# Fabrication of $ZnAl_2O_4$ from Corresponding Metals Nitrate in the Co-existence of Natural $SiO_2$ and it Application as Adsorben of Mercury Nitrate

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**Abstract.**In situ fabrication of $ZnAl_2O_4$ from precursorof zinc nitrate and andaluminium nitrate aqueous solutions was carried out in a rice husk's $SiO_2$ suspension. The reaction's mixture was heated at 100 °C in open air under stirring and the solvent was evaporated to form white gel. The gel was cooled to room temperature and a solid material was obtained, subsequently heated at 1100 °C for 5 hours. The obtained material was applied as adsorbent for mercury ions at room temperature

## INTRODUCTION

It was known and confirmed that the differences on the $ZnAl_2O_4$ preparation give different morphology, acidity and also in some cases will affect the application of the produced materials. Recently, some synthetic methods of $ZnAl_2O_4$-$SiO_2$ including their applications was emphasized. Previously, $ZnAl_2O_4/SiO_2$ containing $89SiO_2–6Al_2O_3–5ZnO$ was synthesized [**1**]. More recently the $ZnAl_2O_4@SiO_2$ was prepared via sol-gel processes from zinc nitrate, aluminium nitrate and tetraehylorthosilicate, including their application for catalyst of acetylation of alcohols, phenols and amines without any solvent [**2**]. Based on the recent information, $ZnAl_2O_4$was used in many purposes, therefore many researchers are working in the preparation and some modification in this ceramic material. For example synthesize of $ZnAl_2O_4$ as a transparent by using of development optic method [**3]**. On the other hand synthesis of $ZnAl_2O_4$ by different methods and used as catalytic support of platinum metal was reported recently [4]. The $ZnAl_2O_4$ was also used as a filler in $LiClO_4$-PEO polymer electrolyte system[**5**]. Moreover, the preparation of cobalt ion supported by $ZnAl_2O_4$was carried out and their properties was investigated [**6**]. Currently, research development on preparation of $ZnAl_2O_4$as a supportingmaterial for iron compound by solid-state reaction has been created and applied as a catalyst in a transesterification reaction of triglyceride. Unfortunately the catalytic system did not give the desired product. Therefore, more efforts should be developed to increase the activity of the material as a catalyst [**7**]. Furthermore, a facile synthesis of highly thermostable mesoporous $ZnAl_2O_4$ with adjustable pore size was developed [**8**]. The reseach result give a new information for the formation new material to host for some metals to increase the reactivity of $ZnAl_2O_4$ itself.

Based on the these results, the development of synthetic method of $ZnAl_2O_4$ in the presence of a natural based compound such as silica from rice husk was carried out to create a material that could give new characteristics and further appplication development.In almost cases the $SiO_2$ was obtained in the reported reactions were from tetra-orthosilicates as precursors at same time of the $ZnAl_2O_4$ formation [**1-2**]. Since the $SiO_2$ could be obtained from nature, a study on the preparation of $ZnAl_2O_4$ from metals nitrates in the co-existence of $SiO_2$ from rice husk via sol-gel method has been carried out. The study was also continued to the application for adsorption of mercury ions in a solution.

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## MATERIALS AND METHOD

$Zn(NO_3)_2.4H_2O$ and $Al(NO_3)_3.9H_2O$ were obtained from Merck and used as received. $SiO_2$ was isolated from rice husk of Oryza sativa var glutinose following reported procedures with a litle modification [**9**]. $H_2O$ in this research is demineralized water. Synthesis of $ZnAl_2O_4$ in the presence of $SiO_2$ was carried out as follow: 25 mmol (6,536 gram) $Zn(NO_3)_2$ $4H_2O$ and 50 mmol (18,76 gram) $Al(NO_3)_3$ $9H_2O$ were added to an erlemenyer containing $SiO_2$ (25 mmol, 1,502 gram) suspension in demineralized water (100 ml), stirred until all metal nitrates were dissolved well. The reaction mixture was heated at 100 °C until the solvent was in small amount and the transparent white gel formed in the bottom of erlenmeyer. The gel was removed to crucible and heated using oven at 110 °C for 3 hours and subsequently heated at 1100 °C for 5 hours. The product was characterized using XRD, IR spectrophotometer, DTA and TGA. A representative procedure for adsorption study is as follow: mercury nitrate solution (29,2 ppm, determined using cold vaopur atomic absorption spectrophotometry) was added to an erlenmeyer (200 ml) and followed by addition of $ZnAl_2O_4$-$SiO_2$ to the solution. The mixture was shaked using automatic shaker for 1 hour and kept for 12 hour. The aliquots were taken from the reaction mixture around 50 ml and measured using atomc absortion spectrophotometer (AAS) cold vapour system.

## RESULTS AND DISCUSSIONS

The in situ fabrication of $ZnAl_2O_4$ from Zinc (II) nitrate and aluminium (III) nitrate under heating at boiling point of water in the presence of natural $SiO_2$ without any addition of basic compounds was performed. During the heating of reaction mixure in a household, annitrogen oxide smell was observed by nose. It was assumed that nitrous gas was released during the reaction. The white powder was analyzed using XRD and the result is shown in Fig 1.

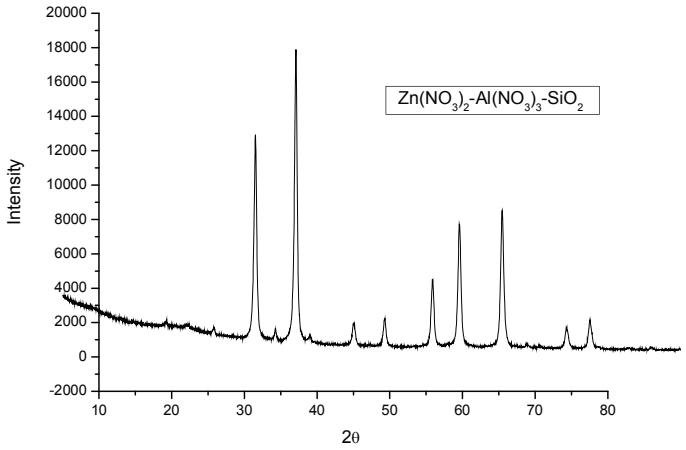



**FIGURE 1**. XRD patternas-prepared $ZnAl_2O_4$ in the presence of natural $SiO_2$

The XRD patern of the obtained material as shown in Fig 1, revealed that the desired $ZnAl_2O_4$ was obtained in the presence of $SiO_2$ (broad peak around $2\theta = 20°$). Small amount of impurity of ZnO was also observed. This result gives another alternative for preparation of $ZnAl_2O_4$. In some reports, the presence of basic compounds such as ammonium hydroxide, NaOH were essential for synthesis of $ZnAl_2O_4$ [**10**] or ammonia [**11**], but in the present report, the presence of such compounds were not needed. Further characterization using DT/TG analysis is shown in Fig. 2. The DT/TG analysis were carried out in the normal atmospheric pressure under air condition

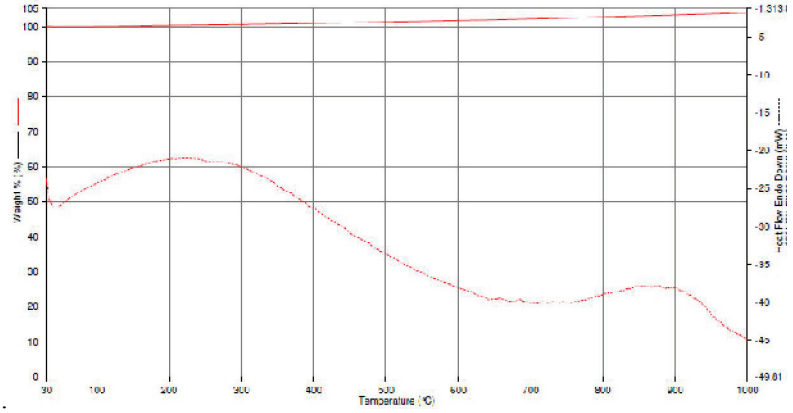


**FIGURE 2**. DTA - TGA as-prepared $ZnA_{l2}O_4$ in the presence of natural $SiO_2$ (the measurement have been done at air condition)

As shown in Fig. 2, the absence of any significant exothermic peak on the DTA curve of the mixed material shows that no recrystallization process occurs at temperature up to 1000 °C. This result suggested that the material could be used in some reactions at high temperature due to their thermal stability. Furthermore, to know the composition and morphology of the obtained materials, the product was subjected to EDX (Figure 3).

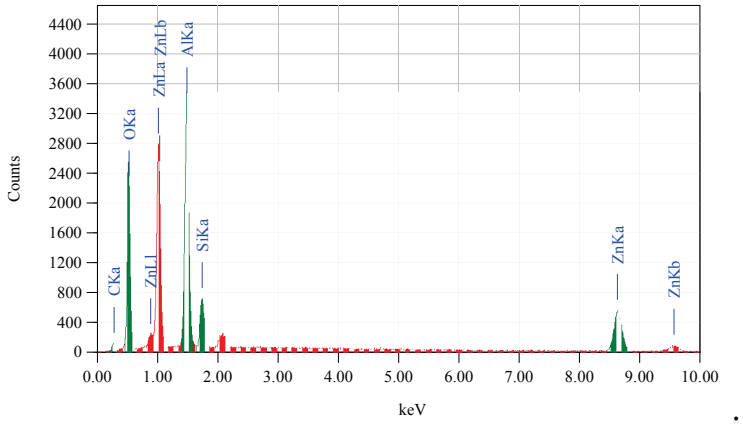
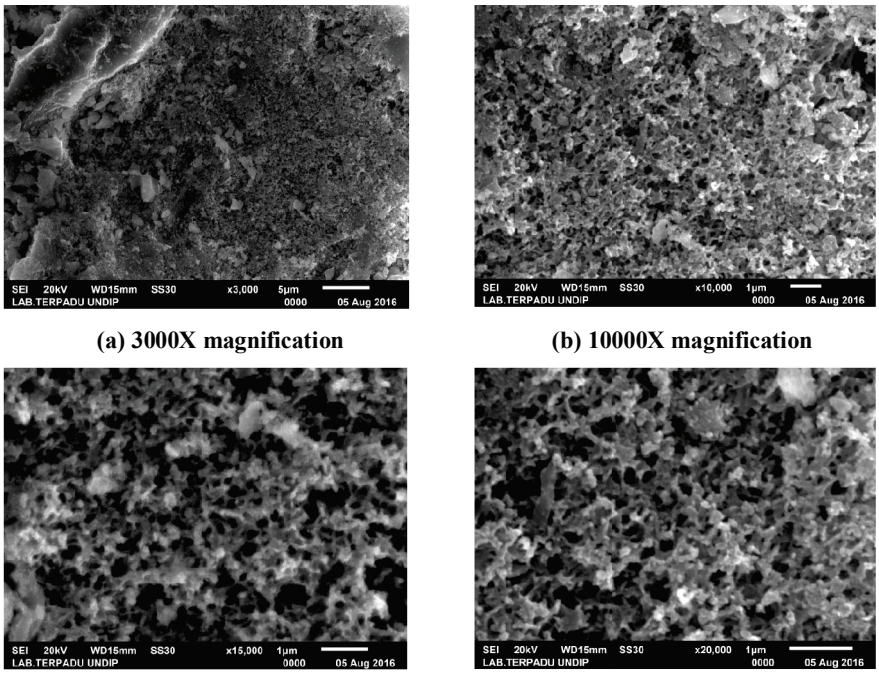



**FIGURE 3**. Energy Dispersive X-ray analysis result of the as-prepared material

Fig. 3 shows the presense of Zn, Al and Si metals as major element in the materials and it was in line with evidence of the obtained XRD profile for $ZnAl_2O4$ in the presence of natural $SiO_2$. Scanning Electron Microscopy (SEM) analysis was performed to investigate the morphology of the obtained materials and the results are shown in Figure 4.




**(a) 3000X magnification** **(b) 10000X magnification**

**(c) 15000X magnification** **(d) 20000 X magnification**

**FIGURE 4**. SEM analysis results of $ZnAl_2O_4$-$SiO_2$

Fig. 4 show that the current material was dominated by the porous particles (part b, c and d). This result will give an oportunity to use the material as adsorbent. The application of the obtained material as adsorbent of mercury nitrate solution is summarized in Table 1.

**TABLE 1.** Adsorption efficiency of mercury nitrate solution using $ZnAl_2O_4$-$SiO_2$

| No | Adsorbent Amount (gr) | Final Concentration Mercury (mg/L) | % Efficiency* |
|---|---|---|---|
| 1 | 0.3 | 27.00 | 7.53 |
| 2 | 0.5 | 25.10 | 14.04 |

*% efficiency was calculated from equation $[(C_0 - C_f)/C_0] \times 100$ ; where $C_0$ is initial concentration and $C_f$ is final concentration

Table 1 show the ability of the synthesized material as adorbent of mercury nitrate (29,2 ppm). The final concentration is lower than the mother solution after treatment using two variations of adsorbent weights (0,3 gram and 0,5 gram). These resuts clearly show that the current as-prepared materials become alternative material for heavy metal adsorbent.

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