

Synthesis of Zeolite from Coal Fly Ash by Fusion Method

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Abstract

Coal fly ash has been regarded as waste and are typically produced in large quantities in power plants. However, not many know that it can be used for the synthesis of zeolites. Zeolites are known for its porous characteristic that helps in absorbing charged ions. In this report, the synthesis of zeolite from coal fly ash using fusion method was studied. The synthesis was made by mixing coal fly ash with Sodium Hydroxide (NaOH). Sodium Hydroxide (NaOH) are used to produce NaP type zeolite. The parameters used were temperature (80°C, 100°C, 120°C, and 140°C), molarity of sodium hydroxide (2M, 4M, and 6M) and the reaction time is 6 hours. The samples are then characterized using Fourier-transform infrared spectroscopy (FTIR) and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Pb²⁺ was being used as heavy metal sample for the ICP-OES testing. The absorption test shows that the highest absorption was by using a sample with the parameter of 140°C temperature and 4M NaOH molarity with 84.36% Pb²⁺ removal percentage. However, it can also be seen that 100°C samples have an increasing Pb²⁺ removal percentage as the molarity used increases. This proves that 100°C is the optimum temperature for synthesis of zeolite using fusion method. For comparison, a commercial zeolite was also tested in Pb²⁺ removal.

Keywords: Fusion method, Fly ash, Sub-bituminous coal fly ash, Synthesis, Zeolite

1.0 Introduction

Coal is a combustible carbonaceous rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, sulphur and mineral matter. It is an important energy resource necessary to meet the future demand of electricity and also as a major contributors to CO₂ emission problem. This environmental problem is further increased by coal fly ash (fly ash and bottom ash) generated in these plants as a solid waste residue which creates not only a solid waste disposal problem but also a dusting problem in the atmosphere and in the surrounding land area (Al-Harashseh et al., 2015). In Malaysia, there are hundreds of thousands tons of coal fly ash produced from coal fired power plant. From this amount, only a small portion are used as a raw material for concrete and construction cause, the remainder are easily dumped on the landfill sites (Das, 2011). Majority of the fly ash are disposed as a solid waste in landfills and ash ponds are causing an alarming rate of disposal activity.

A promising new approach to improve the application of coal fly ash is to convert the coal fly ash into zeolite. Zeolites are known due to its widespread utilization in diversified fields and for its properties that have high porosity, which translates into high surface area and high content of reactive material like aluminosilicate. Besides, converting fly ash into zeolite not only eliminates the disposal problem, but also turns a waste material into a marketable product. Few examples of today's synthesized zeolite are zeolite X, zeolite NaP1, zeolite Y, zeolite – A and etc. Zeolites are safe and non-toxic at any level and have been used in agriculture, water treatment, aquaculture, paper manufacturing, industry such as adsorption, ion exchange in domestic and commercial water purification, specific separation of gases, and many more (Amrhein et al., 1996). According to a study by (Shaila et al., 2015) zeolites are also able to remove radioactive ions from contaminated water.

Some researchers have utilized the one step fusion treatment to produce fly ash zeolites in the past. However due to the low production of zeolites in mass production and high content of impurities, the research has taken a different direction which is to use hydrothermal method in producing zeolites from fly ash as it produces high purity of fly ash zeolites. The cons of hydrothermal though is that it requires more time and steps in producing zeolites which makes it less economical than fusion method. Fusion method favors in the speed of reaction and purity of the final product as high as 62%. Different temperatures and molarity of Sodium Hydroxides (NaOH) are being used in this process. The molarity of Sodium Hydroxide (NaOH) used are 2M, 4M and 6M while the temperature used are 80,100,120 and 140°C.

2.0 Methodology

2.1 Materials

Sub-bituminous coal fly ash was obtained from Manjung's coal-fired power plant located in Perak. The sample received was dried in the oven at 110°C for 24h to remove any surface moisture. The dried coal fly ash was sieved to various sizes using sieve shaker. Then, the coal fly ash sample was stored in a sealed container before use. Sodium Hydroxide (NaOH) was used in this experiment. The sodium hydroxide (NaOH) was liquefied from pellets by mixing it with water. Three different molarities were used in the experiments which are 2M, 4M and 6M. Distilled water was used in the washing process of the synthesized zeolite. Deionized water was the recommended type of water used to enhance the solubility of the solute in the washing process.



Figure 1. Coal Fly Ash produced by the industry



Figure 2. Coal Fly Ash

2.2 Fusion method

2.2.1 Synthesis of zeolites

A mixture of 2 M of NaOH solution (4 g of NaOH in 50 mL distilled water) and 20 g of coal fly ash was heated in a ceramic crucible in an oven at 80°C for 6 hours. During heating, dissolution of silicon and aluminium occurs first. Then, condensation takes place and aluminosilicate gel rapidly starts to deposit on the surface of Coal Fly Ash particulates. Increasing the heating time leads to the formation of aluminosilicate gel to crystalline zeolitic phase. During the heating process, dissolution is followed by the condensation and crystallization of NaP zeolite on the surface of the coal fly ash particles (Behin et al., 2016)

2.2.2 Washing process

Zeolitized coal fly ash particles obtained in synthesis of zeolites process were then added to 50 mL of distilled water. The mixture was then stirred. A proper washing procedure removes most of the toxic components, such as cadmium and arsenic, from the synthesized zeolite. This process was only done once but can be repeated multiple times to effectively remove toxic components. If repeated, the filtrate collected from the first washing stage, which had the highest pH was recycled back in the synthesis of zeolites process. This solution was then added a certain amount of NaOH and recycled back to the synthesis of zeolites process as a new alkali solution for the next synthesis. This operation can minimize process water consumption as well as minimizing chemicals consumption (Behin et al., 2016)

2.2.3 Drying process

After the washing process, the mixture was then filtered to further remove any unwanted solids. The solution was then put in a ceramic crucible and was heated on a hot plate until white zeolite crystals are formed in the crucible. The crucible does not have a lid on top of it to ensure the steam could be released to the air. The temperature of the hot plate was 250°C. The sample of zeolite was left to be cooled and placed in a plastic sealed bag and labelled accordingly.

2.3 Characterizations of synthesized zeolites

The chemical composition of the synthesized zeolite was determined by using Fourier-transform infrared spectroscopy (FTIR) and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The goal of the FTIR process is to obtain an infrared spectrum of absorption and emission of silica and alumina in the synthesized zeolite and the commercialized zeolite 3A. By using infrared, molecular vibration was conducted thus produces a wavenumber readings which each type of component have their own specific wavenumber. Vibrational infrared was used because it is different than other type of vibration such as X-ray, ultraviolet, and microwave. The reason vibrational infrared were being used as it has the lowest wavenumber frequency which it can detect up to 2.5 μm to 15 μm .

2.4 Adsorption of Lead (Pb^{2+})

The test was performed at room temperature using samples with the best properties. Fly ash, synthesized zeolite and commercialized zeolite 3A were tested to see the performance of each adsorbent. 2g of iodine dye was added to 3 conical flasks containing 10 ml of distilled water each. Then, 5g of fly ash, synthesized zeolite and commercialized zeolite were added to the three conical flasks respectively. The flasks were gently shaken for 2 to 3 minutes. The change in colour was analysed.

3.0 Results & Discussion

3.1 Fourier Transform Infrared spectroscopy studies

3.1.1 Characterization of Zeolite

Zeolite material are often used as adsorbent because of it special structure of its crystal. Natural zeolite with uniform pores of molecular dimensions only allow certain hydrocarbon molecules to enter crystal while other molecules are rejected based on molecular size or in other words, it is a shape selectivity of ion exchange properties (Li, 2005). The region or peak in table are the criteria for zeolite characterization.

Table 1. List of Component, wavenumber and tentative assignment of zeolite.

Wavenumber (cm^{-1})	Component	Tentative Assignment
1200 - 950	Si-O-Si (T-O Stretching mode)	Internal tetrahedron vibrations
800 - 500	Pseudo-Lattice Pattern Region	Connect with internal tetrahedron bond for crystal structure
3200 - 3600	Zeolite Water (Broad Band)	Broad band represents the characteristic of OH to O_2 ions.
3700 - 1600	OH (Stretching Region)	Hydroxyl group attached to zeolite structure

Table 1 above indicates a certain specific wavenumber (cm^{-1}) along with their roles for a good adsorption characteristics of zeolite.

The terminal silinol group (Si-O-Si) are important in crystallization of zeolite as it will make the zeolites to have relatively large external surface area which can intensify the adsorption of hydrocarbon molecules (Li, 2005) . The relative intensity of the absorption band is at $\sim 3745 \text{ cm}^{-1}$ depending on the primary size of the zeolite crystals.

The pseudo-lattice pattern region that are connected to the internal tetrahedral bonds are typical for the ordered crystal structure to make the zeolite to have smaller structure which can increase the surface area and thus increasing adsorptions (Deng et al., 2016).

The hydroxyl group attached to the zeolite structure is the key element in zeolite. The OH⁻ act as an active site on the zeolite structure. The OH groups will attach to cations which compensate the negative charge of the framework (Li, 2005).

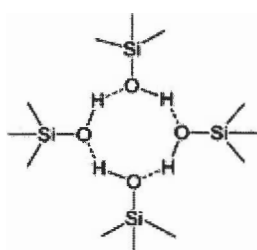


Figure 3. The terminal silinol structure of Si-O-Si. (Kawai & Tsutsumi, 1998)



Figure 4. The pseudo-lattice pattern of Si-O-Si that form crystal structure (Jurkić et al., 2013)



Figure 5. Figure above shows that only selected hydrocarbon can only enter the zeolite. (Jurkić et al., 2013)