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Review on Zeolite Mesoporous Structure: To Keep Nutrient for Fertiliser Purposes

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Abstract: Reduction in crop production and plant growth is one of the major problems faced by the agriculture industry. This problem can be solved by increasing the nutrient uptake of the plants with the addition of zeolite additive that able to hold the nutrient within its mesoporous structure. The ability of zeolite not only can trap nutrient within microporous structure but also provide cation exchange mechanism that will better improve the ion diffusivity and absorption. Hence, this study will do a review on the synthesis factor of zeolite, the characteristic properties mesoporous structure of zeolites and its ability to keep nutrient for fertilizer purposes. The main raw material is kaolin that will be discussed and focused with different composition and the synthesis method of zeolite will focusing more on hydrothermal synthesis technique. Few parameters and results from previous author's findings will be discussed and analyzed further in this study. The focused parameters were heating temperature, NaOH concentration and Si/Al ratio to determine the CEC and crystallinity of zeolite type A.

Keywords: Zeolite, Kaolin, Hydrothermal Synthesis, Crystallinity

1. Introduction

Early research regarding plant nutrient's need was devoted largely to determining important factors to the growth, development, and maturation of plants [1]. Various ways were introduced in order to increase the nutrient in the crop, one of the methods is by adding the additive and using zeolite. Zeolite is a type of minerals that has the characteristics of being microporous with aluminosilicate mesoporous structure and are often used as adsorbents and catalysts. Crystalline zeolites have precisely defined pores with diameters matching the size of micro molecules with valuable size-shape-selectivity. Therefore, zeolites were known as being important selective absorbers and separators. Furthermore, zeolites also has the capability of being indispensable as solid acids in size-selective catalysis [2]. However, despite being extremely beneficial, micropores tend to impose restrictions on the mass transport of reactants, concerning size of the molecules [2].

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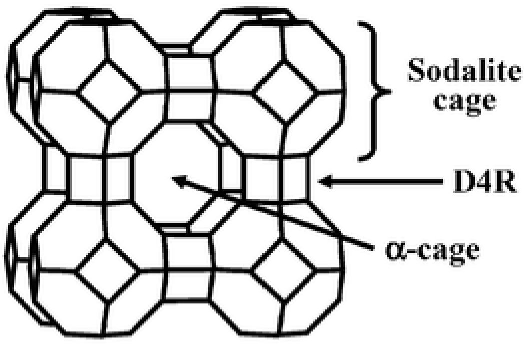
Processing parameters in the process of zeolite synthesis from kaolin will affect the formation and phase and properties of the zeolites produced. For example, zeolites with different type and structure possessed a mixture of silicone dioxide (SiO_2) and aluminium oxide (Al_2O_3) and this ratio of silica: alumina may affect the formation of zeolite. Hence, this study will highlight on the formation of zeolite based on different value of silica: alumina ratio, the influenced factors that will generate different zeolite CEC and shape produced. The effect of hydrothermal and calcination process effect towards zeolite properties and performance also reviewed to analyses the characteristics, properties and structure of zeolites produced. should describe general information on the subject matter area of study. The effect of zeolites on nutrient uptake efficiency, plant growth and quality of soil will be reviewed as well in ensuring its ability for the targeted application

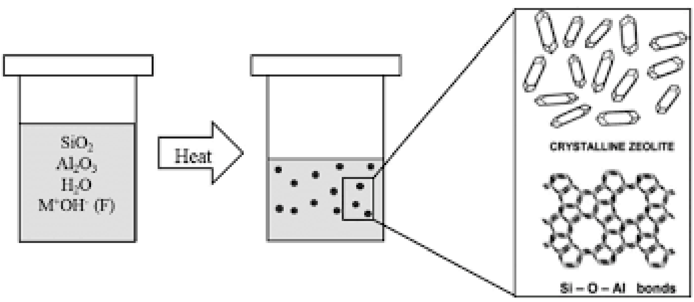


2. Materials and Methods

The raw material that will be discussed in this study as a source of zeolite is a mineral called kaolin. Kaolin generally contain various amounts of minerals such as muscovite, quartz, feldspar and anatase and it is usually white in colour [3]. Kaolin has low adsorption capacity for the reason that it has low CEC which is why a zeolite synthesis process from kaolin is highly beneficial because adsorption rate of a zeolite is way higher [4]. Kaolin is a also cheap and abundant in nature which is considered an economical raw material.

2.1 Hydrothermal synthesis of zeolites

Zeolites that were treated using hydrothermal will have to go through the calcination process or the metakaolinisation, for temperature below than 700-800 °C to transform the kaolin to zeolite. It will be done in a sealed autoclave for several hours at certain temperature. Then it will undergo the heating process mainly at 100 °C with NaOH that will act as an alkali solution base to enhance the formation of zeolite structure [5–7].



2.2 X-Ray Diffraction (XRD)

The characterization of zeolite formation needs to use a device called the X-Ray Diffraction (XRD) machine. This machine will identify an image of a molecular structure of a crystalline material in an x-rays form. Specifically, an XRD analyser will acquire patterns of interference that mirrors the lattice structure by varying the incidence angle of the X-Ray beams. This technique can be used to calculate the relative crystallinity of zeolites sample using a certain custom C-program [8].

2.3 Scanning Electronic Microscope (SEM)

Zeolites will undergo various phases after this XRD treatment which is the scanning of zeolite structure using SEM microscope as stated above to analyse the morphology of the surface of zeolites. The structure of zeolite will be analysed based on the pore size and crystallinity Relative crystallinity of synthesized zeolites can be calculated using this formula [9]:

$$Relative\ Crystallinity \left(\frac{I}{I_o}\right) = \frac{\sum \quad intensity\ of\ XRD\ peak\ of\ product}{\sum \quad intensity\ of\ XRD\ peak\ of\ standard\ zeolite} \qquad \text{Eq. 1}$$

3. Results and Discussion

The results and discussion presented in this section based on the previous recorded data and analysis of the previous researchers. Comparison and analysis of the result is presented based on the considered parameter/factors towards the determined output i.e properties and performance. All the selected considered parameter/factor such as parameters of zeolites synthesis: shape, crystallinity, NaOH concentration and Si/Al ratio. will be analyzed further and discussed towards the formation of zeolites based on their output such as CEC, absorption and plant growth.

3.1 Comparison of zeolite synthesis from hydrothermal method

Results is presented in the form of comparison tables to review different findings from previous author in synthesizing zeolite.

Table 1 shows the parameter of zeolite synthesis from kaolin using hydrothermal method which is ratio of Si/Al, NaOH concentration and CEC or shape of zeolites obtained from four authors. [5–7,10]. High temperature (300 to 1300 °C) in calcination process is essential because it influences the framework of zeolites as it increase the surface area and volume of micro-porous and mesoporous and the mass of zeolite (LTA) were also reduced [11]. Higher temperature lead to shorter time of reaction results to happen [12].

Table 1: Comparison table of zeolite synthesis from hydrothermal method: NaOH molarity and Si/Al ratio

Author	Title	Si/Al ratio	NaOH Concentration	CEC/ Shape
(a) Monica A. Villaquira´ N-Caicedo, Ruby M. De Gutie´Rrez, Marisol Gordillo and Nidia C. Gallego (2016)	Synthesis of zeolites from a low-quality Colombian Kaolin	**INTERMEDIATE (2.32)**	NaOH alkaline solution	• CEC = 442 cmol(+)/kg of zeolites • Cubic with sharp and rounded edge
(b) Lijalem Ayele, Joaquín Pérez-Pariente, Yonas Chebude, Isabel Diaz (2015)	Synthesis of Zeolite A from Ethiopian kaolin	**INTERMEDIATE (2.04)**	Optimum crystallinity at 3M NaOH (90%)	• CEC= 295 mg $CaCO_3$/g • Cubic crystal shaped
(c) Mousa Gougazeh, J-Ch. Buhl (2014)	Synthesis and characterization of zeolite A by hydrothermal transformation of natural Jordanian kaolin	**LOW (1.65)**	Optimum result at 1.50M to 3.50M of NaOH	Cubic-shaped crystals with lephisheric morphology of hydroxysodalite
(d) A. S. Kovo, O. Hernandez and S. M. Holmes (2009)	Synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique	**INTERMEDIATE (3.0)**	NaOH alkaline solution	Octahedral crystals of zeolite Y

From Table 1, author (a) to (d) claimed that they used NaOH to enhance the zeolite formation and the best molarity of NaOH reported by two authors (a to b) is 3M. Author (a) reported high CEC value of zeolites which is 442 cmol/kg of zeolites, way higher than commercial zeolite which is only 408 cmol/kg[10]. Author (b) also reported a CEC value but they compare it with $CaCO_3$ which shows a value of 295 mg $CaCO_3$/g of zeolites. CEC value of zeolite from author (a) and (b) shows that zeolite is capable of exchanging cations, which is essential in its role for keeping nutrients for fertiliser purposes. Both author (b) and (c) reported to have a created a zeolite with excellent crystallinity at the molar ratio of 3M. Also we can see that the Si/Al ratio affect the shape formation of zeolite as author (a) to (c) gained a cubic shaped zeolite which is zeolite type A while author (d) gained an octahedral shape of zeolite which is known as zeolite Y. The Si/Al ratio of author (d) is slightly higher than other author which affect the formation of zeolite.

3.2 Comparison of zeolite effects on plant growth and nutrient uptake efficiency

The papers in this table discussed the effects of zeolites on growth of plants and its nutrient uptake efficiency [13–16] The CEC and crystallinity of zeolites are as shown below:

Table 2: Comparison table of zeolite effects on plant growth and nutrient uptake efficiency

Author/ Year	Research Title	Types of Zeolite	CEC /crystallinity/	Nutrient Uptake Efficiency	Plant Growth Measurement
(a) Ramesh. V Jyothi, Jissy S Shibli, SMA (2015)	Effect of zeolites on soil quality and nutrient uptake efficiency in sweet potato (Ipomoea batatas L.)	Zeolite A	254.1 cmol/kg	Nitrogen (214.1 %) Phosphorus (337.5 %) Potassium (127.2 %)	90 days of observation: ● Number of leaves (136 to 212) ● Number of branches (10.7 to 17.7) ● Vine length (cm) (99 to 86.5) Yield and biomass (g/plant): ● Tuber yield (113.3 to 177) ● Total plant biomass (147.3 to 221)
(b) Khan, Amir Zaman Khan, H. Khan, R. Nigar, S. Saeed, B. Gul, H. Amanullah Wahab, S. Muhammad, et.al (2011)	Morphology and yield of soybean grown on allophanic soil as influenced by synthetic zeolite application	Na-P1 Zeolite	260 cmol/kg		● Pods plants increased by 7.06% ● Seed yield and dry matter accumulation of pod plant increased. ● Leaf surface area increased

(c) A.Al-Busaidi, T.Yamamoto, M. Inoue et al. (2008)	Effects of zeolite on soil nutrients and growth of barley following irrigation with saline water	Ca-type zeolite		Absorbs and retain cation which is Ca^{2+}, K^{+}, Mg^{2+} and Na^{+} Increased cation concentration in upper layer of soil and decrease the concentration down the profile Filtered harmful salts in the root zone of plant	● Plant height increased by 25%, ● Leaf area increased by 44% ● Dry weight increased by 60%
(d) Bansiwal, Amit Kumar Rayalu, Sadhana Suresh Labhasetwar, et.al (2006)	Surfactant-modified zeolite as a slow release fertilizer for phosphorus	Zeolite A	85% crystallinity	Maximum sorption of Phosphorus (P) 454.5 mmol/g	

Table 2 presents data of nutrient uptake of zeolites in three papers by author (a),(c) and (d) have shown that zeolites are able to increase the sorption of nitrogen, phosphorus, potassium significantly and also manage to retain cations as stated by author (c). This were supported by the CEC data by two authors, author (a) and (b) presented a high CEC value of zeolite that shows a directly proportional relationship with the rate of plant growth. The plant growth was described based on the size of leaf surface area, height of plant and their yield which shows an absolute increase in amount. In addition, zeolite also can act as a filtration agent, by allowing good minerals and filtrating harmful salts/substance in the root zone of the plant, as reported by author (c) which correlates directly with the plant growth.

4. Conclusion

In conclusion, zeolite can be synthesized using hydrothermal method and have good relative crystallinity and high CEC value by using these parameters which is 3M of NaOH, heating temperature 100 °C and has low and intermediate Si/Al ratio. Further investigation also proven zeolite has the ability to improve the growth of plant and has great nutrient uptake efficiency which makes it suitable for fertilizer purposes in agriculture industry. In fact, zeolite is one of the substances that is considered nature friendly which it does not harm and contaminate the environment, hence will provide green technology. This is beneficial to maintain the sustainability of the nature and maintaining good environment. Future study in reducing the time taken to synthesize zeolite using hydrothermal method and increase the major phase of zeolite formation is encouraged.

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