

Hydrogen Sulfide Removal by using Zeolite from Coal Bottom Ash

[Rewadee Anuwattana, Narumon Soparatana, Worapong Pattayawan,
Pattamaphorn Phungngamphan, Atiporn Jinpayoon and Siriwan Tepinta]

Abstract— The aim of this work is to synthesis zeolite by using coal bottom ash from power plant and used as hydrogen sulfide (H_2S) adsorbent to removal H_2S from synthetic biogas. The zeolite was synthesized by fusion hydrothermal process of coal bottom ash, which was source of starting materials. Moreover, the obtained zeolite products were used for preparation of polyethylene composite material by using twin-screw extrusion process, polyethylene-grafted maleic anhydride (PE-g-MA) as compatibilizer at various PE-g-MA: zeolite ratio (0.5:1, 1:1, 2:1 and 3:1, respectively) and different composition of Titanium Dioxide (TiO_2) (0.25, 0.5, 0.75, 1, 1.5 and 2 phr). The results showed that the optimum condition for composite material as PE-g-MA: zeolite ratio of 2:1 exhibited the highest adsorption capacity. Moreover, the equilibrium time and adsorption capacity at equilibrium increased with increasing the TiO_2 loading. The results suggested that the polyethylene composite material filled with zeolite has a potential to be used as adsorbent for removing hydrogen sulfide.

Keywords— Coal bottom ash, NaA zeolite, Hydrogen Sulfide Removal, Waste Utilization

I. Introduction

Nowadays coal is derived as a major source for energy generation, especially in developing countries, for many decades. Use of coal in thermal power plants produced tons of ashes during power generation productions. [1] Coal ash often is considered as “non-hazardous”. Eventually, most of the produced ashes are being deposited in landfills. It is possible cause environmental impacts due to its high volume of generation which requires a large area for disposal and consequently contaminating soils and groundwater [2-3].

The coal ash from thermal power plants is commonly divided into two categories which are fly ash (light grey fine particle size of less than 0.15 mm) and bottom ash (coarser particle size of more than 0.15 mm) Several potential applications of coal ash are under developed in the construction and building materials [4] such as civil engineering applications [5], geo-polymer [6], sand replacement material [7] and cement composites [8].

Rewadee Anuwattana, Narumon Soparatana, Worapong Pattayawan,
Pattamaphorn Phungngamphan, Atiporn Jinpayoon and Siriwan Tepinta
Expert Centre of Innovative Clean Energy and Environment,
Thailand Institute of Scientific and Technological Research
Thailand.

Moreover, the chemical composition of coal ash mainly consists of silica (SiO_2) and alumina (Al_2O_3) and other mineral compounds which can convert to silicon-base material by hydrothermal treatment for alternative adsorbent such as zeolite. It is therefore possible to synthesize zeolite from coal ash by the hydrothermal treatment or in aqueous solution at elevated pressure and temperature. [9] Several articles have proposed various methods for the hydrothermal activation of coal ash in zeolite synthesis, using for this variation of several parameters involved in this synthesis [10, 11-13].

Zeolite is a crystalline hydrated alumino silicate minerals with structures based on a three-dimensional framework of SiO_4 and AlO_4 tetrahedra of a highly regular porous structure. Zeolites exhibit features as high selectivity, high stability and high exchange capacity, which together with the properties of sorption and catalysis, provide their technological application in various sectors. Zeolites have been proved to be successful adsorbents for hydrogen sulfide (H_2S) removal [14-15].

Hydrogen Sulfide (H_2S) is a highly toxic gas, flammable and corrosive substance. It is present naturally in natural, biogases and landfills as well as in several synthesis gases. [16] H_2S in biogas formed with the anaerobic digestion of organic substances by a consortium of microorganisms. [17] H_2S is also extremely hazardous compound which causes a potential risk to humans, odor problems and acid rains when oxidized to SO_2 and so it should be removed from the environment.

Photocatalysis is newest generation of proactive air treatment technology. It's well-known advantage for the abatement of volatile organic pollutants via oxidation process at mild conditions and very suitable for trace pollutant concentrations removal. [18] Titanium dioxide (TiO_2) is non-toxic compound, chemically and biologically inert in its natural form with relatively low cost and high availability. TiO_2 has been extensively studied in many fields related to the environmental purification. It's most commonly used as photocatalyst for the removal of pollutants both in water and gas-phase is well known. [19]

The purpose of this study was to synthesize zeolite by using coal bottom ash from power plant and applied to use as the H_2S adsorbent from biogas.

II. Experimental

Preparation of zeolite.

The raw material for this work was the coal bottom ash (lignite), which supported by Electricity Generating Authority of Thailand (EGAT), Mae Moh Power Plant in Lumpang Province, Northern Thailand. The chemical composition of coal bottom ash was analyzed by X-Ray fluorescence (XRF). The pretreatment of the coal bottom ash consist of mechanical, acid and thermal treatments. Synthesis of Na-A zeolite was studied by fusion prior hydrothermal treatment, activated by 3 M NaOH under hydrothermal treatment at 105 °C for 1-5 hours. The synthesized samples were characterized by X-Ray diffraction (XRD) using Shimadzu.

Zeolite Characterization

The synthesized zeolite products were characterized by XRF, XRD and SEM-EDX analysis. The X-Ray Diffraction patterns (XRD) of zeolite synthesis from bottom ash and zeolite standard were recorded in 2θ ranging between 5° and 60° with scanning rate of $2^\circ/\text{min}$ and $\text{CuK}\alpha$ radiation (Lab X (XRD 6000), SHIMADZU). The %crystallinity of zeolite products was calculated according to equation (1) [20] with the commercial zeolite A as the standard.

$$\% \text{Cryst} = \left(\frac{\sum \text{intensity of XRD peaks area of the zeolite product}}{\sum \text{intensity of XRD peaks area of the standard zeolite}} \right) \times 100 \quad (1)$$

Furthermore, the morphology and elemental compositions of the zeolite products were investigated using a scanning Electron Microscope (SEM) JSM-5410 LV. (JEOL, Japan). The samples were sputtered with a thin film of gold to minimize the charging effects. Energy dispersive X-ray spectroscopy (EDXS) was performed in Oxford ISIS 300 model. An X-ray Fluorescence, XRF (Bruker AXS S8 Tiger model) was used to measure the chemical composition of the raw materials and zeolite A obtained.

Preparation of Zeolite/TiO₂/LDPE composite

Low Density Polyethylene (LDPE) was supplied by PTT Global Chemical, with a melt flow index (MFI) = 1.9 g/10 min. and density of 0.924 g/cm³. Titanium Dioxide (TiO₂) was purchased from Loba Chemie Pvt. Ltd. and Polyethylene-graft- Maleic anhydride was purchased from Sigma-Aldrich, Schnelldorf (Germany).

The Zeolite/TiO₂/LDPE composite was formulated with 1 phr zeolite loading with polyethylene-grafted maleic anhydride (PE-g-MA) as compatibilizer at various PE-g-MA: zeolite ratio (0.5:1, 1:1, 2:1 and 3:1) at different content of TiO₂ (0.25, 0.5, 0.75, 1, 1.5 and 2 phr).

The Zeolite/TiO₂/LDPE composite were prepared by using twin-screw extruder with a screw diameter of 16 mm and an L:D ratio of 40. Zeolite, PE-g-MA, TiO₂ and LDPE were mixed and placed in the hopper. The temperatures were ramped from 160°C to 190°C with screw speed of 150 rpm in the extruder.

Adsorption Experiments

The adsorption tests were carried out by using a self-assembled fixed-bed reactor (stainless tube with the inner diameter of 13.05 mm and height of 216 mm.). 10 grams of the adsorbent was packed in reactor supported by silica wool. The hydrogen sulfide (H₂S) in synthetic biogas (CH₄ 47%, CO₂ 47%, H₂S 105 ppm. balanced in Nitrogen) flowed through the sorbent with the flow rate of 0.1 lit/min at the room temperature. After the adsorption process completed, the H₂S concentration was measured by MRU OPTIMA 7 Biogas Analyzer, Germany. For studying the adsorption capacity of zeolite composite for H₂S removal was defined when the breakthrough concentration of H₂S is 50% of the initial concentration and completed when the outlet H₂S concentration reaches the breakthrough concentration.

III. Results and Discussion

Synthesis of zeolite from coal bottom ash

The coal bottom ash was obtained from Electricity Generating Authority of Thailand (EGAT), Mae Moh Power Plant in Lumpang Province, Thailand. The coal bottom ash contains the highest amounts of SiO₂ and Al₂O₃ (35.8% and 19.2%, respectively) and rich in TiO₂ and SrO. The SiO₂/Al₂O₃ molar ratios of coal bottom ash is 3.15. It indicated that coal bottom ash can used as raw material to synthesis zeolite. Figure 1 shows XRD patterns of the zeolite A products from coal bottom ash at various times of alkali hydrothermal reaction (1, 3 and 5 hours) compared with the commercials zeolite A as the standard. It indicated the most crystalline phases of synthesized NaA zeolite from coal bottom ash is Sodium Aluminum Silicate Hydrate, (ICDD No. 00-038-0241).

Morphology images of synthesized zeolite product from coal bottom ash by fusion with NaOH in the weight ratio of 1:3 at 550 °C for 1 hours and activated with 3M NaOH for 5 hours is shown in Figure 2. Zeolite product clearly shows that the particles have a cubic morphology and that their particles are aggregated together.

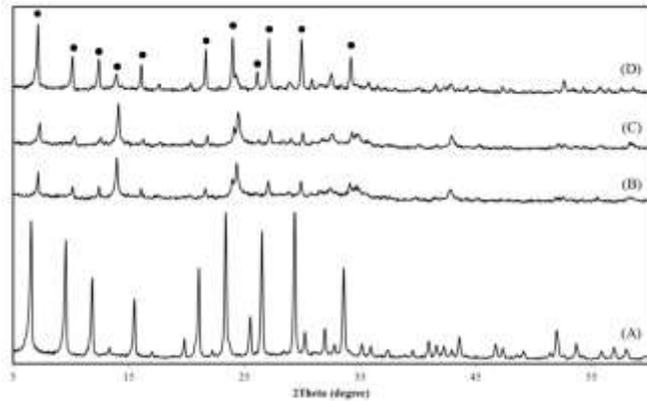


Figure 1 X-Ray Diffraction (XRD) patterns of Zeolite Standard (A), Synthesized zeolite from coal bottom ash at 1 hour (B), 3 hour (C) and 5 hour (D) (• Peak position of Zeolite)

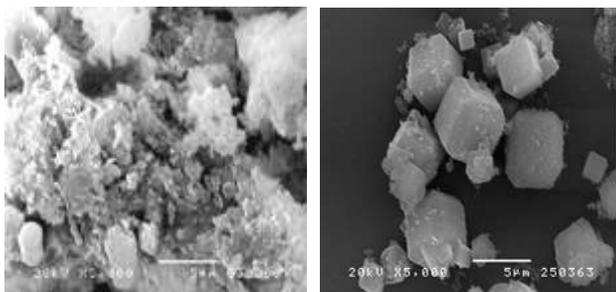


Figure 2 Scanning electron microscope (SEM) of raw coal bottom ash (A) and Synthesized zeolite from coal bottom ash (B)

Hydrogen Sulfide Adsorption Capacity

The hydrogen sulfide adsorption capacity at equilibrium time and the breakthrough curves of H₂S adsorption of Zeolite/TiO₂/LDPE composite at various PE-g-MA: zeolite ratio is shown in Table 1 and Figure 3(A), respectively.

The result indicates that the composite filled with zeolite and TiO₂ has a potential to remove hydrogen sulfide. Because, zeolites are crystalline microporous frameworks, based on a threedimensional network of silica and alumina, the cations in aluminosilicate zeolites may allow the possibility of strong interactions with the polar gas molecules [21]. Moreover, the composite was prepared from PE-g-MA: zeolite ratio of 2:1 provides good H₂S adsorption capacity at low initial concentration of H₂S (105 ppm) because PE-g-MA improves dispersion of zeolite and TiO₂ in LDPE matrix.

TABLE 1 THE EQUILIBRIUM TIME AND ADSORPTION CAPACITY AT EQUILIBRIUM OF ZEOLITE/ TiO₂/LDPE COMPOSITE WITH ZEOLITE 1 PHR AND TiO₂ 0.5 PHR AT VARIOUS PE-G-MA: ZEOLITE RATIO

PE-g-MA: zeolite ratio	Equilibrium time (sec)	Adsorption capacity at equilibrium (mol/g)
Neat LDPE	90	6.25
0.5:1	108	6.89
1:1	94	5.95
2:1	96	7.11
3:1	88	5.05

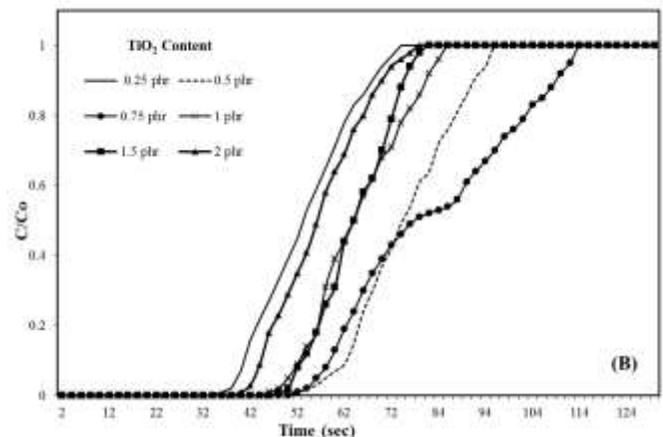
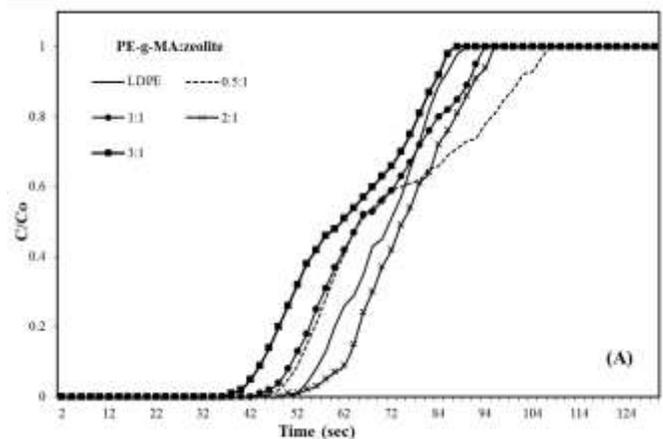


Figure 3 The breakthrough curves of H₂S adsorption over the composite with various PE-g-MA: zeolite ratio (A) and different TiO₂ loadings (B). (C₀ and C represent the influent and effluent H₂S concentration, respectively)

TABLE 2 THE BREAKTHROUGH TIME, EQUILIBRIUM TIME, ADSORPTION CAPACITY AT BREAKTHROUGH AND ADSORPTION CAPACITY AT EQUILIBRIUM OF ZEOLITE/TIO₂/LDPE COMPOSITE WITH ZEOLITE 1 PHR, PE-G-MA 2 PHR AT DIFFERENT COMPOSITION OF TIO₂

Sample	TiO ₂ content (phr)	Breakthrough time (sec)	Equilibrium time (sec)	Adsorption capacity at breakthrough (mol/g)	Adsorption capacity at equilibrium (mol/g)
LDPE 1	0.25	54	78	3.2	3.68
LDPE 2	0.5	74	96	6.2	7.11
LDPE 3	0.75	80	114	6.46	8.53
LDPE 4	1	64	86	4.6	5.34
LDPE 5	1.5	64	82	4.5	5.18
LDPE 6	2	56	80	3.49	4.08

In this study, the different ratios of Zeolite/TiO₂/ LDPE composite were prepared by twin screw extrusion to investigate the effect of PE-g-MA: zeolite ratio and TiO₂ loading on the H₂S adsorption performance. Table 2 gives the information about the breakthrough time, equilibrium time, adsorption capacity at breakthrough and adsorption capacity at equilibrium of Zeolite/TiO₂/LDPE composite at various amounts of TiO₂ (0.25, 0.5, 0.75, 1, 1.5 and 2 phr. represent in LDPE1, LDPE2, LDPE3, LDPE4, LDPE5 and LDPE6, respectively). The operating conditions were as follows: adsorption temperature, 25 °C and influent velocity, 0.1 lit/min and atmospheric pressure. The breakthrough curves of H₂S adsorption are presented in Figure 3.

The composite at low TiO₂ loading (0.25 phr) show low adsorption capacity. As shown in Table 2, the H₂S adsorption capacity of zeolite composite at equilibrium time increased as the TiO₂ loading increased. For the Zeolite/TiO₂/LDPE composite with amount of TiO₂ was 0.75 phr, the equilibrium time and adsorption capacity at equilibrium reached 114 second and 8.53 mol/g. However, when the loading of TiO₂ was beyond 0.75 phr, the adsorption capacity was decreased as can be seen in Figure 4. It was suspected due to the reaction between TiO₂ and H₂S produced TiS₂ on the surface of the sample which inhibited the adsorption performance.

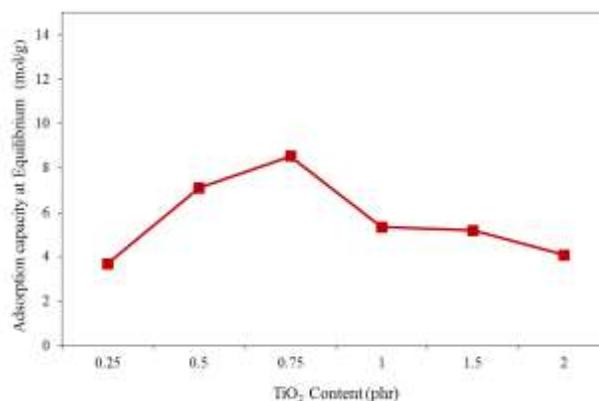


Figure 4 The adsorption capacity at breakthrough and adsorption capacity at Equilibrium of Zeolite/TiO₂/LDPE composite with 1 phr of zeolite, 2 phr of PE-g-MA at different composition of TiO₂

IV. Conclusion

Zeolite products from coal bottom ash was synthesized via a fusion and hydrothermal process with 3 M NaOH at 105°C for 1-5 hours. Which can be applied to Zeolite/TiO₂/LDPE composite at various PE-g-MA: zeolite ratio and different composition of TiO₂ for the purpose of removing hydrogen sulfide (H₂S) from landfill gas. The results of H₂S removal efficiency indicated that the composite prepared from PE-g-MA: zeolite ratio of 2:1 exhibited the highest adsorption capacity. The optimum condition for TiO₂ loading of 0.75 phr shows the adsorption capacity at equilibrium of 8.53 mol/g. The results suggested that Zeolite/TiO₂/LDPE composite has a potential to be used as H₂S adsorbent.

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