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Study on the modification of fly ash as a coagulant

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Abstract:

This study was carried out to produce a complex coagulant containing aluminum and iron salt from coal fly ash by H_2SO_4 acid. An application of this extracted solution as a coagulant was also investigated by the jar-test process. Fly ash collected at the Electrostatic precipitation (ESP) system in Mong Duong thermal power plant are mainly round and fine particles with diameters ranging from 0.2-8 µm, containing aluminum and iron of 15 and 6% respectively. At a room temperature of 25°C, with 1 M H_2SO_4 acid solution and the retention time of 20 minutes, the maximum contents of around 60.16 $mg.l^{-1}$ of Fe and 4.37 $mg.l^{-1}$ of Al were the most favorable to convert aluminum and iron from mineral forms to sulfate salt-based forms. The produced complex coagulants from fly ash of the Mong Duong power plant are proved to be effective for total suspended solids (TSS) removal from wastewater where the highest efficiency achieved 83.6% at the coagulant solution ratio of 5% (w/w) with a concentration of TSS in the initial wastewater was 60 $g.l^{-1}$. The positive results from this study open a meaningful approach toward a huge of fly ash produced from thermal power plants as well as other coal-burn-related activities in Vietnam.

Keywords: **coagulant, coagulation, fly ash, modification, wastewater treatment.**

Classification numbers: **2.2, 5.3**

1. Introduction

Fly ash is a byproduct generated from burning coal in thermal power plants. In Vietnam, with consumption of nearly 100 million tons of coal per year for running thermal power plants in recent years, it is estimated that the average amount of created fly ash collected from the ESP filter system will be increased from 30 million tons in 2025 to 38 million tons in 2030 [1]. The main response to this solid waste is only being disposed of in ash ponds surrounding the plants [2]. Some environmental problems related to this unsafe restoration are soil, water and air pollution as well as soil malfunction.

With a huge amount created every year over the world, fly ash has been widely utilized as an amendment for highway road bases [3, 4], construction products such as cement or brick [5, 6] as well as stabilizing clay-based building materials [7, 8]. In the field of environmental treatment, the promising use of fly ash for wastewater treatment was classified based on either physical method (absorption, filtration) or chemical method (photocatalysis and Fenton process) [9]. In terms of the physical method, utilization to synthesize zeolite materials for water treatment absorption was widely applied [10-12]. Ceramic filtration made from fly ash is an inexpensive micro-porous inorganic membrane [13, 14]. For chemical applications, fly ash with a high surface area for the deposition and growth of metal oxide nanoparticles (Fe, Ag, ZnO and TiO_2) led to utilizing of this by-product for photocatalytic support [15, 16]. Fly ash contains different metals Fe, Al, Mn, Cu, Ni and/or its oxides was investigated as a supporter of Fenton processes [17, 18].

Using ores as raw materials for manufacturing commercial coagulants is largely applied in recent years. The main composition of popular coagulants is ferric sulfate - $Fe_2(SO_4)_3$ and aluminum sulfate $Al_2(SO_4)_3$. These coagulants are widely used for both wastewater and drinking water treatment. The coagulation process is the major physicochemical treatment method for the reduction of suspended solids and turbidity. Iron coagulant in the ferric form behaves similarly to aluminum sulfate and forms ferric hydroxide floc in the presence of bicarbonate alkalinity. Fly ash is rich in iron and aluminum oxides. Converting these oxides to sulfate forms is the scientific basis of recycling fly ash as a coagulant material.

Aluminum and iron salts were created by soaking fly ash in H_2SO_4 acid. The extracted solution is then to be used

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as a mixed coagulation agent. Jar-test process has shown the efficiency in removal of TSS from wastewater. This successful result is considered as a suitable solution to open a new approach to reducing huge fly ash in Vietnam, suggesting further work on fly ash.

2. Methodology

2.1. Research materials

Fly ash was collected from Mong Duong 2 thermal power plant in Cam Pha city, Quang Ninh province, Vietnam. The fly ash was captured by an ESP filter system. The density of fly ash was 2.24 g.cm^{-3} and 2.1% moisture.

2.2. Research methods

2.2.1. Fly ash analysis

The morphological and chemical compositions of the fly ash material were examined by scanning electron microscopy (SEM) coupled with - energy-dispersive X-ray spectrometry (EDS) (FESEM S-4800, Hitachi). SEM analysis was conducted with 500x and 2000x magnifications. EDS analysis was at 1.060 keV.

Fig. 1. Fly ash collected from the ESP system at Mong Duong 2 thermal power plant.

2.2.2. Aluminum and iron extraction experiment

The oxides of aluminum and iron in fly ash were decomposed by using sulfuric acid at different concentrations at 0.5, 1, 2, 3 and 4 M (Table 1). Each 20 gram of dried fly ash was mixed with 45 ml of sulfuric acid at concentrations ranging from 0.5, 1, 2, 3, and 4 M, the retention time of the experiments remained at 20 minutes. All of the experiments were carried out at room temperature (22-25^{o}C). All experiments were performed in triplicate.

Table 1. Experimental conditions.

Acid Cont. (M) / Temp. (^{o}C)	0	0,5	1	2	3	4
25	Control	TM1	TM2	TM3	TM4	TM5

2.2.3. Chemical analysis

The content of Al^{3+} and Fe^{3+} ions in the extracted solution were measured by AAS (AAS 300 - Perkin Elmer).

2.2.4. Jar-test

The jar-test method was used to determine the efficiency of the complex coagulant (Fig. 2). The modified solution with different ratios of 1, 3 and 5% was added to 300 ml of artificial wastewater with the TSS concentration of 500 mg.l^{-1}. The solution was stirred at approximately 100 rpm for 1 minute then reduced the stirring speed to 35 rpm for 20 minutes. The containers were allowed to settle for 20 minutes.

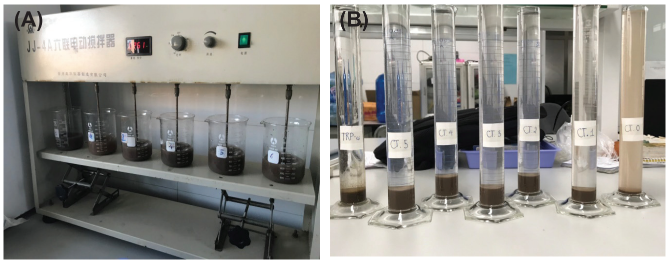

Fig. 2. The jar-test experiment (A) and the coagulation process (B).

2.2.5. Data processing

T-test was used to clarify the significant difference at $p<0.05$. All of the analytical data were processed and indicated by SignmaPlot 14 software.

3. Results and discussion

3.1. Physio-chemical properties of fly ash

3.1.1. Size distribution of fly ash

The resultant combustion product from coal-fired thermal plants includes bottom ash and fly ash. While the bottom ash was easily collected from the furnace because of its heavyweight and large dimension, the fly ash with a very fine particle and low weight was only captured from the ESP filter system.

The ESP fly ash at Mong Duong 2 thermal power plant has a round and very fine particle ranging from 0.2-8 µm. Fig. 3 shows that these fine particles are aggregated into micron and sub-micron sizes. This result is compatible with other researches. L.V. Thien, et al. (2019) [19] showed that the fly ash from some coal power plants such as Pha Lai, Ha Khanh and Ninh Binh was primarily silt-size particles (0.2-5 µm) and that number of fly ash diameter of the Soma thermal power plant was from 4.5-7.5 µm according to the work of A. Bicer (2018) [20].

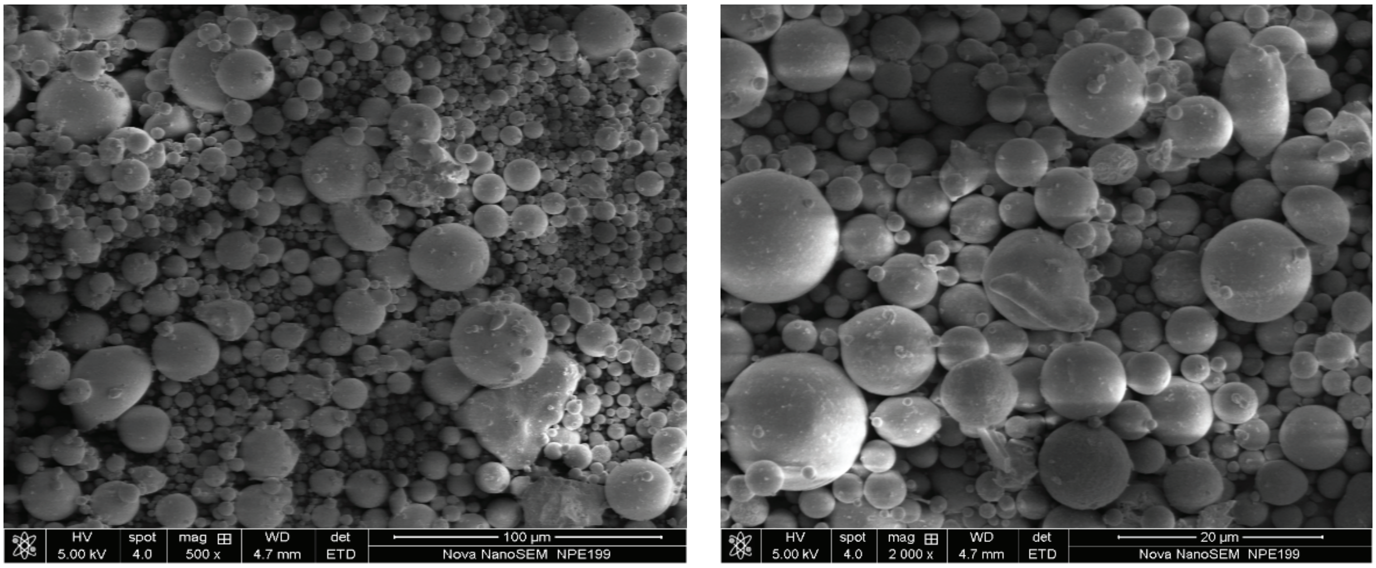

Fig. 3. Scanning electron micrograph of the fly ash (Mong Duong).

3.1.2. Chemical composition of the fly ash

Iron and aluminum sulfate salts play an important role in the coagulation process for waste and wastewater treatment.

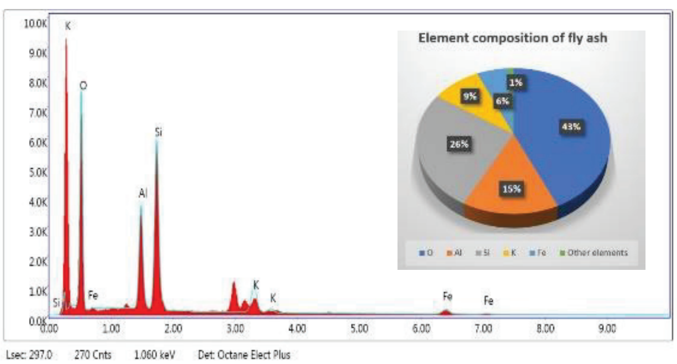

Fig. 4. Chemical composition of fly ash by EDX technique.

Figure 4 shows that the fly ash is mainly composed of oxygen (43%), Si (26%), Al (15%), K (9%), Fe (6%) and others (1%). According to Le Van Thien, et al. (2019) [19], the composition of elements detected in fly ash was the highest percentages of Si, Al and Fe, and significant percentages of Mg, K and Ca. These aluminum and iron in fly ash may play an important role in producing coagulation agents based on aluminum and iron sulfate salt content [21].

3.2. Aluminum and iron extraction

Aluminum and iron sulfate play an important role in the coagulation process. That means, in this research, converting aluminum oxide and iron oxide to sulfate salt forms will determine the efficiency of the coagulation process. The impact of H_2SO_4 acid concentration on the conversion efficiencies of Al and Fe was shown in Fig. 5.

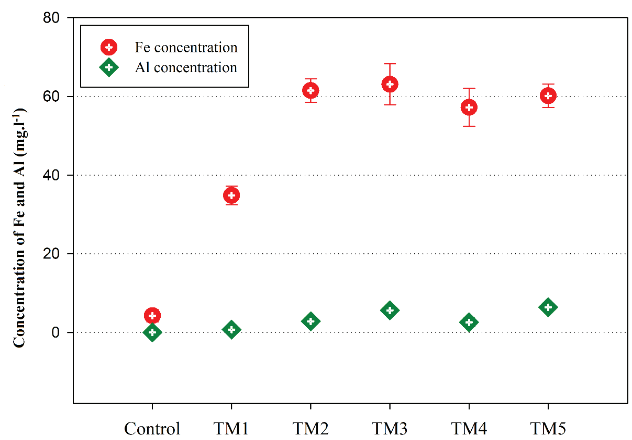

Fig. 5. The converting efficiencies of Al and Fe.

Figure 5 shows that the leaching processes of both Al and Fe increase with an increase in acid concentration. While the leached concentration of Fe rose sharply when the H_2SO_4 concentration from 0.5 to 1 M was then kept stable at a higher acid concentration from 1 to 4 M. The concentration of extracted Al tended to remain stable between 0.75 M to 6.43 M when the acid concentration changed from 0.5 to 4 M. Fig. 5 also showed that the leaching capacity of Fe from fly ash was always higher than that of Al, getting the maximum value around 60.16 mg.l^{-1} Fe, compared to 4.37 mg.l^{-1} Al. In other words, the higher the H_2SO_4 concentration, the higher the concentration of aluminum and iron obtained. In our study, the maximum conversion efficiency of Fe was realized with 1 M H_2SO_4 acid solution at room temperature (22-25^{o}C), with a retention time of 20 minutes.

The difference in leaching between Fe and Al in this study may be explained by the reason that aluminum is an amphoteric metal oxide so self-organized porous anodic oxide films are produced when reactive metals such as aluminum and titanium are electrochemically oxidized in baths that dissolve the oxide [22]. M. Fan, et al. (2005) [23] reported the conversion efficiencies of 84.8% for iron and only 55.1% for aluminum at 120°C and after 4 hours of reaction time. The phases of iron oxides in raw fly ash are mainly of hematite, magnetite and/or maghemite which could be easily dissolved in acid solution than aluminum oxides [24].

3.3. Application of the complex coagulant solution

The modified complex coagulant solution of aluminum and iron sulfate was applied to remove TSS in water by the jar-test process. The volume ratio of extracted solution applied in this study was 1, 3, and 5% (w/w). The coagulation efficiency was determined by the amount of collected TSS (mg.l^{-1}, Fig. 6) and by the transmittance (T%, Fig. 7).

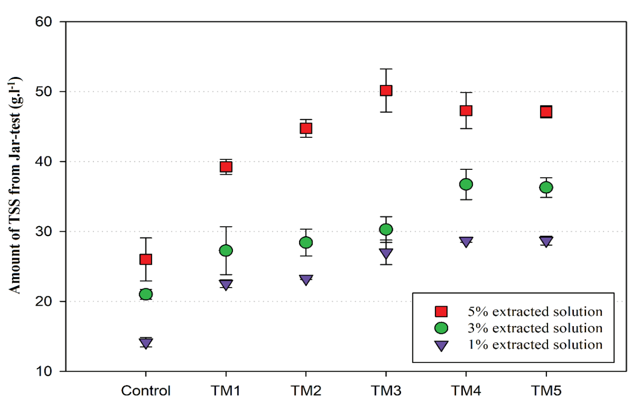

Fig. 6. The efficiency of TSS removal by the complex coagulant.

The most common tendency is that the treatment efficiency increases gradually with the amount of added coagulant solution. With the treatment adding 5% extracted solution, the amount of settled TSS was twice as high as the control sample, achieving 50.16 g.l^{-1} compared to only 26.0 g.l^{-1} of the control. In the lower extracted solution, 3% and 1%, TSS removal efficiency is significantly lower than that in the 5% solution. With a concentration of TSS in the initial wastewater is 60 g.l^{-1}, it was achieved the highest TSS removal efficiency of 83.6% at the coagulant solution ratio of 5% (w/w). L. Forminte, et al. (2020) [25] synthesized new material from fly ash with sulfuric acid and used this complex material in the coagulation process. It obtained a TSS removal efficiency of 84% at the coagulant dosage of 60 mg.l^{-1}. According to H. Saleem (2013) [26], using ferrous and aluminum sulfate from fly ash as a coagulant condensed about 75% of turbidity, 73% of color, and 93% of TSS.

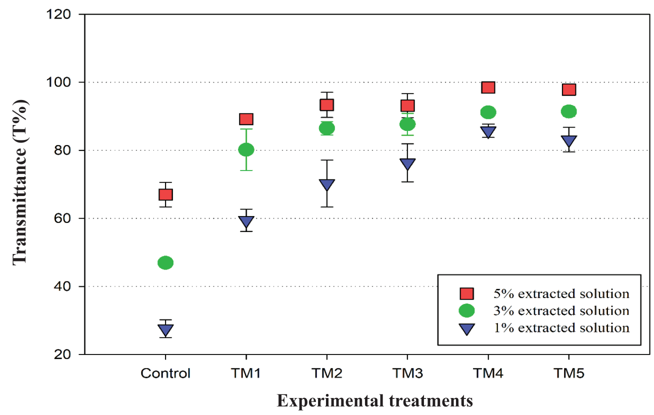

Fig. 7. The efficiency of transmittance by the complex coagulant.

Similar to TSS removal efficiency, the transmittance of water after treatment has also the same result (Fig. 7). In all of the experimental formulas, the highest TSS removal capacity, as well as the transmittance efficiency, were always achieved at TM3 (treated with H_2SO_4 2 M) and TM4 (treated with H_2SO_4 3 M). These TM3 and TM4 treatments were also the best conversion ratio of aluminum and iron into the solution which was mentioned above.

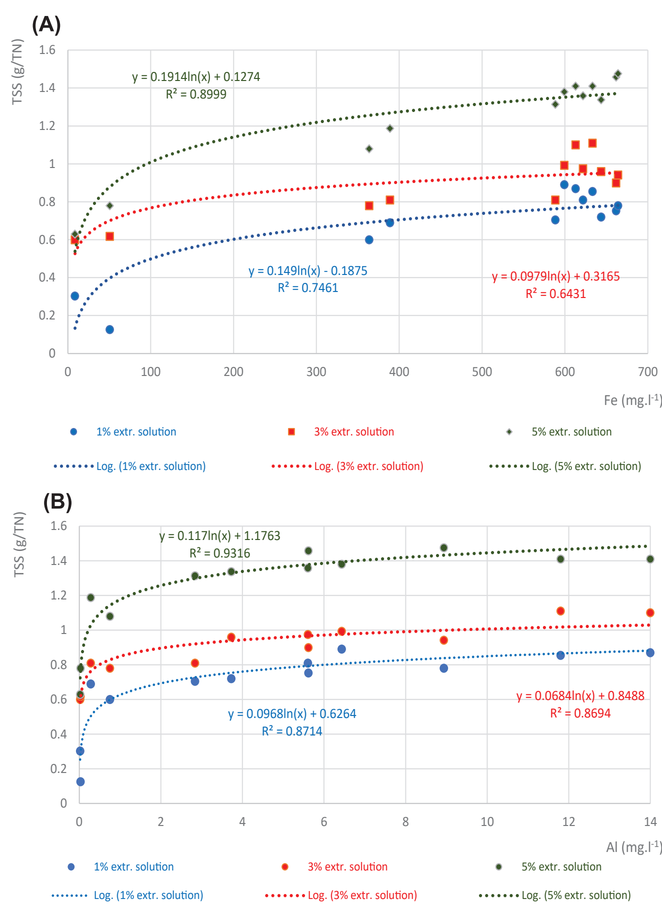

Fig. 8. Correlation between coagulation efficiency and Fe (A), Al (B) contents.

To determine the factors affecting the coagulation efficiency, the significant correlation (t-test) between Fe and Al concentrations (via the volume of complex coagulant solution) with the amount of settled solid was collected after the coagulation processes. The results in Fig. 8 show that the correlations coefficient (R^2) between the settled solid amount and the leached Fe content were 0.746, 0.643 and 0.899 at 1, 3, and 5% dosage of the complex coagulant solution, respectively. These correlation coefficients for aluminum were 0.871, 0.869 and 0.932, respectively. All correlations are significant at the p=0.001 significance level with n=11 samples. From the Fig. 8, it can be seen that the effect of aluminum sulfate on the TSS removal efficiency was remarkably higher than that of iron sulfate. With the same amount of TSS removed, the change in the concentration of aluminum sulfate was always lower than the concentration of iron sulfate. Moreover, the correlation factors that showed the relationship between the amount of coagulant and removed TSS, the of aluminum sulfate was also higher compared to the iron factors. According to X. Huang, et al. (2016) [27], the floc properties in the coagulation process were affected by the initial solution pH and flocs created by aluminum sulfate coagulant were the largest in size among those of the coagulants of iron and titanium sulfates at a pH of 5.

4. Conclusions

Fly ash collected at the ESP system in Mong Duong thermal power plant are mainly round and fine particles with diameters ranging from 0.2-8 µm. With containing aluminum and iron of 15% and 6% respectively, this fly ash was considered a resource of Al and Fe to produce a potential complex coagulant solution.

The produced complex coagulant from fly ash of Mong Duong thermal power plant containing both aluminum and iron ions are proved to be effective for TSS removal in the wastewater. At a room temperature of 25°C, with 1 M H_2SO_4 acid solution and a retention time of 20 minutes, the maximum contents of around 60.16 mg.l^{-1} of Fe and 4.37 mg.l^{-1} of Al were the most favorable to convert aluminum and iron from mineral forms to sulfate salt-based forms. In this study, the H_2SO_4 acid concentration is the factor that has the greatest influence on converting iron into a sulfate salt-based form. Meanwhile, aluminum is less affected because of its amphoteric metal.

The application of this extracted coagulant solution to remove TSS in wastewater has shown its potential results when the highest efficiency achieved 83.6% at the coagulant solution ratio of 5% (w/w) with the concentration of TSS in the initial wastewater was 60 g.l^{-1}. Positive results from this study open a meaningful approach toward a huge of fly ash produced from thermal power as well as other coal-burn-related activities in Vietnam.

CRediT author statement

Ngoc Tu Nguyen: Conceptualization, Methodology, Supervision, Writing original draft; Quang Huy Trinh: Validation, Taxonomic identification, Review and Editing; Thi Thu Ha Nguyen: Data curation, Validation; Van Duc Tran: Supporting data analysis, Sample analysis; Thi Thuy Hang Ho: Supervise and comment on editing the manuscript for completeness.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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