Synthesis and characterization of magnetic adsorbent based on Fe$_2$O$_3$-fly ash from Pulang Pisau’s power plant of Central Kalimantan

D A P Wardani*, L Rosmainar, R M Iqbal and S N Simarmata
Department of Chemistry, Faculty of Mathematics and Natural Science, University of Palangka Raya, Kampus Tunjung Nyahu, Palangka Raya 73112, Kalimantan Tengah, Indonesia
Email: dayupwardani@mipa.upr.ac.id

Abstract. One of the biggest producers of fly ash in Central Kalimantan is Pulang Pisau’s power plant. Fly ash, which is produced from burning coal or biomass, is a mixture of oxides with less combustible carbon and other minor inorganic compounds so that it has a dominant-negative surface charge and is a promising adsorbent. Modification of fly ash with Fe$_2$O$_3$ can affect the structure and morphology of the adsorbent, and the magnetic properties of the adsorbent can help in the process of separating the adsorbent after treatment. This study aims to study the synthesis and magnetic characteristics of magnetic adsorbent based on Fe$_2$O$_3$-fly ash from Pulang Pisau’s power plant. The proximate test results obtained showed that the SiO$_2$ compound contained in fly ash was the highest with a percentage level of 32%. The optimum composition of fly ash and Fe$_2$O$_3$ ratio is 1: 2. Morphology of magnetic adsorbent based on Fe$_2$O$_3$-fly ash was observed using SEM EDX. The results showed Fe$_2$O$_3$ particles impregnated to the pores of fly ash particles which had 29,11% of O and 70,22% of Fe. The magnetic properties of magnetic adsorbent based on Fe$_2$O$_3$-fly ash from Pulang Pisau’s power plant were simply proven using an external magnetic field.

1. Introduction
Fly ash in this research was coal ash waste that was used as a source of energy in the industry. Steam power plant is a producer of fly ash in very large numbers. One of the biggest producers of fly ash in Central Kalimantan is Pulang Pisau’s power plant. Coal production in Indonesia in 2015 was 425 million tons and estimated to be in the range of 400 million tons/year until 2019 (Direktorat Jenderal Mineral dan Batubara, 2016). If all the coal is consumed domestically and the average ash content is 8% (ash content generally varies from 3 to 20% by weight), then there are around 32 million tons/year of coal ash produced. Most of the ash is fly ash while the rest is bottom ash (bottom ash). Meanwhile, the global production of fly ash from industry is estimated at 800 million tons/year in 2010 [1, 2].

Fly ash is categorized as hazardous and toxic waste so that it is not allowed to be disposed of without being processed [3]. This is what causes the use of fly ash in the world is still very low at only 20-30%. Fly ash, which results from burning coal or biomass, is a mixture of oxides with less combustible carbon and other minor inorganic compounds so that it has a dominant-negative surface charge and is a promising adsorbent. Many applications in wastewater treatment have been reported, most of them on a fairly large scale. Fly ash is widely used in the adsorption of heavy metals [4] and fly ash has been reported as an adsorbent for dyes from the textile industry waste batik [5].
Iron oxide and hydroxide are interesting subjects because they can be utilized in the fields of geochemistry, mineralogy, metallurgy, and environmental protection [6]. Iron oxide exists in a variety of polymorph variations. Anhydrous iron oxides including hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃), and β-Fe₂O₃ are less common. Fe₃O₄ (magnetite) and Fe₁-xO (wüstite) contain both ferrous and ferrous iron [7]. Fe₂O₃ is a conventional semiconductor material, which has been widely used as an active catalytic, magnetic, nonlinear optical, and gas sensitive material. These properties are caused by the high surface area and porosity of the Fe₂O₃ particles. Fe₂O₃ is commonly found in regional soils, and can also be easily synthesized in a laboratory in a short time. Synthesis of Fe₂O₃-Fly Ash is reported to be able to increase the ability of Pb metal ion adsorption due to increased surface area [8]. Maghemite (γ-Fe₂O₃) is an inexpensive magnetic material, and if the composition of fly ash has magnetic properties, it will be easier to separate the multiphase system by using an external magnetic field. This shows the regeneration of absorbent substances, waste management, and types of separation which are of safe value.

Fly ash contains some silicon and aluminum. In addition, fly ash can also contain calcium, iron, potassium, magnesium, titanium, sulfur, and so on. These elements are reported in their oxide form, for example, silicon in the form of SiO₂ and iron in the form of Fe₂O₃. The oxides can be either amorphous or crystalline.

Fly ash which is classified as N class is a natural calcined material. Class F of fly ash is produced from the burning of anthracite or bituminous coal which is pozzolanic while class C comes from the burning of lignite or sub-bituminous type coal which is pozzolanic and cementitic. Further research shows that the CaO content in class F is below 20%, whereas in class C it is more than 20%. The high calcium and SO₃ content in fly ash can also be caused by the cleaning process that occurs in the chimney’s power plant, especially the removal of flue gases from sulfur gases. One of the cleanings can be done by adding calcium which will bind sulfur gases. High calcium content can reduce the compressive strength of geopolymers if the fly ash is used as raw material for geopolymers. According to Damilola et al. [9], this can be overcome by adding NaOH to the water glass, both of which are geopolymers activators, to avoid decreasing the workability of samples containing lots of calcium, thereby increasing the compressive strength of geopolymers [9].

The particle size and shape characteristics of fly ash depend on the source and uniformity of the coal, the degree of destruction before combustion, the combustion environment, the uniformity of combustion, and the type of collection system used. The fly ash from the coal combustion powder has gone through a liquid stage at high temperatures, and subsequently, this is generally round in shape with diameters ranging from below 1 μm to above 150 μm [10]. The size distribution of fly ash particles can be measured in various ways but is usually measured by sieve analysis, a method suitable for particles larger than about 45 μm [11, 12]. The particle size distribution shows how the highest contribution to total mass comes from fly ash particles less than 38 in m size, which is broadly consistent with some of the studies described by Helmuth [13].

Physico-chemical surface characteristics of fly ash, such as site density, acidity constant, specific surface area, and surface electrical characteristics, metal adsorption constant, determination of capacity, strength, and potential of organic compounds bind the surface of fly ash. Surface characteristics such as specific surface area and zero charge point pH (pH ZPC) have been assessed [14–16]. The specific surface area from <1 m²/g to tens of m²/g depends on carbon content [14–16]. Research has shown that pH ZPC is between 2.4 and 7.0. Alkaline metric titrations are used to determine site density and solid surface acidity constants [17], [18]. On the other hand, Magnetic minerals in nature can be classified in the oxide family iron-titanium, iron sulfide, and iron oxide hydroxides. The iron-titanium oxide family is most often found in rocks. This family consists of minerals that meet the triangle diagram (ternary diagram) with edge members consisting of TiO₂, FeO, and Fe₂O₃.

Hematite is the most prominent iron ore. Most high-grade iron ore is subject to simple dry process beneficiation to meet the size requirements. This involves multi-level crushing and screening to obtain chunks of products (−31.5 + 6.3 mm) and plates (about −6.3 mm). Low-grade hematite ore needs to be increased to achieve the required iron content, which involves a more complicated ore beneficitation
process. Comminution rates are needed for low-grade hematite ore similar to high-grade ore to provide the same product [19]. Hematite (α-Fe₂O₃), is the most thermodynamically stable iron oxide phase in the family and iron oxide has many advantages, such as natural abundance, biocompatibility, and low cost [20]. Hematite has been reported to be able to bind with Sb (III) closely through the inner-sphere complex. Hematite nanoparticles can remove Sb (III) metal and are easily separated after treatment [21].

Various chemical methods have been developed to synthesize maghemite nanoparticles, including precipitation, thermolysis, and electrochemistry. From these methods, the electrochemical method is simple because this method is easy to control and the equipment used is simple. In the electrochemical method, the reaction that occurs is the oxidation-reduction reaction on the electrode surface, where the reaction is influenced by several factors such as the electrode used (type, surface area, the distance between the two electrodes), electrolyte as a precursor (type and concentration), potential difference, temperature, pH and current density [22].

The electrochemical synthesis of maghemite nanoparticles was successfully carried out using the FeCl₃ solution. It was concluded that with increasing current density, the average size of the resulting maghemite particles gets smaller [22]. The synthesis of maghemite by the electro-oxidation method was also carried out using a solution of tetrabutylammonium bromide dissolved in DMF (N, N-dimethylformamide). The resulting maghemite particles have an amorphous size of 3-8 nm deposited in the anode [23]. Based on the above explanation, our research aims to synthesize a potential magnetite adsorbent based on a combination of Fe₂O₃ and fly ash from Pulang Pisau’s power plant.

2. Materials and methods

2.1. Equipment and materials

The types of equipment that we used in this work were X-Ray Diffraction (XRD) (Rhigaku Miniflex600), Spectrophotometer Scanning Electron Microscopy (SEM) (Hitachi SU3500), and glassware. The materials that we used in this work were fly ash from Pulang Pisau’s power plant of Central Kalimantan, Fe₂O₃, and methanol.

2.2. Methods

The method in this study was divided into three stages, first, the characterization of coal and fly ash from Pulang Pisau’s power plant of Central Kalimantan, second, The synthesis of magnetic adsorbent based on Fe₂O₃-fly ash, and third, the structural characterization of magnetic adsorbent based on Fe₂O₃-fly ash.

2.2.1. The characterization of coal and fly ash from Pulang Pisau’s power plant of Central Kalimantan

Coal was tested proximately and ultimately to find out its characteristics, then analysis was also carried out on fly ash to determine the composition of the oxide compounds contained by methods that were compliant with ASTM D 3-682 13 standards.

2.2.2. The synthesis of magnetic adsorbent based on Fe₂O₃-fly ash

Fly ash and Fe₂O₃ were mixed into a beaker with a ratio of 1: 1, 2: 1: 3, and 1: 4, then each solid mixture was dispersed into 50 mL of methanol and stirred on a hotplate stirrer for 2-3 hours until homogeneous. Then, the homogeneous mixture was allowed to stand until the filtrate and sedimentary phases were formed, then decanted to separate the filtrate and Fe₂O₃-fly ash. Fe₂O₃-fly ash deposition was heated into the oven at 75 °C for 1 hour to vaporize the methanol which was still trapped on the surface of the Fe₂O₃-fly ash composite.

2.2.3. The structure characterization of magnetic adsorbent based on Fe₂O₃-fly ash

Fe₂O₃-fly ash adsorbent was characterized by Panalytical X-Ray Diffraction (XRD) using a Cu-Kα light source (λ = 1.5406 Å) which was operated with a current of 30 mA and a voltage of 40 kV. The analysis rate was
1 ° C.min- 1 and step size 0.02°. The morphological of magnetic adsorbent based on Fe₃O₆-fly ash was characterized by Scanning Electron Microscopy (SEM).

### 3. Results and discussion

#### 3.1. The structure characterization of coal and fly ash from Pulang Pisau's power plant of Central Kalimantan

The ultimate analysis of coal was used to study the properties and compositions in coal from Pulang Pisau’s power plant of Central Kalimantan. The result of the analysis is shown in figure 1. According to figure 1, the coal from Pulang Pisau’s power plant contained volatile matter which reached 38.53%. It means that the matters contained in the coal were easy to vaporize. The second highest composition was fixed carbon that reached 36.23%. It was because the coal consisted of hydrocarbon chains with many carbon compositions. On the other side, the lowest matter contains in coal was ash which reached 4.01%. The ash that was produced from the steam power plant gave some problems because it was hazardous waste which consisted of two types; fly ash and bottom ash.

**Figure 1.** The ultimate analysis result of coal from Pulang Pisau’s power plant.

The next analysis for the coal is proximate analysis and the result is shown in figure 2. The composition of C, H, O, and N shows that the coal generally consisted of organic matter formed by hydrocarbon chains.

**Figure 2.** The proximate analysis result of coal from Pulang Pisau’s power plant.
The results of electricity production at the power plant produce side products in the form of fly ash. Fly ash was characterized to identify compounds contained in the fly ash sample. Figure 3 shows the oxide compounds contained in the fly ash of Pulang Pisau's power plant.

![Figure 3. The compounds compositions in fly ash from Pulang Pisau's power plant.](image)

The fly ash from Pulang Pisau’s power plant had 32% of SiO$_2$, 23% of CaO, 15% of Fe$_2$O$_3$, and Al$_2$O$_3$, MgO, and Na$_2$O below 10%. According to its classification, the class of the fly ash from Pulang Pisau’s power plant was classified as class C because the amount of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ was more than 50% but less than 70% of the total components. The abundant component of metal oxide in the fly ash had the potential to be used as an adsorbent feedstock that could be improved by its physical and chemical properties by composting fly ash with Fe$_2$O$_3$.

The next characteristic studied is the particle size identified in various circumstances, namely AR, ADB, DB, and DAFB. The highest particle size was 98 nm and the most explosive was 18 nm. All particle measurements show that the Pulang Pisau’s power plant fly ash was classified as nanomaterial (material that has a size of less than 100 nm). The particle size of the fly ash is shown in table 1.

| Sample | Particle Size (nm) |
|--------|--------------------|
| AR     | 98                 |
| ADB    | 96                 |
| DB     | 76                 |
| DAFB   | 18                 |

Table 1. The particle size of fly ash from Pulang Pisau’s power plant.

3.2. The study of synthesis and characterization of magnetic adsorbent based on Fe$_2$O$_3$-fly ash from Pulang Pisau’s power plant of Central Kalimantan

This section describes several studies related to the synthesis and characterization of magnetic adsorbent based on Fe$_2$O$_3$-fly ash including XRD confirmation of fly ash and the influence of Fe$_2$O$_3$ and the fly ash composition variation, morphological analysis using SEM, and the magnetic properties of magnetic adsorbent based on Fe$_2$O$_3$-fly ash using an external magnetic field.

3.2.1. XRD confirmation of fly ash and the influence of Fe$_2$O$_3$-fly ash composition variation. The analysis using X-ray diffraction was conducted to find out the types of minerals contained in fly ash and Fe$_2$O$_3$ which is shown by a peak at 20. The qualitative analysis result of fly ash and magnetic adsorbent based on Fe$_2$O$_3$-fly ash refers to the database of JCPDS No. 39-1364, 46-1045, 02-0431,
which is the minerals database of maghemite (γ-Fe₂O₃), quartz (SiO₂), and mullite (Al₆Si₂O₁₃). The 2θ database showed in table 2.

| Mineral                  | 2θ Database (°)         |
|-------------------------|-------------------------|
| Quartz (SiO₂)           | 20,82; 26,62; 36,52; 39,44; 40,26; 42,41; 45,75; 50,10; 54,83 |
| Mullite (Al₆Si₂O₁₃)     | 16,5; 23,4; 29,5; 31,2; 33,1; 35,4; 39,2; 41,0; 48,3; 52,8; 59,8 |
| Maghemite (γ-Fe₂O₃)     | 18,3; 23,77; 26,1;30,3; 35,7; 37; 42,2; 53,6; 57,3; 62,8; 72,3; 74,8 |

Figure 4. X-ray diffractogram of (a) fly ash from Pulang Pisau’s power plant of Central Kalimantan; magnetic adsorbent based on Fe₂O₃-fly ash in ratio (b) 1:1; (c) 2:1; (d) 3:1; (e) 4:1. Note: Q= Quartz; M= Mullite; M*=Maghemite.

Figure 4(a) shows the X-ray diffractogram of the fly ash from Pulang Pisau’s power plant of Central Kalimantan and figures 4(b), (c), (d), and (e) shows the X-ray diffractogram of magnetic adsorbent based on Fe₂O₃-fly ash composition variation. Figure 4(a) is dominated by the characteristic mineral peak of quartz at 2θ = 20.82°; 26.62° and mullite at 2θ = 31.2°; 33.1°; 35.4°; 39.2°; 59.8°. Figures 4(b), (c), (d), and (e) shows that the characteristic mineral peak of maghemite appeared at 2θ= 26.1°;30.3°; 35.7°; 42.2°; 53.6°; 62.8°; 65.7°;72.3°. According to the result, the optimum of Fe₂O₃-fly ash is showed in figure 4(c) magnetic adsorbent based on Fe₂O₃-fly ash 2:1, because the characteristic mineral peak of fly ash still appeared and the maghemite formed in the pores structure of fly ash.

The addition of Fe₂O₃ in the composition to form maghemite (γ-Fe₂O₃) in the pores structure of fly ash increased the peak. It indicates that Fe₂O₃ in the pores formed perfectly. But, the addition decreased the peak intensity of quartz and mullite. The decreases in peak intensity occurred because of destructive interference increased caused by the Fe₂O₃ particles impregnation in the pores of fly ash. In general, the introduction of material into the interlayer space would increase the phase that
eliminated each other which was scattered by the wall and that which was scattered by the interlayer space, thereby reducing the intensity of scattering in the reflection of Bragg.

3.2.2. Morphological analysis using SEM EDX. Analysis using SEM EDX instrumentation was carried out to study the morphological of magnetic adsorbent based on Fe$_2$O$_3$-fly ash. Figure 5 shows the morphological of magnetic adsorbent based on Fe$_2$O$_3$-fly ash using SEM, in which there were Fe$_2$O$_3$ particles formed in the pores of fly ash. Small spherical particles with agglomerated particles in the fly ash pores can be observed in figure 5.

![Image of SEM EDX analysis](image)

**Figure 5.** The morphological of magnetic adsorbent based on Fe$_2$O$_3$-fly ash.

![Image of EDX analysis](image)

**Figure 6.** The result of magnetic adsorbent based on Fe$_2$O$_3$-fly ash using SEM EDX.

Figure 6 shows that the pores of magnetic adsorbent based on Fe$_2$O$_3$-fly ash contained elements of O, Al, and Fe. The percentage of the elements are written in table 3. Magnetic adsorbent based on
Fe₂O₃-fly ash had 29.11% O, 00.67% Al, and 70.22% Fe. It proves that Fe₂O₃ impregnated to the pores of fly ash.

Table 3. The elements contained in magnetic adsorbent based on Fe₂O₃-fly ash.

| Element | Wt (%) |
|---------|--------|
| OK      | 29.11  |
| AlK     | 00.67  |
| FeK     | 70.22  |

3.2.3. The magnetic properties of magnetic adsorbent based on Fe₂O₃-fly ash using an external magnetic field. One of the characteristics of maghemite iron oxide (γ-Fe₂O₃) is magnetic properties. If there is a stronger magnetic field effect, the maghemite will be attracted. Figure 7 shows a simple magnetic properties test using an external magnetic field. Fe₂O₃ has ferromagnetic properties, where pure Fe₂O₃ has no superparamagnetic properties because Fe₂O₃ tends to agglomerate so that the particle size becomes larger (> 25 nm). Meanwhile, it is estimated that the analysis results of the magnetic adsorbents based on Fe₂O₃-fly ash would have superparamagnetic properties and had a size of <25 nm which occurred because Fe₂O₃ was distributed into the fly ash pores.

Figure 7. The magnetic properties test using an external magnetic field.

4. Conclusion

Based on the results of the research, it can be concluded that proximate test results show that the total carbon reached 53%. The level of fly ash resulting from coal combustion at Pulang Pisau’s power plant of Central Kalimantan was 4.01%. The SiO₂ compounds contained in the fly ash of Pulang Pisau’s power plant were the highest with a percentage level of 32%. The addition of the composition of Fe₂O₃ indicated a better formation of Fe₂O₃ in the fly ash pores. However, the addition of this composition decreased the intensity of the characteristic peaks of the constituent minerals of fly ash. The decrease in intensity occurred because of the decreasing crystallinity of the constituent minerals of fly ash. The optimum composition of fly ash and Fe₂O₃ ratio was 1:2. The analysis result using SEM-EDX shows that Fe₂O₃ impregnated to the pores of magnetic adsorbent, which had 29.11% of O and 70.22% of Fe. Magnetic adsorbent based on Fe₂O₃-fly ash from Pulang Pisau’s power plant of Central Kalimantan had magnetic properties.

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