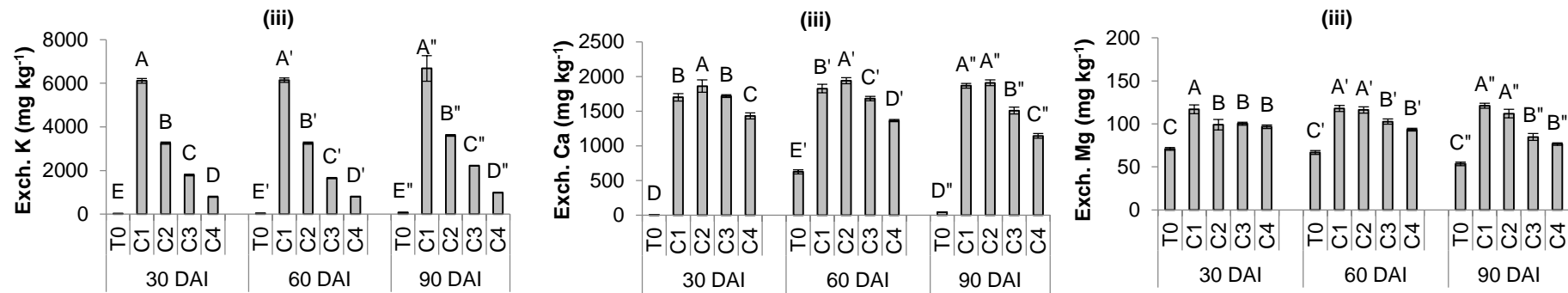


Figure 3: Effects of treatments on soil exchangeable K, Ca, and Mg at 30, 60, and 90 DAI. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$ . (i), (ii), and (iii) represent treatments with TSP, ERP, CIRP, and clinoptilolite zeolite, respectively. Note: Letters without prime represent 30 DAI, single prime superscript represents 60 DAI, and double prime superscript represents 90 DAI

*Effects of amending fertilizers with clinoptilolite zeolite on soil total and available phosphorus*

Soil total P and available P at 30, 60 and 90 days after incubation (DAI) are presented in Figure 4. The reducing trend in soil total and available P regardless of incubation time and type of P fertilizer was due to the reduction rates of the P fertilizer used. Sorption of P may have also possibly decreased with increasing soil pH (Figure 2). This relates to the increase of negative charges on soil particles as amorphous Fe and Al oxides precipitated and greater competition of hydroxyl ion (OH<sup>-</sup>) with phosphate ions for the adsorption sites when soil pH increased (Naidu and Syers, 1990). Limited availability of P to satisfy sorption sites also explains the increase in soil exchangeable Fe with reducing P fertilizer rate. Larger sorption capacity of Al implies better saturation of Al compared to Fe (Maguire *et al.*, 2000; He *et al.*, 1992).

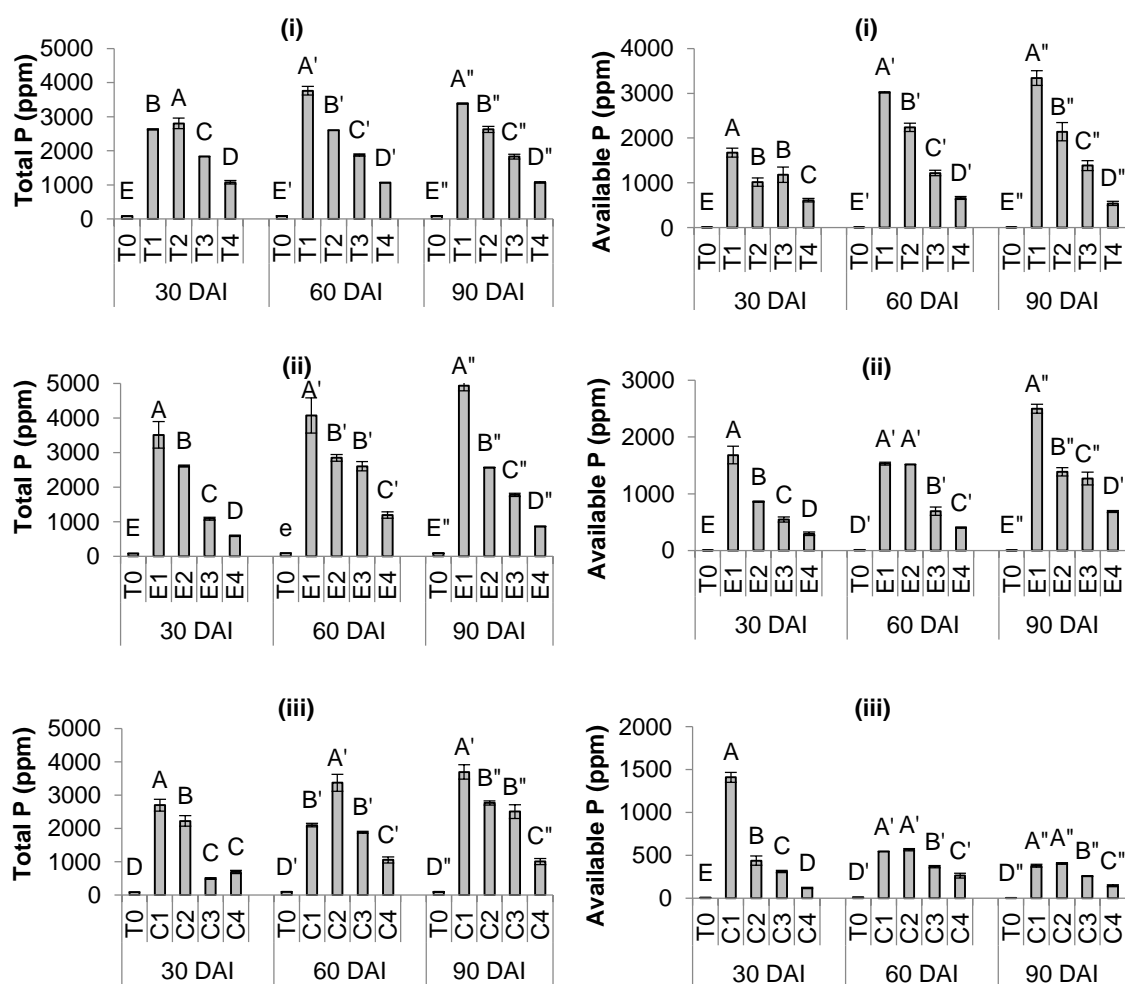


Figure 4: Effects of treatments on soil total and available P at 30, 60, and 90 DAI. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$ . (i), (ii), and (iii) represent treatments with TSP, ERP, CIRP, and clinoptilolite zeolite, respectively. Note: Letters without prime represent 30 DAI, single prime superscript represents 60 DAI, and double prime superscript represents 90 DAI

### Effects of amending fertilizers with clinoptilolite zeolite on soil inorganic phosphorus fractions distribution

The percentage of inorganic P following application of TSP, ERP, and CIRP are summarized in Table 6. At 30 DAI, active P fractions (Fe-P > Ca-P > Al-P) constituted 80% but increased to 90% at 90 DAI under soil alone (T0). Iron bound P showed the largest fractions of inorganic P regardless of time of incubation. At 30 DAI, Fe-P was approximately 58% and the fraction increased with time to 68% at 90 DAI. Application of fertilizer regardless of type and rate altered the distribution of soil inorganic P in this study.

Upon application of TSP (Table 6), Fe-P fraction reduced by 2 to 4 folds, whereas Al-P increased by 5 folds (dominant inorganic P fraction). The observation is however contrary to the soil treated with rock phosphates as Ca-P was the dominant fraction regardless time of incubation and rate of rock phosphate applied. Application of ERP resulted in more than 90% Ca-P fraction whereas CIRP showed almost 60% to 70% Ca-P regardless of time of incubation. Figure 6 shows the effects of treatments on Sol-P. Treatments with TSP showed Sol-P recovery from 30 DAI to 90 DAI whereas for ERP and CIRP treatments started from 60 DAI to 90 DAI. The higher recovery of Sol-P in TSP treatments compared with those of rock phosphates was due to the solubility of TSP. The significantly higher content of Sol-P in T1 regardless of day of incubation was due to the higher rate of TSP applied (normal fertilization which is 100% TSP). The reduction trend in T2, T5, and T8 was attributed to reduction of TSP application by 25%, 50%, and 75%, of the recommended rate respectively. Application of higher P rates was able to quench the P fixation sites such that P buffering capacity was exceeded. Hence, the higher amount of Sol-P recovery following the application of TSP (Buresh *et al.*, 1997).

Loosely soluble-P recovery from 60 DAI due to increase in soil pH (Figure 2) following application of clinoptilolite zeolite and rock phosphates as relatively higher pH impedes release of P from rock phosphates. This, could partly explain the insignificant differences regardless of fertilization. In addition, in this incubation study, there was no leaching, no roots exudates, and no nutrients uptake to induce dissolution of the rock phosphates. The transformation of inorganic P fractions is mainly governed by soil pH.

Regardless of time of incubation, TSP application in soils showed higher Al-P content compared with rock phosphates (Figure 5) suggesting that a portion of P applied (TSP) to the soil

might have been adsorbed at a faster rate to allophane and Al oxides more than that converted to any other forms. This observation is consistent with a report that Al-P varies with rate of fertilization, high sesquioxides content, and low pH (Amaizah *et al.*, 2013). Hence, the relative increase in Al-P recovery following the application of TSP in this study suggests the strong effect of fertilization on Al-P.

Rock phosphates are generally made up of calcium apatite, so they considerably increase Ca-P fraction in soils (Hongqing *et al.* 2001). As soil pH increased (Figure 2), dissolution of rock phosphate was impeded. The absence of plant-soil association in this study could not significantly affect induced-exchange mechanism with which clinoptilolite zeolite induces rock phosphate dissolution. The higher Ca-P content in the rock phosphate treatments compared with TSP treatments suggests that undissolved rock phosphates remained in the soil and dissolved slowly (Figure 5). A lower Ca-P in CIRP could be due to the better solubility of CIRP than ERP. Regardless of rate of P application, the reduction of Ca-P with time could be related to the recovery of Sol-P in the TSP treatments as previously discussed. Appreciable amounts of the solubilized P (TSP) might have also been partly fixed by Al and Fe to form Al-P and Fe-P pool in this high P fixing soils (Figures 5 and 6). This observation is consistent with a report that in high P fixing Ultisol, Al-P and Fe-P dominated upon application of TSP (highly soluble P) whereas Ca-P dominated in soils was high with rock phosphate application (Hongqing *et al.*, 2001; Zoysa *et al.*, 1997). However, some of the heavily fertilized acid soils might contain significant amounts of Ca-P (Lookman *et al.*, 1996) and hydroxyapatite has also been found as a product of the superphosphates dissolution in acidic and slightly acidic soils (Kumar *et al.*, 1994).

Reductant soluble-P is assumed to be P associated with poorly crystalline Fe oxides that is stable under oxidized condition (Figure 6). Reductant soil soluble-P as affected by fertilization regardless of rate showed a decreasing trend with time of incubation. This could be related to transformation of Red-P into other forms of P with increasing time. The level of Red-P in the natural environment can be manipulated as an index of potential P release into soil that is subjected to redox conditions (Sharpley, 2000; Gu and Qin, 1997). In a study on waterlogged rice fields, it was reported that Red-P, Al-P and Fe-P were positively correlated with P availability, suggesting their contributions to supply of the P to crops in the areas under stress condition ( $\text{Fe}^{3+}$  could release adsorbed P when reduced to  $\text{Fe}^{2+}$ ) (Adhami *et al.*, 2013). However, in this study, there was no redox potential involved and thus, implicates high content of Occl-P because adsorbed P might have been physically encapsulated or surrounded by secondary minerals such as Fe and Al oxyhydroxides with time (Figure 6).

Table 6: Percentage of soil inorganic P fractions as affected by TSP, ERP and CIRP treatments at 30, 60 and 90 DAI. Note: T0: soil alone; T1, E1, C1: recommended P fertilizer, T2, E2, C2: 75% fertilization + 85% zeolite; T5, E5, C5: 50% fertilization + 100% zeolite and T8, E8, C8: 25% fertilization + 115% zeolite

DAI	Pi-Type	TSP					ERP					CIRP					
		T0	T1	T2	T5	T8	T0	E1	E2	E5	E8	T0	C1	C2	C5	C8	
30	Sol-P	0.0	12.0	8.0	5.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Al-P	10.0	56.0	56.0	54.0	51.0	10.0	1.0	1.0	2.0	6.0	10.0	2.0	2.0	3.0	6.0	
	Fe-P	59.0	14.0	17.0	24.0	26.0	59.0	0.0	1.0	1.0	5.0	59.0	9.0	12.0	12.0	16.0	
	Red-P	12.0	0.0	0.0	0.0	1.0	12.0	0.0	0.0	0.0	1.0	12.0	0.0	1.0	1.0	1.0	
	Ca-P	11.0	17.0	18.0	16.0	18.0	11.0	97.0	94.0	93.0	75.0	11.0	78.0	69.0	62.0	51.0	
	Occl-P	8.0	1.0	1.0	1.0	2.0	8.0	2.0	4.0	4.0	13.0	8.0	11.0	16.0	22.0	26.0	
60	Sol-P	0.0	16.0	15.0	9.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	Al-P	9.0	48.0	55.0	58.0	56.0	9.0	2.0	2.0	1.0	3.0	9.0	4.0	3.0	6.0	5.0	
	Fe-P	64.0	12.0	15.0	13.0	23.0	64.0	1.0	1.0	1.0	3.0	64.0	15.0	11.0	16.0	21.0	
	Red-P	8.0	0.0	0.0	0.0	0.0	8.0	0.0	0.0	0.0	1.0	8.0	0.0	0.0	0.0	1.0	
	Ca-P	6.0	20.0	13.0	17.0	17.0	6.0	92.0	88.0	96.0	88.0	6.0	71.0	77.0	64.0	53.0	
	Occl-P	13.0	4.0	2.0	3.0	1.0	13.0	5.0	9.0	2.0	5.0	13.0	10.0	9.0	14.0	20.0	
90	Sol-P	0.0	13.0	10.0	8.0	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	Al-P	10.0	74.0	73.0	64.0	47.0	10.0	2.0	1.0	1.0	2.0	10.0	1.0	4.0	6.0	4.0	
	Fe-P	68.0	8.0	9.0	18.0	26.0	68.0	0.0	1.0	1.0	2.0	68.0	13.0	15.0	10.0	11.0	
	Red-P	2.0	5.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	1.0	
	Ca-P	13.0	0.0	7.0	9.0	20.0	13.0	95.0	94.0	97.0	92.0	13.0	68.0	63.0	61.0	60.0	
	Occl-P	7.0	0.0	1.0	1.0	2.0	7.0	3.0	4.0	1.0	4.0	7.0	18.0	18.0	23.0	24.0	

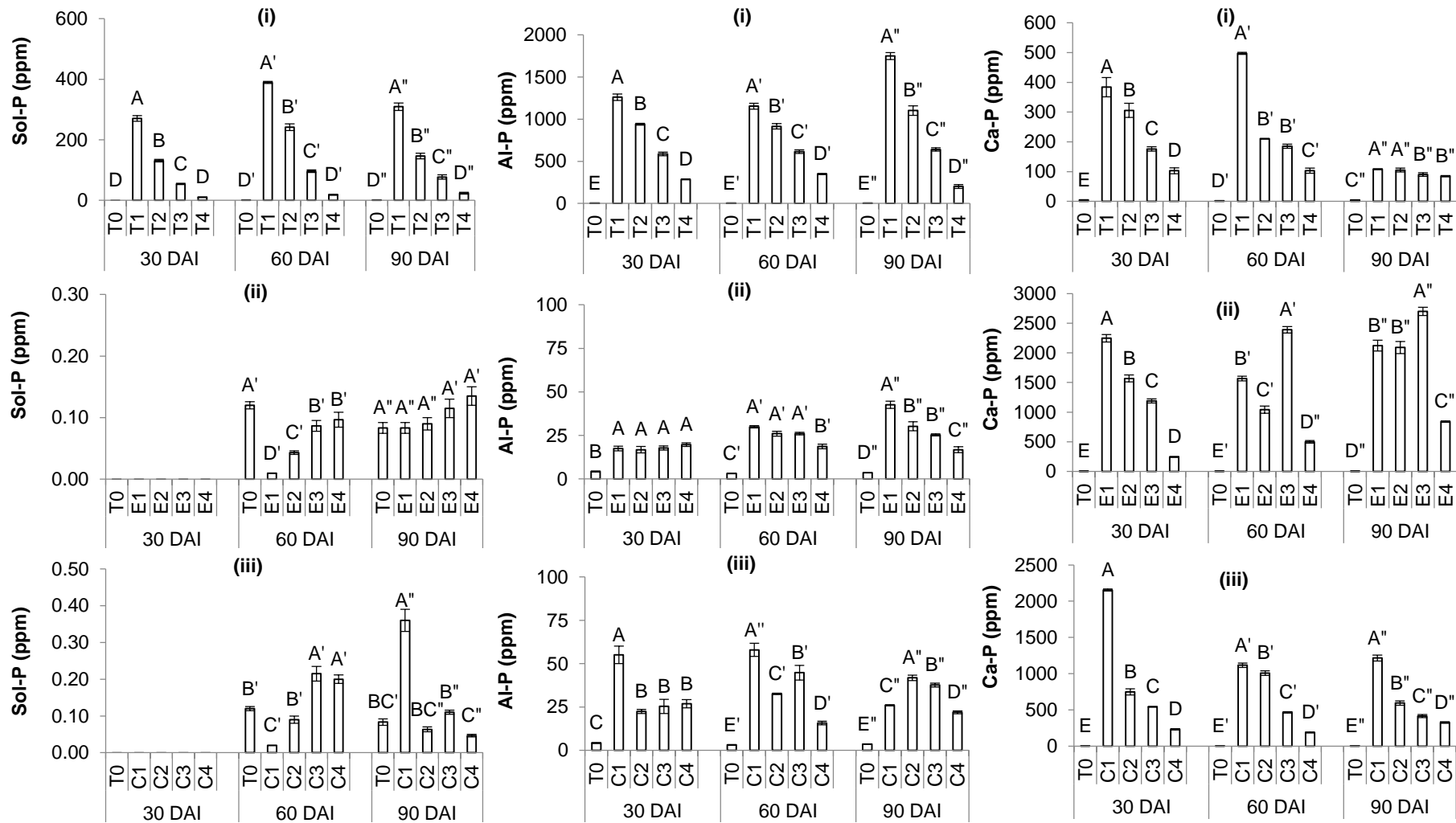


Figure 5: Effects of treatments on Sol-P, Al-P, and Ca-P at 30, 60, and 90 DAI. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$ . (i), (ii), and (iii) represent treatments with TSP, ERP, CIRP, and clinoptilolite zeolite, respectively. Note: Letters without prime represent 30 DAI, single prime superscript represents 60 DAI, and double prime superscript represents 90 DAI

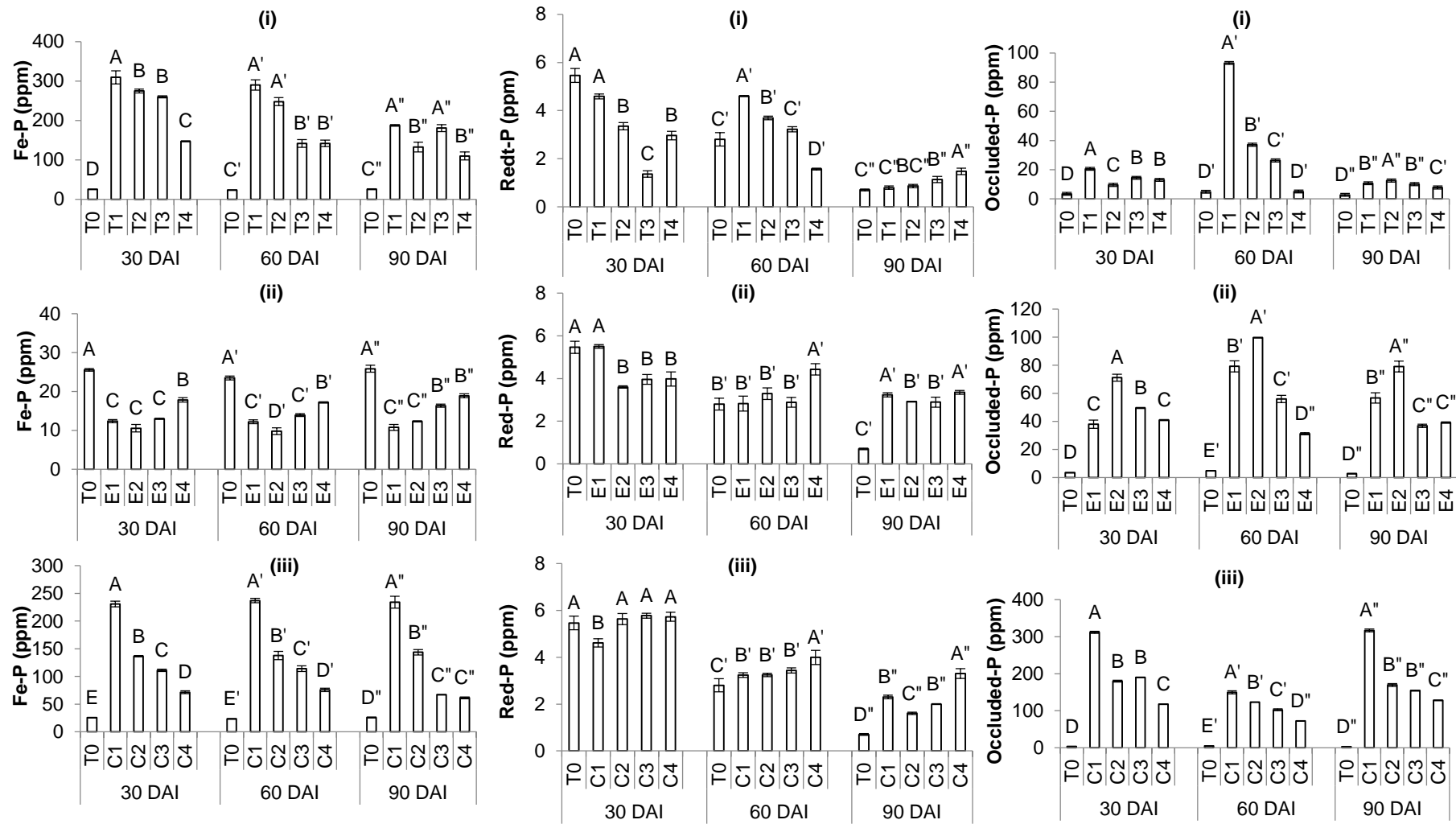


Figure 6: Effects of treatments on Fe-P, reductant-P and occluded-P at 30, 60, and 90 DAI. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$ . (i), (ii), and (iii) represent treatments with TSP, ERP, CIRP, and clinoptilolite zeolite, respectively. Note: Letters without prime represent 30 DAI, single prime superscript represents 60 DAI, and double prime superscript represents 90 DAI



## Conclusions

Reduced rate of fertilizers with increasing rate of clinoptilolite zeolite significantly increase soil pH. As a result, reduction of exchangeable Al was comparably to the recommended rate of fertilizer which also reduced soil titratable acidity. Retention of Ca and Mg in the treatments with 85% clinoptilolite zeolite and 25% fertilizers reduction (T2, E2 and C2) was comparable to the standard recommendation. However, treatments with clinoptilolite zeolite neither significantly reduced exchangeable Fe, P fixation (Al-P, Fe-P, Ca-P, Red-P, and Occl-P) nor increased soil total P and availability of P. Although retention and availability of P was not striking with the of inclusion clinoptilolite zeolite in this study, results could be different if the soil is cultivated with crops. Root exudation and uptake of nutrients may contribute to release of organic acids to compete for adsorption sites and reducing Ca availability in the soil to trigger induced-exchange dissolution of RP-clinoptilolite zeolite. The treatment with 25% fertilizer reduction amended with 85% clinoptilolite zeolite is suggested for further evaluation in pot and field studies as its effects are similar to that of the recommended fertilizer rate.

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## Chapter 6

### Effects of amending nitrogen, potassium, and phosphorus fertilizers with clinoptilolite zeolite on soil pH buffering capacity and nutrients leaching of an acid soil

Hasbullah Nur Aainaa,<sup>1</sup> \*Osumanu Haruna Ahmed,<sup>1,2</sup>  
Nik Muhamad Ab Majid,<sup>3</sup> Kasim Susilawati<sup>4</sup>

<sup>1</sup>Department of Crop Science, Faculty of Agriculture and Food Sciences, Universiti Putra Malaysia, Bintulu Sarawak Campus, 97008 Bintulu, Sarawak, Malaysia

<sup>2</sup>Institute of Tropical Agriculture and Food Security (ITAFoS), Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>3</sup>Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>4</sup>Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

\*Corresponding author email: [osumanuharuna@gmail.com](mailto:osumanuharuna@gmail.com)

#### Abstract

Amending fertilizers with clinoptilolite zeolite may improve nutrients availability and selected soil chemical properties by exploiting the large surface area, high negativity, and alkaline nature of clinoptilolite zeolite to reduce environmental pollution due to unbalanced use of chemical fertilizers and mobility of toxic elements on acid soils. The acidity, nutrients, and toxic metals bound in acid soil tend to unlock as soil capacity to bind to the positively charged ions depletes in high weathering, rainfall, and heat of the tropics. A laboratory leaching experiment was carried out to evaluate nutrients retention from soils treated with different amounts of clinoptilolite zeolite as fertilizers rate reduced over 30 days. Leachates and soil were analyzed using standard procedure. Results indicated clinoptilolite zeolite inclusion reduced pH buffering capacity in the soil and reduced the leaching losses of Ca and Mg. The availability of N, P, K, and Fe in the soil significantly reduced following the application clinoptilolite zeolite at 25% fertilizer reduction. The effect of the clinoptilolite zeolite on nutrients was not glaring because of the fertilizer reduction.

**Keywords:** pH buffering capacity, nutrients leaching, clinoptilolite zeolite, nutrients retention, environmental sustainability

#### Introduction

In the humid climates, nutrients losses through leaching are higher than in the dry climates (Havlin *et al.*, 1999). Sandy soils with high water infiltration rate and low nutrients retention capacity are prone to nutrients leaching (von Uexküll, 1986). In acid soils, nutrients leaching tend to increase

because roots development is impeded. Mobility of anions such as nitrate and phosphates in highly weathered acid soils is also impeded because of the high anion exchange capacity of those soils. In contrast to nitrate, phosphate movement (through diffusion) is very low in most soils because of P precipitation and adsorption to mineral surfaces. However, excessive application and inefficient use of P fertilizers could cause water pollution such as eutrophication as available P in soils may enter water bodies through soil erosion (Zhou and Zhu, 2003) rather than through leaching (Ruban, 1999) except in very sandy and organic soils (Wild, 1988).

In a study where clinoptilolite zeolite was used in the fertilization programme of maize cultivation on an acid soil, the Clinoptilolite zeolite neither significantly increased soil pH, P availability, bases cations nor reduced P fixation, soil acidity, and exchangeable Al (Ahmed *et al.*, 2016). However, dry matter production, yield of fresh cobs, nutrient uptake, and agronomic efficiency were similar for the maize plants with or without clinoptilolite zeolite (Ahmed *et al.*, 2016). With the exception of soil pH which improved with clinoptilolite zeolite and 75% fertilizer application (Urea, Egypt Rock Phosphate, and KCl) the aforementioned results obtained in the first maize plant cycle were similar to those obtained in the second cycle (Ahmed *et al.*, 2016; Aainaa *et al.*, 2015). These results suggest that the use of clinoptilolite zeolite in agriculture is beneficial as it can be used to reduce the unbalanced use of N, P, and K fertilizers of *Zea mays* L. and related crops cultivated on acid soils. Perhaps, in a long term, soil chemical properties could significantly improve due to carry over effects of clinoptilolite zeolite.

However, further assessment on nutrients leaching for environmental consideration besides minimizing environmental pollution due to excessive use of chemical fertilizers needs to be clarified. Thus, this study was conducted to determine retention and leaching of nutrients added to soil as affected by clinoptilolite zeolite application in the fertilization programme of *Zea mays* L. In this present study, clinoptilolite zeolite was adopted as an amendment to improve P use efficiency and to also reduce N, P, and K fertilizers use.

## Materials and methods

### *Soil Sampling, Preparation, and Characterization.*

The clinoptilolite zeolite used in this study was imported from Indonesia. The mineral soil used in the study is typical of Bekenu series (Typic Paleudults) and it was sampled at an uncultivated area of Universiti Putra Malaysia, Bintulu Campus Sarawak, Malaysia. The coordinates of the soil sampling site are latitude 03° 12.241' N and longitude 113° 04.270' E. The soil samples taken at 0-15 cm depth were air-dried, ground, and sieved to pass to a 2 mm sieved. Soil samples were characterized for physical and chemical properties before and after the leaching study. Soil texture was determined using the hydrometer method (Tan, 2005). pH of the soil and clinoptilolite zeolite

were determined in distilled water (at ratio of 1:2.5 soil:water) using a digital pH (Peech, 1965). Soil organic matter and total carbon were determined using the loss-on-ignition method (Piccolo, 1996). Soil bulk density was determined using the method described by Tan (2005). Soil total P (extracted using aqua regia) and available P (extracted using Mehlich No.1) (Tan, 2005) were determined using spectrophotometer (Lambda 25, Perkin Elmer) after blue color development (Murphy and Riley, 1962). Soil cation exchange capacity (CEC) was determined using the ammonium acetate method (Cottenie, 1980) whereas CEC of the clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). The CsCl method used avoids underestimation of CEC of the zeolites as this method does not lead to entrapment of ammonium ions in the channels of zeolites. Exchangeable cations were extracted using double acid as extractant following the method of Mehlich No.1 (Mehlich, 1953). Afterwards, the exchangeable cation concentrations of the solution extracted from the soil were determined using Atomic Absorption Spectrometer (AAAnalyst 800, Perkin Elmer Instruments, Norwalk, CT), Total titratable acidity was determined using acid-base titration method (Rowell, 1994) whereas Kjeldahl method was used to determined total N (Bremner, 1965),

The selected physico-chemical properties of Bekenu series and clinoptilolite zeolite are shown in Table 1 whereas the chemical properties of P fertilizers (TSP, ERP, and CIRP) are shown in Table 2. The soil used was acidic (pH=4.32), low in CEC (5.33 cmol(+)kg<sup>-1</sup>) and total N (0.06%). Soil total carbon, exchangeable K, Ca, and Mg were slightly higher than the standard range for this soil type (Paramanathan, 2000) because of litter decomposition with time at the soil surface as the soil used in this study was taken from an uncultivated area.

Table 2: Selected soil physico-chemical properties of Bekenu series

Soil properties	Soil		Clinoptilolite zeolite
	Value obtained	Standard range*	
pH (water)	4.32	4.6-4.9	8.54
Bulk density (g cm <sup>-3</sup> )	1.01	Nd	Nd
CEC (cmol(+)kg <sup>-1</sup> )	5.33	3.86-8.46	75.4
Total N (%)	0.06	0.04-0.17	0.22
Total P (%)	0.005	Nd	0.01
Available P (mg kg <sup>-1</sup> )	2.48	Nd	Nd
Organic matter (%)	5.60	Nd	Nd
Total carbon (%)	3.25	0.57-2.51	Nd
Total Fe	7.51	Nd	0.11
Total acidity	1.38	Nd	Nd
Exchangeable Al	0.9	Nd	Nd
Exchangeable H	0.48	Nd	Nd
Exchangeable K	0.24	0.05-0.19	6.16
Exchangeable Ca	0.76	0.01	22.30
Exchangeable Mg	0.45	0.07-0.21	2.36
Exchangeable Na	3.60	0.01	18.99
Texture	SL	SL	Nd

Note: Nd= not determine, SL= sandy loam, asterisk (\*) subjected to the soil development, standard data range by Paramanathan (2000)

The total P<sub>2</sub>O<sub>5</sub> of TSP, CIRP, and ERP were 41%, 24%, and 27%, respectively (Table 2). Calcium in TSP, ERP, and CIRP were 4%, 47%, and 51%, respectively. The higher amounts of Ca in ERP and CIRP were due to inherent contents of Ca in the parent materials of the fertilizers. High Ca in the apatite of the rock phosphates contributes to alkalinity of these phosphate fertilizers compared with that of the acidulated TSP.

Table 3: Selected chemical properties of phosphorus fertilizers

Property	TSP	ERP	CIRP
pH (water)	2.46	7.42	7.93
Total P (%)	18.09	11.96	10.62
Total P <sub>2</sub> O <sub>5</sub> (%)	41.12	27.19	24.15
Total K (%)	0.42	0.25	0.31
Total Ca (%)	4.88	47.55	51.73
Total Mg (%)	0.35	0.17	0.24
Total Fe (%)	0.38	0.61	0.52

### *Determination of soil pH buffering capacity*

Prior to soil pH buffering capacity determination, 250 g of soil (Bekenu Series) were mixed thoroughly with clinoptilolite zeolite. Three clinoptilolite zeolite rates were evaluated represent the rate applied in combination with different P fertilizers (TSP, ERP, and CIRP).

- T0 : Soil only (controlled)
- Z0 : Clinoptilolite zeolite only
- T2 : Soil + 0.34 t ha<sup>-1</sup> clinoptilolite zeolite
- E2 : Soil + 0.43 t ha<sup>-1</sup> clinoptilolite zeolite
- C2 : Soil + 0.42 t ha<sup>-1</sup> clinoptilolite zeolite

Following the method of Rowell (1994), soil pH buffering capacity was determined using 0.1 M NaOH and 0.1 M HCl. The samples were equilibrated for 7 days as described by Aitken and Moody (1994). A 10 g of air-dried soil was weighed into a plastic vial, and 25 mL of distilled water were added. A 1 mL of 0.05 M CaCl<sub>2</sub> was added to minimize variation in ionic strength and 0.25 mL of toluene addition was to inhibit microorganism activity. Suspensions were shaken for 24 hours at 180 rpm after which they were equilibrated for seven days. Samples were shaken for 2 minutes daily until the seventh day of equilibration. Titration curves were established by repeatedly adding 0.1 M HCl to the suspensions and pH measured until the required pH range was obtained. The amount of acid required to reduce pH by one unit was calculated as the negative reciprocal of the slope of the linear regression. The values of pH buffering capacity were obtained from the slope of titration curves of acid (0.1 M HCl) or base (0.1 M NaOH) additions plotted against pH (pH range 4 to 7). With the exception of soil alone, the other treatments were titrated with 0.1 M HCl. The soil alone treatment was titrated with 0.1 M NaOH to avoid underestimation of the acidity of the soil.



### Laboratory leaching experiment

A laboratory leaching experiment was carried out at the Soil Science Laboratory of Universiti Putra Malaysia Bintulu Sarawak Campus Malaysia. Based on the bulk density of Bekenu series, 250 g soil were filled in polypropylene container. Nitrogen, P, and K fertilizers, and clinoptilolite zeolite were mixed thoroughly with soil prior to the leaching experiment. Distilled water was sprayed every three days to every pot with soil such that leachate (through leaching) was collected to determine the amount of nutrients leached from the soil. The volume of distilled water (48 mL) used in this leaching study was based on rainy days over 30 days. A 5 year rainfall data was obtained from the Malaysian Meteorological Department from which average amount of rainfall per month was used. Leachates were collected at 3 days interval over 30 days of leaching for determination of pH, available N, P, K, Ca, Mg, Al, and Fe whereas soil samples were collected at 30 days of leaching. The soil samples were air-dried, and analyzed for pH, titratable acidity, total P, available P, exchangeable Al, Fe, K, Ca, Mg, and total N using the aforementioned procedures.

### Experimental design and treatments

The experimental design was completely randomized with three replicates. The treatments were based on treatments evaluated in our previous field trials (Aainaa, 2016). The rate of the fertilizers used was based on standard recommendation (Malaysian Agricultural Research and Development Institute, 1990). The recommended rates of N, P, and K fertilizers used were as follows: 60 kg N ha<sup>-1</sup> (130 kg ha<sup>-1</sup> urea), 60 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> (130 kg ha<sup>-1</sup> TSP: 214 kg ha<sup>-1</sup> ERP: 200 kg ha<sup>-1</sup> CIRP), and 40 kg K<sub>2</sub>O ha<sup>-1</sup> (67 kg ha<sup>-1</sup> MOP). The rates of the fertilizers applied in this study were scaled down to per plant basis (Table 3).

Table 4: Treatments evaluated in leaching study

Treatment			Urea	P fertilizer	MOP	Clinoptilolite zeolite
			----- g pot <sup>-1</sup> -----			
Control	Soil only	T0	:	-	-	-
TSP	100%	T1	:	4.85	+ 4.84	+ 2.47
	75%	T2	:	3.64	+ 3.63	+ 1.85
ERP	100%	E1	:	4.85	+ 7.95	+ 2.47
	75%	E2	:	3.64	+ 5.96	+ 1.85
CIRP	100%	C1	:	4.85	+ 7.42	+ 2.47
	75%	C2	:	3.64	+ 5.57	+ 1.85
Clinoptilolite zeolite	Rate for TSP	TZ	:	-	-	-
	Rate for ERP	EZ	:	-	-	-
	Rate for CIRP	CZ	:	-	-	-

### Statistical analysis

### Results and discussion

#### pH buffering capacity

pH buffering capacity of a soil is the resistance of that soil to changes in pH when an acid or a base is added. It is expressed as the amount of protons required to change soil pH by one unit ( $\text{mmol H}^+ \text{ kg}^{-1} \text{ soil pH}^{-1}$ ) (Rowell, 1994). As shown in Figure 1, there was positive linear relationship between amount of  $\text{OH}^-$  and soil pH for soil alone (T0). However, the effects of clinoptilolite zeolite alone (T1) and different rates of clinoptilolite zeolite mixed with soil (T2, T3, and T4) on soil pH buffering capacity reflected or resulted in the negative linear relationship between  $\text{H}^+$  and soil pH.

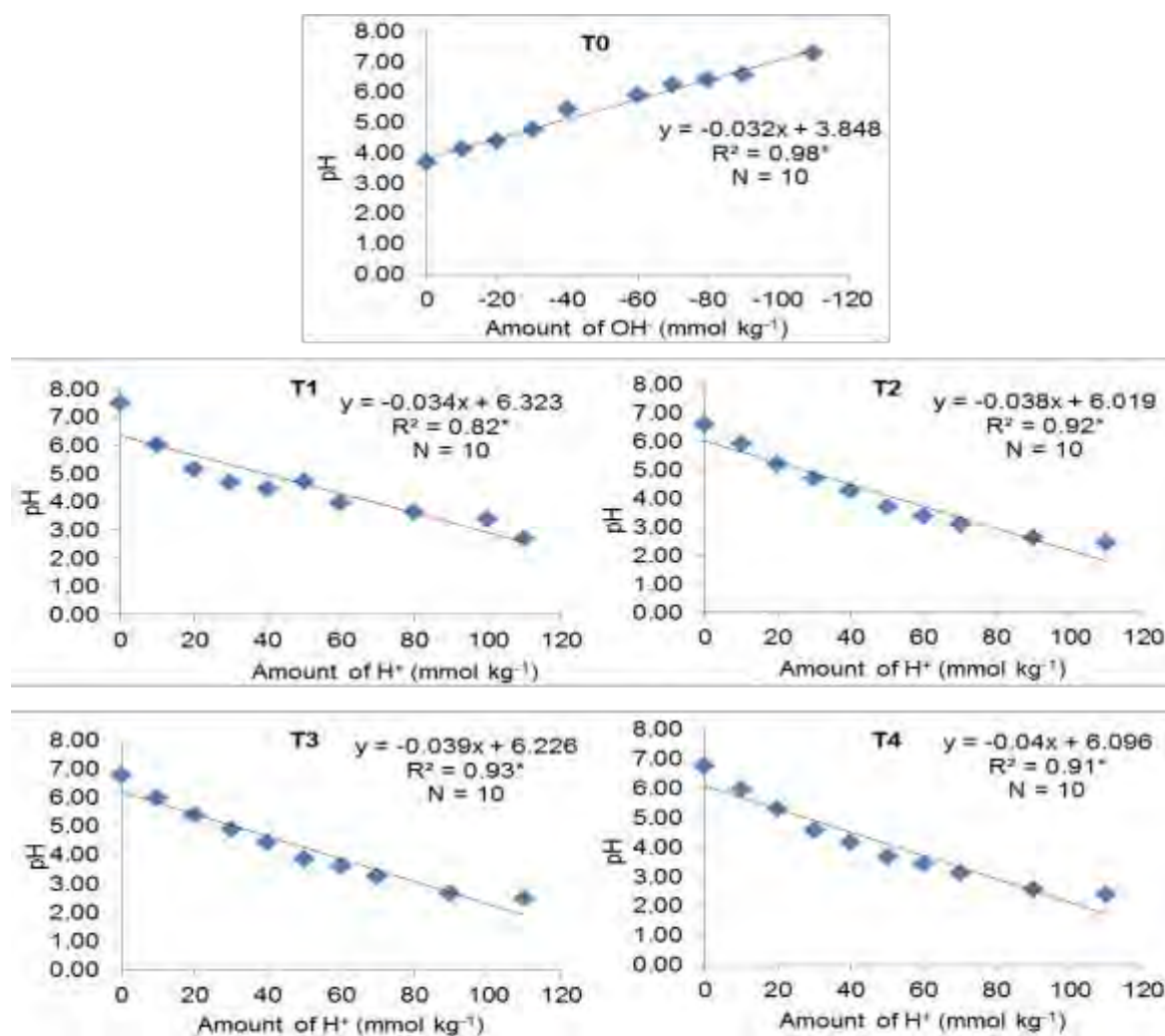


Figure 2: Soil pH buffering capacity. Treatment of soil alone (T0) using 0.1 M NaOH, Clinoptilolite zeolite alone (T1),  $0.34 \text{ t ha}^{-1}$  clinoptilolite zeolite (T2),  $0.43 \text{ t ha}^{-1}$  clinoptilolite zeolite (T3), and  $0.42 \text{ t ha}^{-1}$  clinoptilolite zeolite (T4)

Table 4 summarizes the pH buffering capacity of the treatments. Although the clinoptilolite zeolite had higher CEC (Table 2), a higher pH buffering capacity recorded for soil alone could be due to organic matter in the soil. The declining pH buffering capacity observed is related to the changes in the mineral composition of the soils with clinoptilolite zeolite. Dissolution of primary minerals such as feldspar, minerals (allophane), and amorphous materials of the soils also explains the higher pH buffering capacity at low pH (Nelson and Su, 2010). The high pH buffering capacity recorded at pH >6.0 with the inclusion of clinoptilolite zeolite might be due to precipitation of  $Al^{3+}$  as  $Al(OH)_3$  (Bloom 2000). The difference in this buffering capacity determines the degree of soil acidification.

High weathering and strong leaching processes due to high rainfall and heat of the tropics cause depletion of base cations from soils. This accelerates soil acidification which negatively affects crop productivity. As example, mobility of toxic elements such as Al is detrimental to crop roots besides creating chemical stress in crops (Stevens *et al.*, 2009). Soil acidification also enhances mobility and bioavailability of heavy metals such that they (heavy metals) cause plant injuries (Liao *et al.*, 2005).

Table 5: Summary of soil pH buffering capacity as affected by treatments

Treatments	pH	Buffering capacity	Adjusted R <sup>2</sup>
T0 Soil alone	3.84	31.10	0.98*
T1 Clinoptilolite zeolite alone	7.50	29.37	0.83*
T2 Rate of Clinoptilolite zeolite for TSP	6.57	26.12	0.92*
T3 Rate of Clinoptilolite zeolite ERP	6.77	25.50	0.94*
T4 Rate of Clinoptilolite zeolite for CIRP	6.76	25.29	0.91*

Note:

Asterisk (\*) represent significant difference at  $p \leq 0.05$

Soil alone was titrated with base giving the BC unit of  $mmol OH^- kg^{-1}$  soil

Other treatments were titrated with acid giving the BC unit of  $mmol H^+ kg^{-1}$  soil

In a related study on Ultisols and Oxisols of the tropical and subtropical regions, the pH buffering capacity of these soils were reported to be in the range of 13 to 26  $mmol kg^{-1} pH^{-1}$  (Xu *et al.*, 2012). The buffering capacity was reported to increase with increasing application of biochar (22-38  $mmol kg^{-1} pH^{-1}$ ). The functional groups and organic matter of biochar increase soil negative charges because they are able to absorb and provide protons through association reactions at low pH range (less than 7) and dissociation reactions at high pH range (above than 7) (Yuan *et al.* 2011). These reactions increase pH buffering capacity of acid soils upon biochar application (Xu *et al.*, 2012). However, this observation is contrary to what was found in this study as the mechanism responsible for increasing CEC of clinoptilolite zeolite is substitution of  $Si^{4+}$  by  $Al^{3+}$ . Despite reduction of soil pH buffering capacity, the range recorded in this present study is high (25.29-26.12  $mmol kg^{-1} pH^{-1}$ ). The decrease in soil pH buffering capacity indicates increase in the soil sensitivity to acidic condition (Aitken 1992).

*Effects of amending nitrogen, phosphorus, and potassium fertilizers with clinoptilolite zeolite on selected nutrients availability and leaching*

pH of the leachates over 30 days of the leaching study is presented in Figure 2. Soil alone (T0) recorded the lowest range of pH throughout the leaching study as this treatment had no fertilizer. Initial pH of the leachate for soil alone was high because more Fe was adsorbed on the soil compared to  $H^+$ , an evidence being the lower Al and Fe recorded in the leachate at the initial stage of the leaching study. Application of fertilizers, different rates of clinoptilolite zeolite, and amending 75% fertilizers with clinoptilolite zeolite increased pH of the leachates because cations were leached through displacement of  $H^+$  ions from solution (precipitation applied using distilled water had pH 5.6) by ion exchange (Sun *et al.* 2006; Singer and Munns, 1996).

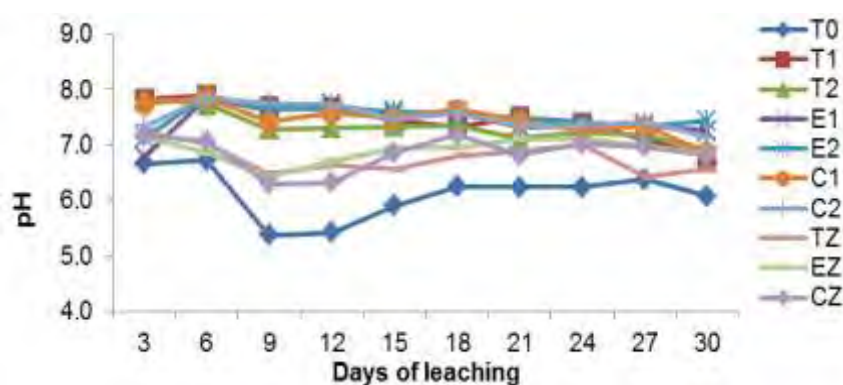


Figure 3: Effects of treatments on pH of leachates over thirty days of leaching

Phosphorus loss from treatments is presented in Figure 3. Phosphorus availability in the leachate was higher from the beginning (day 3) of the leaching study after which it decreased gradually with increasing time for the TSP treatments (Figure 3a). However, the treatments with RPs (Figure 3b) showed contrary results where P in the leachates increased in the second leaching event (day 6) after which it decreased. The fact that the highest P loss from TSP and the RPs occurred on day 3, 6, and 9 and day 6, 9, and 12, respectively suggest that P is prone to leaching. The different trends of P leaching out of the soil indicate that the release of P from loosely adsorbed or water soluble P (for TSP) is a rapid reaction (Yang *et al.*, 2007) whereas for the RPs their solubility to release P was slow. This observation is evident in the higher cumulative loss of P over the leaching periods in the TSP treatments compared with those of the RPs (Figure 3c). The TSP treatment with clinoptilolite zeolite (T2) showed significantly lower P loss compared with the recommended fertilization (T1) due to the lower amount of fertilizer in this treatment.

The lower amount of P leached from the RPs treatments was due low dissolution of calcium phosphates, fixation, and precipitation of P in the soil. Besides, there were no plants to induce RP dissolution via reduction of  $\text{Ca}^{2+}$  availability in soil upon nutrients uptake (Figure 4e). Clinoptilolite zeolite also has low propensity to form anionic complexes due to their negative framework structure (Haggerty and Bowman, 1994). Therefore, in this present study, the availability of P was partly governed by increase in soil pH.

Regardless of treatment, leaching of Fe and Al over 30 days (Figures 4a and 4b) was low at the beginning of the leaching study. Higher amount of Fe was leached from day 9 to 18 day whereas Al in leachate was highest at day 12 of the leaching study after which it decreased with increasing time. Protonation of mineral surfaces (Al and Fe oxyhydroxides) as  $\text{OH}^-$  groups on metal surface accepting  $\text{H}^+$  from the solution might have increased positive surface charges in the soil (Zhu *et al.*, 2005; Zhang *et al.*, 1991). This surface protonation in soils promotes ferric oxides dissolution, thereby solubilizing the metals. This clarifies the higher amount of Fe in the leachate over 30 days of leaching (Figure 5a) compared with Al (Figure 5b). This observation is also consistent with the higher amount of Fe in the soil than Al (Table 1).

The relatively lower amounts of Fe and Al in the leachates of the TSP treatments suggest that some of the P might have been fixed onto the soil colloids and precipitated to form complexes with Fe (strengite) and Al (variscite and various minerals of the plumbogummite group) (Hinsinger, 2001; Whitelaw, 2000; Havlin *et al.*, 1999). However, this explanation is not applicable to RPs treatments as low RP dissolution is related to the parent material of RP (Table 2). Absence of plant also inhibited Ca uptake and exudation of organic acids and  $\text{H}^+$  to favor RP solubilization. This might have impeded metal ions complexation (Welch *et al.*, 2002; Jones 1998). Moreover, the adoption of Fe and Al by the clinoptilolite zeolite resulted in significantly lower Fe and Al leached from the soil compared with those of 100% fertilizer because of 25% fertilizer reduction. The treatments with different rates of clinoptilolite zeolite (TZ, EZ, and CZ) without fertilizer application showed reduction of Fe in the leachate compared with soil alone, suggesting that the clinoptilolite zeolite might have enhanced retention of Fe in the soil. The results obtained in this present study are consistent with those of a report on zeolites use on heavy metal reclamation of acid drainage mine (Motsi *et al.*, 2009; Moreno *et al.*, 2006). As shown in Figure 5e, it is also evident that ion exchange is one of the mechanisms responsible for Fe and Al reduction in the leachates. This is due to an increase in the amount of exchangeable Ca in the soil solution as Fe and Al concentrations increased in the RP treatments in spite of the reduced of the reduced amounts of the RPs used in this present study.

Soil alone (T0) and the treatments with different rates of clinoptilolite zeolite (TZ, EZ, and CZ) had no significant effect on N loss throughout the incubation study (Figure 4c) because the treatments had no nitrogen. Irrespective of treatment, there was rapid decline of available N from day 3 to day 9 followed by gradually decrease of N. At the recommended rate of N, cumulative N loss in

the TSP treatment (T1) was higher than those of the RP treatments (E1 and C1) (Figure 5c). The treatments with clinoptilolite zeolite showed significantly lower N loss compared with the recommended rate of fertilizers due to 25% of the fertilizers reduction. The higher amount of N leached was due to the higher amount of N applied as the soil with low CEC ( $5.33 \text{ cmol}(+)\text{kg}^{-1}$ ) could not significantly retain more  $\text{NH}_4^+$  (Table 1). The fact that the effects of reducing fertilizers by 25% on maize fresh cobs, N uptake, and agronomic efficiency in the field trials were comparable to the recommended fertilizer rates (Ahmed *et al.*, 2016) indicates that clinoptilolite zeolite served as an amendment which temporary captured and released nutrients such as N slowly to ensure timely release of nutrients and use by *Zea mays* L.

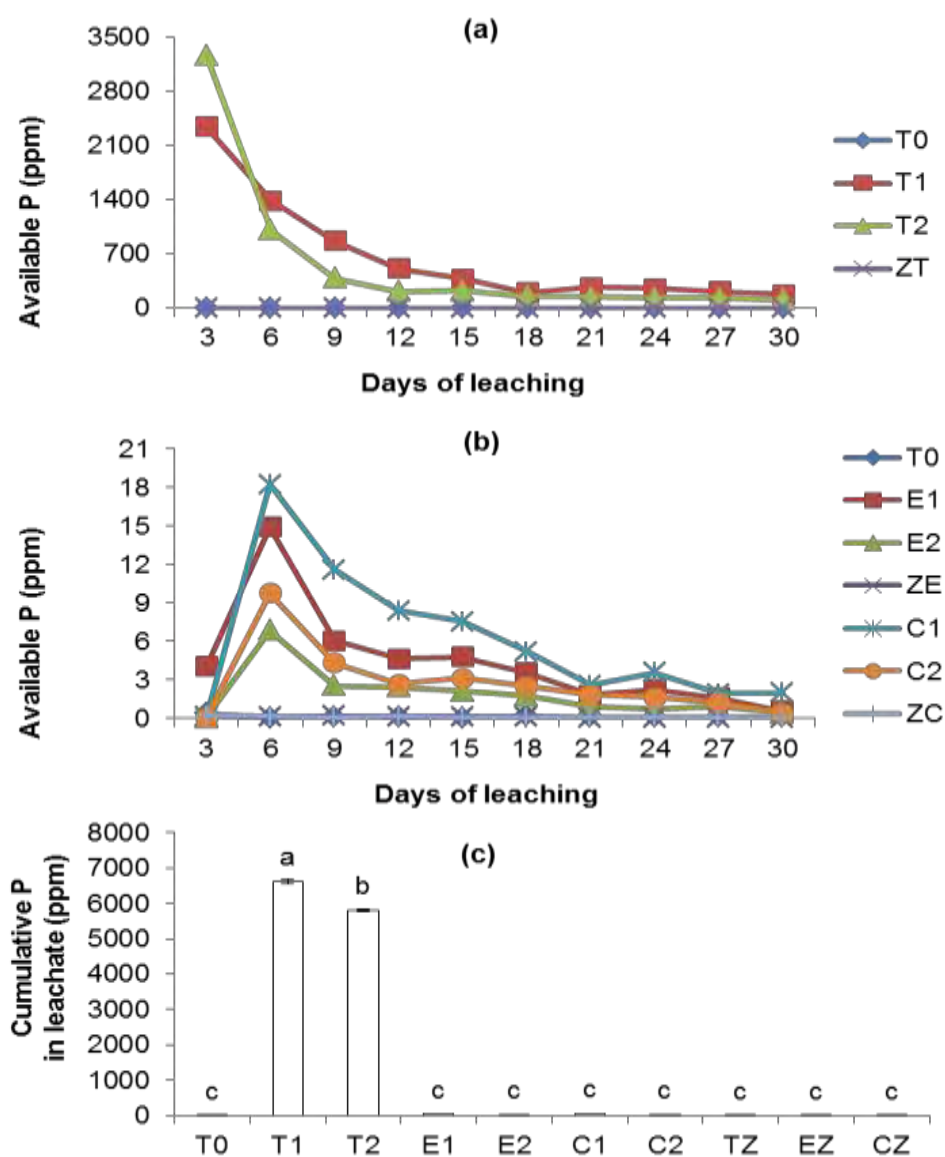


Figure 4: Effects of treatments on available P. (a) and (b) represent treatments with TSP, and rock phosphates and clinoptilolite zeolite, respectively. (c) represent cumulative P in leachates over thirty days of leaching. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$

Leaching of K occurred rapidly until day 12 followed by a gradual decrease (Figure 4d). Regardless of P fertilizer type, higher amount of K was leached from the recommended rate treatments. This finding is related the low CEC of soil used in this leaching study (Table 1) as soils with low CEC and with no amendments such as clinoptilolite zeolite are poor in retaining or adsorbing K. However, it is worth noting that the significantly lower K in the leachate (Figure 5d) over the leaching period is also associated with the 25% fertilizers reduction.

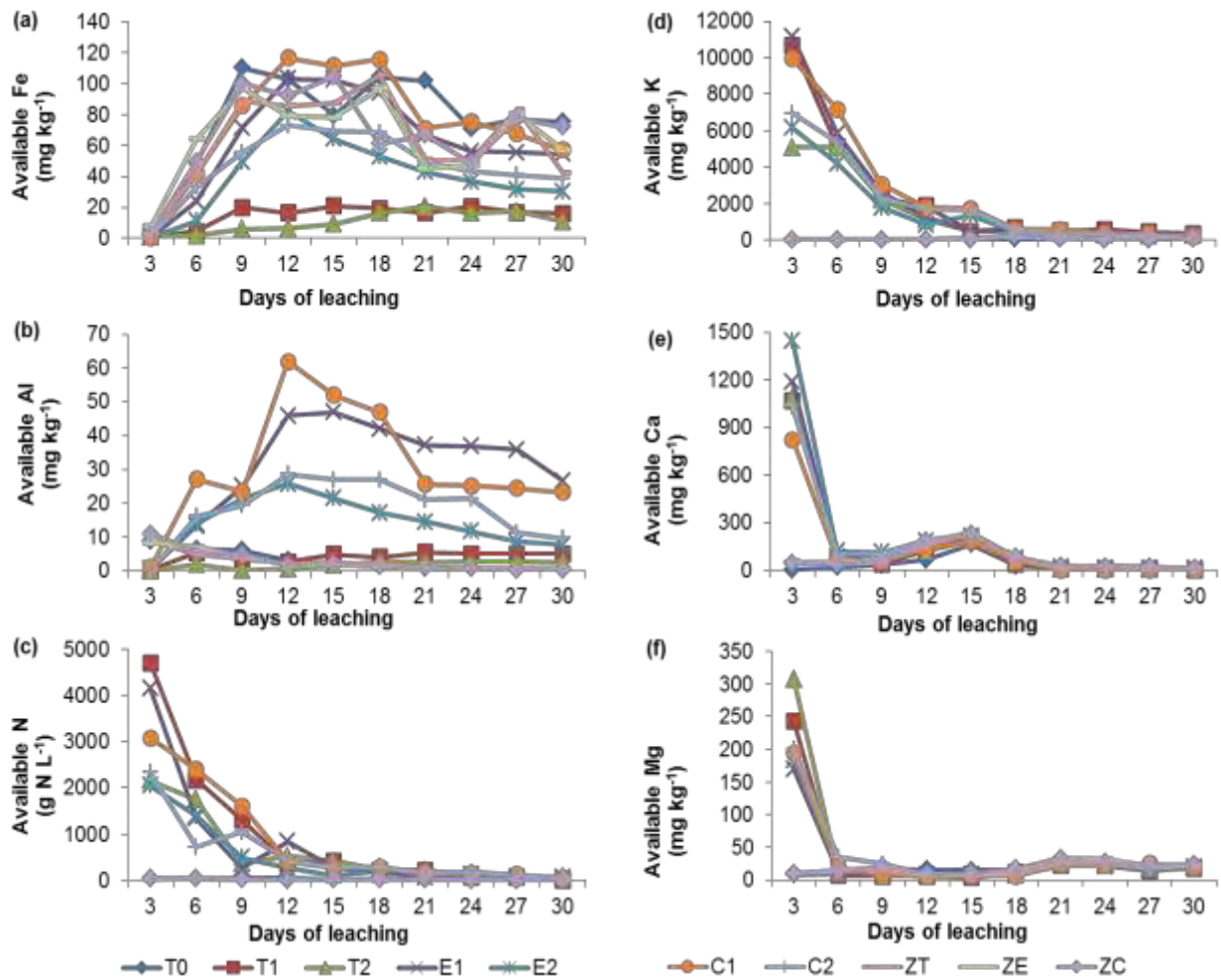


Figure 5: Effects of treatments on available Fe (a), Al (b), N (c), K (d), Ca (e), and Mg (f) in leachates over thirty days of leaching

Leaching of Ca and Mg occurred rapidly until day 9 followed by a gradual decrease (Figures 4e and 4f). The amount of available Ca leached from the treatment with 25% fertilizer reduction and clinoptilolite zeolite was similar to the recommended rate (TSP treatments) (Figure 5e). In contrast, the



RP treatments showed higher Ca in the leachate of treatments with fertilizers reduction but amended with clinoptilolite zeolite. Application of the different rates of clinoptilolite zeolite (TZ, EZ, and CZ) also showed higher amount of Ca loss than soil alone because of the inherent contents of Ca in the clinoptilolite zeolite and the RP fertilizers (Table 2). Although clinoptilolite zeolite provides extra vacant sites for bases retention, the affinity of the sorption depends on valence and hydration of the bases. This partly explains why the losses of Ca and Mg (Figures 5e and 5f) through leaching were relatively lower than monovalent K despite 25% reduction of fertilizers.

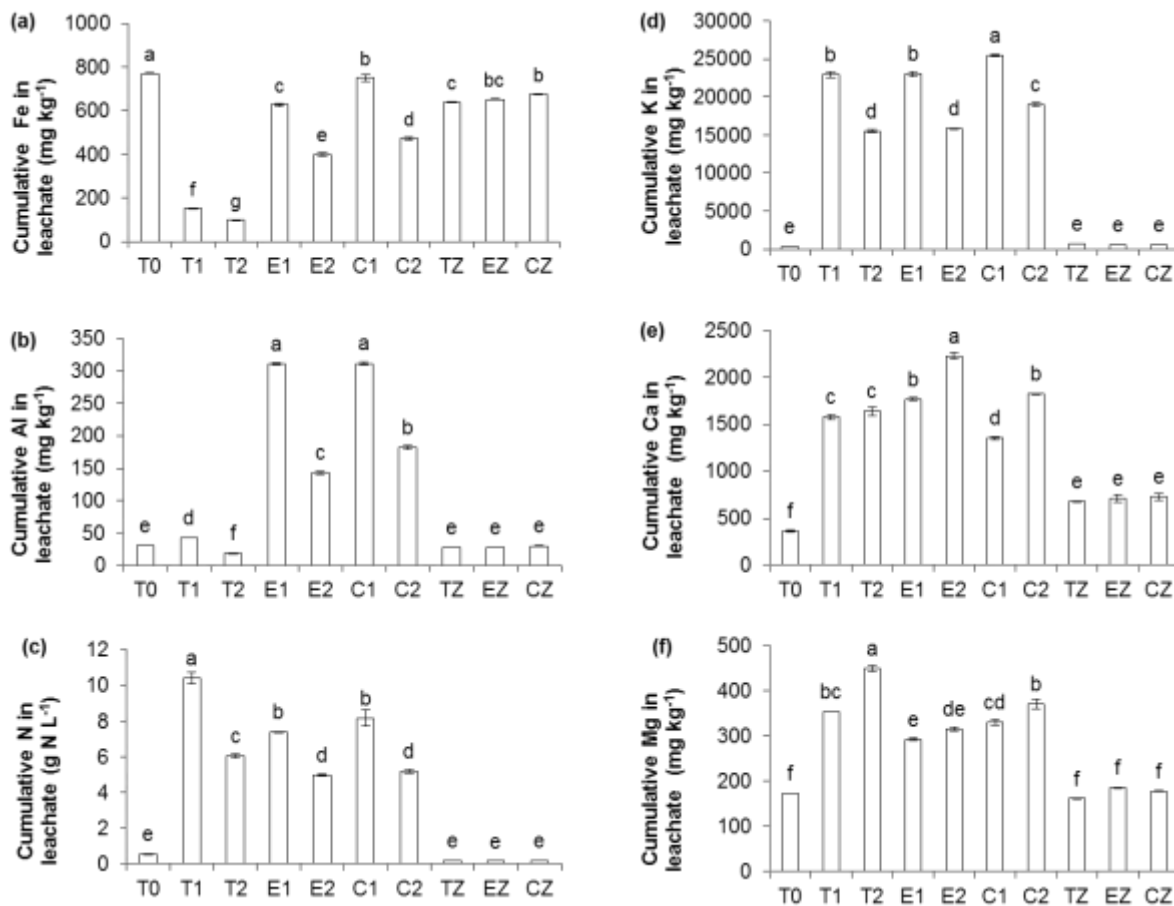


Figure 6: Cumulative Fe (a), Al (b), N (c), K (d), Ca (e), and Mg (f) in leachates over thirty days of leaching. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$

### Soil chemical properties after 30 days of leaching

Soil pH as affected by leaching is shown in Figure 6. The low soil pH of soil alone (T0) is consistent with the higher titratable acidity, exchangeable Al (Figure 7), and exchangeable Fe results (Figure 8) compared with other treatments. The increase in soil pH with fertilization and clinoptilolite

zeolite inclusion reduced exchangeable Fe and Al by reducing solubility of these metal ions to less soluble form due to repeated deprotonation to form precipitate complexes (Krstic *et al.*, 2012; Azura *et al.*, 2011). Hence, Al was negligible whereas exchangeable Fe was reduced.

Application of fertilizers only or amending fertilizers with clinoptilolite zeolite increased soil pH because of the parent materials of these materials. Besides, the high CEC of clinoptilolite zeolite enabled basic cations retention. However, the different rates of clinoptilolite zeolite (TZ, EZ, and CZ) did not increase soil pH because some Ca of the clinoptilolite zeolite leached (Figure 5e) over the 30 days of the leaching study. The clinoptilolite zeolite could not significantly neutralize H<sup>+</sup> (Figure 7) of the soil because of the soil's buffering capacity.

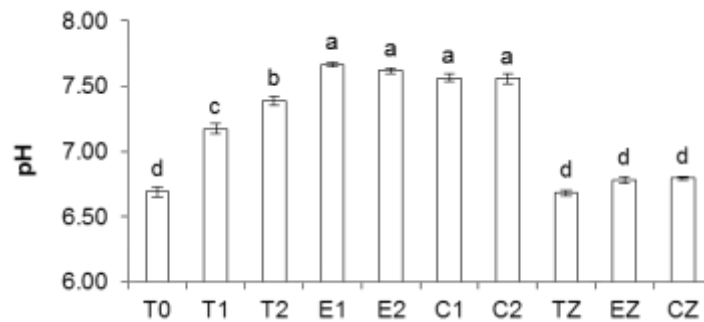


Figure 7: Effect of treatments on soil pH after thirty days of leaching. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$

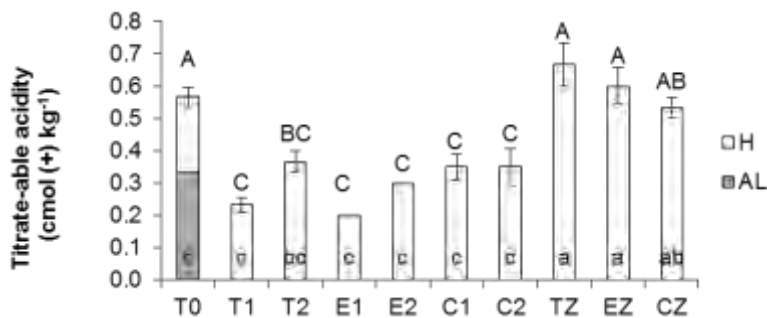


Figure 8: Effect of treatments on soil titratable acidity after thirty days of leaching. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$ . Capital letter indicates means value of titratable acidity whereas small letter indicates H<sup>+</sup> means value

Although soil pH did not increase with clinoptilolite zeolite application alone compared to soil alone, reduction of Al toxicity is reported to be beneficial for improving plant productivity as Al toxicity is the primary factor affecting plant growth (Kong *et al.*, 2008). The presence of  $H^+$  partially alleviates phytotoxic  $H^+$  competes with  $Al^{3+}$  at the root cell plasma membrane (Kochian, 1995). At higher pH values, where monomeric hydroxyl Al species predominates, the activity of  $H^+$  is reduced such that its competitive effects are impeded. This explains the insignificant difference in  $H^+$  in the soil of this present study. This observation is also related to the greater pH buffering capacity recorded for soil alone and clinoptilolite zeolite only (Table 4). More protons are required to change soil pH by one unit ( $mmol H^+ kg^{-1} soil pH^{-1}$ ) (Rowell, 1994).

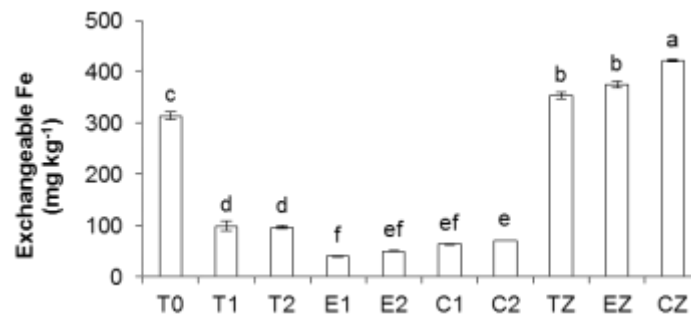


Figure 9: Effect of treatments on soil exchangeable Fe after thirty days of leaching. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$

The amount of available P (Figure 9a) in the treatments with clinoptilolite zeolite was significantly lower compared with those of the recommended rate. This relates to the comparable reduction of Al (Figure 7) and Fe (Figure 8) in the soil because less available P was fixed, precipitated, and leached.

Clinoptilolite zeolite is not a P fertilizer, thus no P was present in the treatments with the different amounts of clinoptilolite zeolite (TZ, EZ, and CZ) to quench Fe sorption site and precipitated soluble Fe. However, significantly higher Fe content in the soil compared with soil alone was due to the high affinity of the clinoptilolite zeolite for Fe. The result obtained is consistent with the significantly lower Fe and Al leached from the soil. The result is also in agreement with a report that zeolites can be used to mitigate acid drainage mines contaminated with heavy metals (Motsi *et al.*, 2009; Moreno *et al.*, 2006).

Figure 9b shows that regardless of treatment, total N in the soil after 30 days of leaching was not significantly different. Although clinoptilolite zeolite improves retention of  $NH_4^+$  and  $NO_3^-$  (Ahmed *et al.*, 2010), the insignificant differences obtained in this study was because of the fertilizers reduction.

Retention of K, Ca, and Mg in the soil are presented in Figures 9c, 9d, and 9e, respectively. Exchangeable K was significantly lower in the treatments with 75% fertilizers amended with clinoptilolite zeolite (for CIRP and TSP), whereas the results of the ERP treatments are comparable. Based on the parent materials of RPs and clinoptilolite zeolite, application of RPs treatments resulted in similar Ca contents compared to the recommended rate except for TSP. This observation is also similar to the exchangeable Mg contents of TSP treatments whose Mg contents were significantly higher than those of the RPs (Refer to Tables 1 and 2).

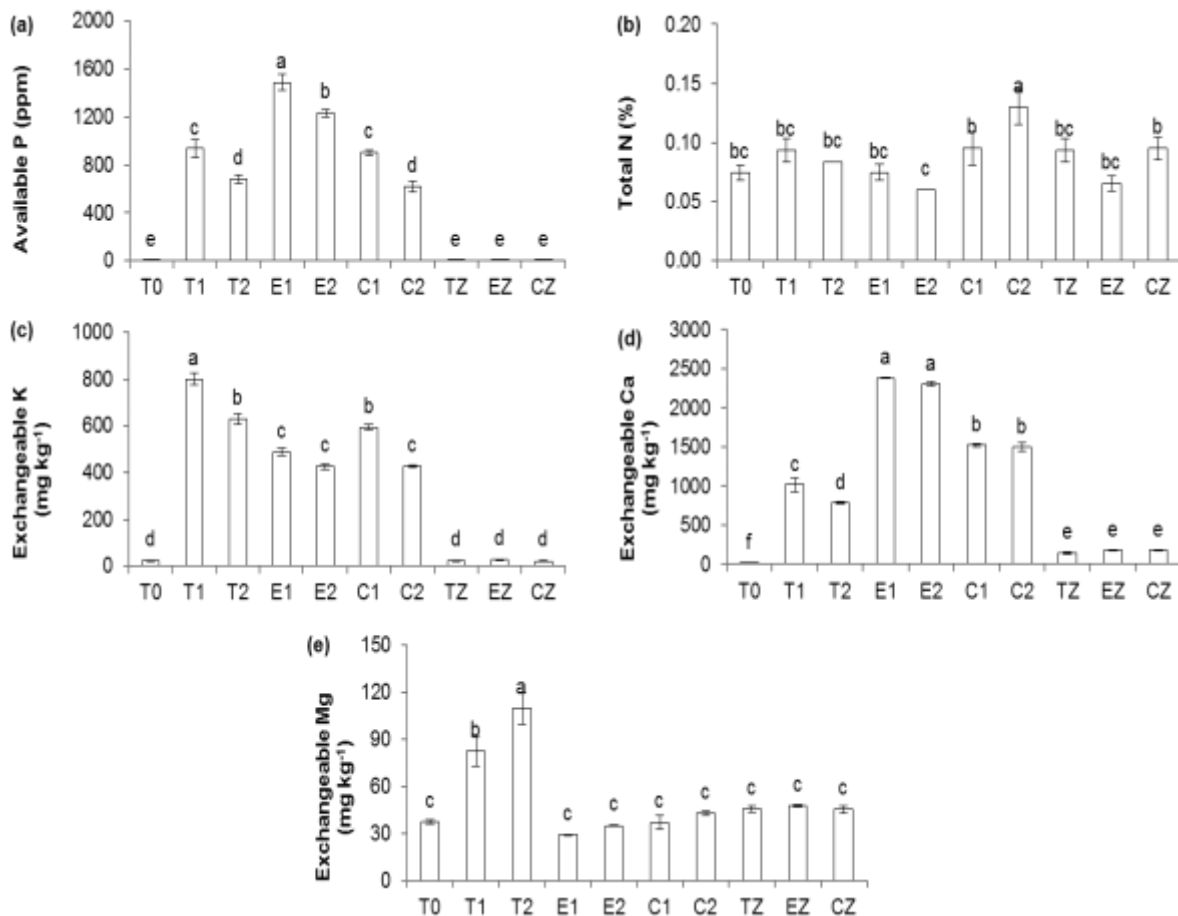


Figure 10: Selected soil chemical properties after thirty days of leaching. Effect of treatments on: (a) available P, (b) total N, (c) exchangeable K, (d) exchangeable Ca, and (e) exchangeable Mg. Means with different letter indicates significant differences using Tukey's test at  $p \leq 0.05$

Zeolites exhibit higher selectivity for monovalent cations compared with multivalent cations (Wong and Ho, 1995). However, competitive adsorption of cations  $K^+$  and  $NH_4^+$  could partly explain the lack of significant difference in N retention. These observations corroborate those of Tarkalson and

Ippolito (2011). The dominance of  $K^+$  over  $NH_4^+$  at the exchange sites of the clinoptilolite zeolite was because of the ion selectivity order of this zeolite, thus supporting the debate of cations competition at the exchange site of clinoptilolite zeolite (Rahmani *et al.*, 2004).

## Conclusion

Although clinoptilolite zeolite inclusion reduced pH buffering capacity in the soil, the pH range recorded in this present study is high. Clinoptilolite zeolite reduced the leaching losses of Ca and Mg. At 25% fertilizer reduction, the availability of N, P, K, and Fe in the soil significantly reduced following the application clinoptilolite zeolite. The effect of the clinoptilolite zeolite on nutrients was not glaring because of the fertilizer reduction. However, the use of clinoptilolite zeolite in maize cultivation on acid soils is beneficial because this zeolite reduces the unbalanced use of N, P, and K fertilizers of maize.

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## ABOUT AUTHOR



**Dr HO SOON MIN** is an associate professor in Faculty of Information Technology-Math & Science at INTI International University, Malaysia. He received his Ph. D in Materials Chemistry at University Putra Malaysia. He taught academic courses in physical chemistry, general chemistry, chemistry & society since last seven years. His research areas include activated carbon, green chemistry, semiconductor, nano materials and thin film solar cells. He has authored or co-authored for more than 130 articles in international referred journals and successfully produced many book chapters as well. He was appointed as journal reviewer, editorial board member, thesis evaluator and head of centre of applied chemistry & green chemistry.

**Dr Nik Ahmad Nizam** is a senior lecturer and Head of Department, Department of Biotechnology and Medical Engineering, Faculty of Biosciences and Medical Engineering and Research Group Leader of Novel Materials Research Group, Frontier Materials Research Alliance, Universiti Teknologi Malaysia (UTM). He has chemistry background from Faculty of Science, UTM, registered chemist under Malaysia Institute of Chemistry and a member of Royal Society of Chemistry, UK. He also has been appointed as Associate Fellow Researcher at Centre for Sustainable Nanomaterials (CSNano), Ibnu Sina Institute for Scientific and Industrial Research (ISI-ISIR), UTM. His research area is applied materials chemistry especially the application of inorganic materials for biological and medical application.



**Professor Ahmed Osumanu Haruna** lectures at Universiti Putra Malaysia. He is affiliated to a number institutes/centres as an associate research fellow. Professor Ahmed serves as an expert reference many national and international institutions. He has supervised a number postdoctoral fellows and postgraduate students. Professor Ahmed has won numerous research grants that have enabled him published numerous scholarly. His research innovations have also won medals, nationally and internationally. He is on several advisory boards and continues to render public services and consultancies to many organizations.

**Peter Adeniyi Alaba** is an Energy and Advanced Environmental engineering expert with a focus on renewable and sustainable energy, climate change, wastewater treatment, solid waste treatment, as well as research and development. He is a graduate of Chemical Engineering from the Federal University of Technology, Minna, building up with postgraduate research in Catalysis and Reaction Engineering from University of Malaya. Peter is an author and has worked in collaboration with several scientists from Australia, Malaysia, Iran, Mexico, United Kingdom and Nigeria on several projects. He also renders professional services to several academic journals.

