CONTRIBUTION TO BENEFICIATION OF COAL FLY ASH FOR THE PRODUCTION OF COAGULANTS FOR WATER AND WASTEWATER TREATMENT

[1]M. Clotilde APUA, [1]M. K. W. KALENGA

[1]*University of Johannesburg, Faculty of Engineering and the Built Environment, Johannesburg, South Africa,* *clotildea@uj.ac.za*, *michelk@uj.ac.za*

https://doi.org/10.37904/metal.2025.5103

Abstract

Wastewater contaminant emissions are currently of global concern because they pose risks to the ecosystem and human health. In the present study, a process of coal fly ash leaching by sulphuric acid was carried out. This process was applied to extract iron, aluminium, magnesium, silicon, and calcium from coal fly ash into a sulphate solution, which can further be used as a coagulant for wastewater treatment. Extraction efficiencies of 57.90% for iron, 33.86% for aluminium, 73.21% for magnesium, 11.12% for silicon, and 25.43% for calcium were achieved under the process conditions discussed in the present study. Wastewater treatment by the obtained sulphates of iron, aluminium, magnesium, silicon and calcium showed good results compared to conventional coagulants.

Keywords: Circular economy, coal fly ash coagulant, metallurgy, waste management, wastewater

1. INTRODUCTION

Water pollution is one of the world’s most undesirable environmental problems, and it requires solutions. Humans use and divert freshwater in many ways to conduct major industrial, agricultural and subsistence activities, discharging wastewater and contributing to the global shortage of freshwater. The main sources of water pollution and contaminants are industrial effluents, municipal wastewater and agricultural activities, due to their high chemical content and wide range of inorganic and organic impurities [1].

The effluent discharged has a devastating impact on the ecosystem and can have long-term adverse effects on the environment. The majority of wastewater contains high levels of dissolved and suspended particles, non-biodegradable compounds, inorganic and organic pollutants, colours and toxic chemicals, which all cause harm to the environment and human health [2]. The elimination of pollutants from wastewater becomes important for the environment through the adoption of an effective treatment technique. Several authors have highlighted the importance of the coagulation process in wastewater treatment due to its efficiency, ease of use and low cost [1,3]. Treatment by coagulation technology has important advantages in the treatment of frequently discharged effluents, such as improving water quality. Coagulation is the process of neutralizing (or destabilizing) the charge in a particular suspension or solution. When a coagulant is used, it neutralizes the charges that repel colloidal particles from one another, causing them to collide and form larger particles (flocs), which are subsequently removed by filtration [4]. The removal of pollutants is usually dependent on the type and dosage of coagulant, the pH of the wastewater, the stirring speed, the stirring time, and the temperature. Physical and chemical properties of the coagulant applied to the wastewater can impact treatment efficiency [1,3]. The choice of an effective coagulant is vital for enhancing treatment efficiency. Thus, researchers have proposed a variety of alternatives, involving the use of chemical coagulants and waste-based coagulants, including coal fly ash-based coagulants and a variety of organic polymers [1-3].

The chemical coagulants utilized in water and wastewater treatment are either metal salts or polymers. Metal salts are inorganic compounds. The most commonly used inorganic coagulants are aluminium and iron salts, such as aluminium sulphate or alum ($Al_2(SO_4)_3$) and ferric sulphate ($Fe_2(SO_4)_3$). Polymers (or flocculants) are synthetic organic substances that consist of a long chain of smaller molecules. They contain repeating units with functional groups such as quaternary amines or carboxyl functions. The molecular weight of a polymer ranges from a few thousand to millions of grams per mole. According to the electrical charge shown by the polymer coagulants in the aqueous phase, polymers are categorized into cationic (positively charged), anionic (negatively charged) and non-ionic (neutrally charged) coagulants. The common polymer coagulants are polyethyleneimine, poly-diallyldimethylammonium chloride, and polyacrylamide [3,4]. Contaminants in water are generally eliminated by sedimentation and then filtration. As they are slow to settle, small particulates are not efficiently eliminated by sedimentation; moreover, they can pass through filters. Moreover, since these particulates carry negative charge, they repel each other; it would be easier to eliminate them by colliding them (coagulation) to form larger particulates. In the coagulation process, using a coagulant such as iron sulphate generates positive charges that neutralize the negative charges of the particulates. This causes particulates to aggregate, producing coarser particles that are more readily eliminated [4,5]. Both inorganic coagulants and synthetic organic polymers act by neutralizing the charge on the particles. Inorganic coagulants destabilize particles by compressing the electrical double layers surrounding them. Polymeric coagulants (organic and inorganic) destabilize particles by adsorption and subsequent particle-polymer-particle bridging [3]. The most widely used of all chemical coagulants in wastewater treatment is alum. The effectiveness of various chemical coagulants for wastewater treatment has been studied [5-7]. However, their use is still being researched. The huge quantities of sludge produced are extremely difficult to regenerate or reuse. Research has suggested that prolonged exposure to these materials can provoke neurodegenerative diseases. Also, the large volume of sludge produced increases the cost of disposal of these potentially hazardous materials [1,3]. The harmful impacts of chemical coagulants on the environment and human health have led recent research to focus on finding alternative techniques for water decontamination. This is why there is increasing emphasis on the development of coagulants based on coal fly ash, a more environmentally friendly and sustainable alternative to chemical coagulants.

Coal fly ash, a waste largely produced by coal-fired power stations, contains a wide range of active compounds, including iron, aluminium, magnesium, silicon, and calcium oxides, which are important raw materials for the synthesis of polymeric coagulants for wastewater treatment by the coagulation process. Many researchers have reported the higher efficiency of coal fly ash coagulants in wastewater treatment and their potential rates of wastewater decontamination due to their characteristics [3,8-10]. Coal fly ash coagulants are commonly employed as a stock solution. Coal fly ash coagulants can be made using a variety of techniques, including extracting essential elements for coagulation from coal fly ash through leaching process. The typical process for synthesizing essential element salt-based coagulant from coal fly ash involves using solutions of sulphuric acid (H_2SO_4), hydrochloric acid (HCl), and sodium hydroxide (NaOH) [8].

The implications of the technological revolution in wastewater treatment are expected to help mitigate the negative effects on the environment. Recently, coagulants based on coal fly ash have been investigated as a sustainable alternative to chemical coagulants [3]. With the global trend towards environmentally friendly materials, research into the use of waste-based coagulants has also been encouraged [1]. A potential resource for wastewater treatment could be coal fly ash, a waste product from coal-fired power stations, since it is inexpensive and effective. In the previous paper [3], the coal fly ash coagulant was used to treat wastewater to remove Mn, Fe, Mg, Al, Ca, Ni, Si, Zn, As, Cr, and Cu. In this research, a preparation method for a coagulant from coal fly ash is provided. A novel wastewater treatment process, using the produced coagulant, was applied to mining wastewater to remove sulphur, chemical oxygen demand (COD), and total suspended solids (TSS).

2. MATERIALS AND METHODS

2.1 Materials and their chemical composition

The coal fly ash used was from the power plant of Kendal, Mpumalanga, South Africa; the main chemical composition is presented in **Table 1**. The wastewater in this experiment was taken from the Witbank coal mine, Mpumalanga, South Africa. **Table 2** shows the wastewater quality. The sulphuric acid used was commercial grade reagent.

Table 1 Chemical composition of coal fly ash (%)

Si	Al	Fe	Mg	Ca	Ti	K	P
23.34	17.01	2.91	0.84	4.47	1.29	0.83	0.46

Table 2 Quality of the wastewater

pH	Colour	Sulphur (mg/L)	TSS (mg/L)	COD (mg/L)
3.23	Yellowish	125.33	17.01	23.34

2.2 Coagulant preparation

The leaching process was carried out by adding 40 g of coal fly ash to a 750 mL high-pressure reactor, then 200 mL of 1.5 M H_2SO_4 was added to the reactor at a stirring speed of 300 rpm, with a pH of 0.5–3.9, and a temperature of 150 °C, for 6 h. The coal fly ash coagulant was thus produced.

The produced coagulant (dosage: 20 mg/L) was then used to treat wastewater in this way: 25 ml of wastewater was poured into a beaker, the initial pH value of the wastewater was adjusted to 7 with concentrated NaOH solution, then a proper quantity of coagulant was added and stirred using a magnetic stirrer. After stirring at a rapid speed for 5 minutes at 300 rpm to homogenise the mixture, the speed was then slowed for 20 minutes at 30 rpm to allow coagulation. Following stirring, the mixture was allowed to settle for 150 minutes, and the supernatant sample was filtered, and the removal % of sulphur, TSS, and COD were determined. And then compare with the results that come from the conventional $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ coagulants.

3. RESULTS AND DISCUSSION

3.1 Coagulant production

The results of maximum extraction efficiencies (using 1.5 M H_2SO_4, pH 0.5–3.9, 300 rpm, 150°C, solid/liquid ratio: 1:5, and leaching time: 6 h) are as follows: 57.90% iron, 33.86% aluminium, 73.21% magnesium, 11.12% silicon, and 25.43% calcium. A diagram of the process of leaching Fe, Al, Mg, Si and Ca from coal fly ash using H_2SO_4 can be proposed based on the above information (**Figure 1**). The chemical properties of the coagulant produced from H_2SO_4 leaching of iron, aluminium, magnesium, silicon, and calcium are shown in **Table 3**.

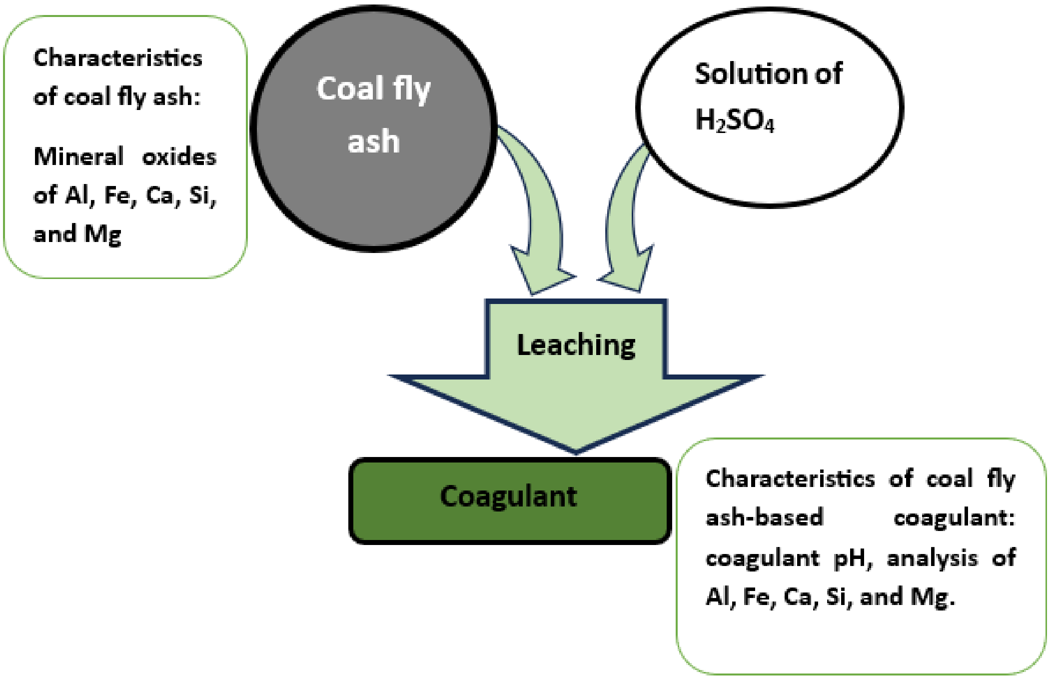

Figure 1 Illustration of the preparation of coal fly ash-based coagulant

Table 3 Chemical composition of the produced coagulant

pH	Colour	Fe	Al	Mg	Si	Ca
0.68–0.75	dark green solution	21,731.89 mg/L	603.18 mg/L	1,366.70 mg/L	96.00 mg/L	796.70 mg/L

The scanning electron microscope (SEM) images show that there were obvious changes in the surface of coal fly ash after leaching with acid. The raw coal fly ash grain (image a) exhibited smooth surfaces compared to the leached coal fly ash grain (image b), which had a pitted and corroded surface. **Figure 2** illustrates the morphology of individual grains with pitted surfaces that form in leached coal fly ash compared to raw coal fly ash.

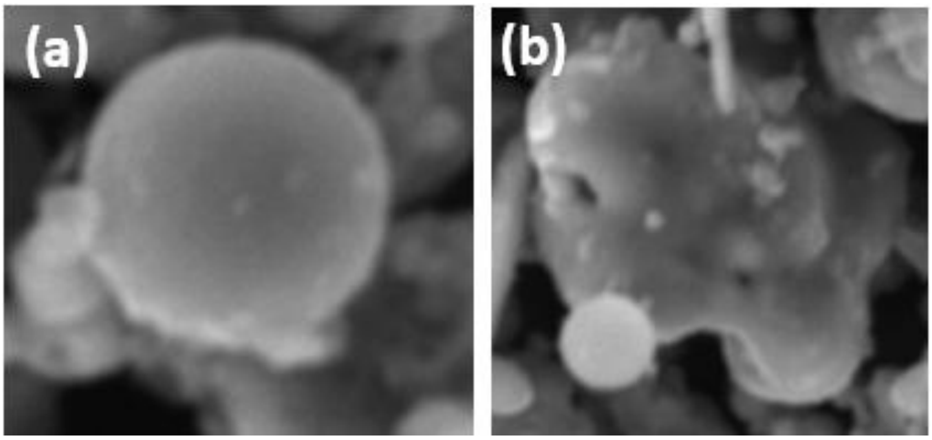

Figure 2 Comparison of SEM images of individual grains of raw and leached coal fly ash: (a) raw coal fly ash and (b) leached coal fly ash

3.2 Wastewater treatment

The results of the performance of the produced coal fly ash-based coagulant on mining wastewater are presented in **Table 4**. The comparison between the coagulation performance of the produced coagulant and that of the conventional monomeric coagulants ($Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$) is presented in **Table 5**. For this comparison, the treatment conditions used for the production of coal fly ash coagulant were applied to $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ coagulants.

Table 4 Results of the treatment of mining wastewater using coal fly ash-based coagulant

Removal rate (%)		
Sulphur	**TSS**	**COD**
83.6	88.2	67.5

Table 5 Results of the treatment of mining wastewater using different coagulants. Removal rate (%)

Pollutants	**$Al_2(SO_4)_3$**	**$Fe_2(SO_4)_3$**	**coal fly ash-based coagulant**
Sulphur	72.7	75.4	83.6
TSS	86.1	81.4	96.2
COD	63.8	61.2	67.5

Table 4 shows that the produced coagulant was effective in removing sulphur, TSS, and COD in mining wastewater. Coal fly ash coagulant contains large amounts of highly charged cations, including Fe^{3+}, Si^{4+}, Al^{3+}, Mg^{2+}, and Ca^{2}+, which greatly attract colloidal particles and offer a high removal rate. It can be seen in **Table 5** that the coal fly ash coagulant is more efficient than the monomeric $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ coagulants. The presence of different cationic salts in the complex coagulant (coal fly ash-based coagulant) is responsible for its effectiveness. This coal fly ash coagulant is a hydrolysed product of different cations (Al^{3+}, Mg^{2+}, Fe^{3+}, Si^{4+}, and Ca^{2+}) containing pre-formed polymeric species of these cations. In addition, their high charge effectively neutralizes the negative charge of pollutants in wastewater and causes significant hydroxide precipitation, leading to sweep flocculation. In addition, the polysilicate species generates a strong adsorbing and bridging effect, which promotes the coagulation of suspended particulates. Consequently, coal fly ash coagulant has a significant advantage over conventional non-prehydrolysed $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ coagulants in terms of pollutant coagulation.

4. CONCLUSION

Sulphuric acid leaching of coal fly ash was used to extract iron, aluminium, magnesium, silicon and calcium from coal fly ash waste, which can then be used as a coagulant for wastewater treatment. Extraction efficiencies of 57.90% for iron, 33.86% for aluminium, 73.21% for magnesium, 11.12% for silicon, and 25.43% for calcium can be obtained under process conditions of 1.5 M sulphuric acid, pH 0.5–3.9, 300 rpm, 150°C, solid/liquid ratio: 1:5, and a leaching time of 6 h.

Coal fly ash-based coagulant was found effective in removing 83.6% of sulphur, 96.2% of TSS, and 67.5% of COD from the mining wastewater sample. Compared to conventional coagulants, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, the coal fly ash-based coagulant showed the best coagulation performance. Coal fly ash coagulants have several advantages over conventional coagulants, including lower cost. Use of coal fly ash for the production of a coagulant for the treatment of wastewater offers a promising avenue for the development of sustainable and effective wastewater treatment technologies and a suitable option for large-scale industrial wastewater treatment applications.

REFERENCES

[1] BADAWI, A.K., SALAMA, R.S., MOSTAFA, M.M.M. Natural-based coagulants/flocculants as sustainable market-valued products for industrial wastewater treatment: a review of recent developments. RSC advances. 2023, vol.13, no. 28, pp. 19335–19355. DOI: 10.1039/d3ra01999c

[2] GUESMI, A., CHERIF, M.M., BAALOUDJ, O., KENFOUD, H., BADAWI, A.K., ELFALLEH, W., HAMADI, N.B., KHEZAMI, L., ASSADI, A.A. Disinfection of corona and myriad viruses in water by non-thermal plasma: a review. Environmental Science and Pollution Research. 2022, vol. 29, no. 37, pp. 55321–55335. https://doi.org/10.1007/s11356-022-21160-7

[3] APUA, M.C. Acid mine drainage treatment by coagulation process using a synthesized sulphate-based coal fly ash coagulant. Johannesburg, 2020. Doctoral thesis. University of the Witwatersrand. https://wiredspace.wits.ac.za/server/api/core/bitstreams/790be7a7-8154-4991-aa6a-0f8fe52ee19b/content

[4] SHENG, D.P.W., BILAD, M.R., SHAMSUDDIN, N. Assessment and optimization of coagulation process in water treatment plant: A review. ASEAN Journal of Science and Engineering. 2023, vol. 3, no. 1, pp. 79–100. https://ejournal.kjpupi.id/index.php/ajse/article/view/319

[5] NASIR, N., DAUD, Z. Performance of aluminium sulphate and polyaluminium choloride in biodiesel wastewater. Journal of Mechanical Engineering and Sciences. 2014, vol. 7, pp. 1189–1195. DOI: http://dx.doi.org/10.15282/jmes.7.2014.18.0116

[6] AZHAR, A.A., HARON, N.F., BALQIS, H. The efficiency assessment of Poly-Aluminium Chloride (PAC) in water treatment plant process: a case study at Sultan Iskandar Water Treatment Plant, Johor. Journal of Sustainable Civil Engineering & Technology (JSCET). 2022, vol. 1, no. 2, pp. 18–16. https://joscetech.uitm.edu.my

[7] MAHMOUDABADI, T., EHRAMPOUSH, M.H., TALEBI, P., FOULADI-FARD, R., ESLAMI, H. Comparison of poly ferric chloride and poly titanium tetrachloride in coagulation and flocculation process for paper and cardboard wastewater treatment. Environmental Science and Pollution Research. 2021, vol. 28, pp. 27262–27272. https://doi.org/10.1007/s11356-021-12675-6

[8] KUMAR, A., KUMARI, M., GUPTA, S.K. Performance study of fly-ash-derived coagulant in removing natural organic matter from drinking water: synthesis, characterization, and modelling. Environmental Monitoring and Assessment. 2022, vol. 194, no. 11, p. 821. https://doi.org/10.1007/s10661-022-10472-3

[9] BINGTAO, L., LI, Z. Experimental study on wastewater treatment by fly ash coagulant. In: IEEE International Conference on Electric Technology and Civil Engineering (ICETCE-2011). Lushan: IEEE, 2011, pp. 1363-1366. DOI: 10.1109/ICETCE.2011.5775805

[10] VALEEV, D., KUNILOVA, I., SHOPPERT, A., SALAZAR-CONCHA, C., KONDRATIEV, A. High-pressure HCl leaching of coal ash to extract Al into a chloride solution with further use as a coagulant for water treatment. Journal of Cleaner Production. 2020, vol. 276, p. 123206. https://doi.org/10.1016/j.jclepro.2020.123206