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Effectiveness of biomass-based fly ash in pulp and paper liquid waste treatment

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ABSTRACT

Adsorption is regarded as one of the most promising and straightforward strategies for reducing organic pollutants from wastewater effluents. The use of adsorbents from economical raw materials, even those from waste, is one recent concern. This study aims to test the effectiveness of biomass-based fly ash in treating liquid waste from pulp and paper production activities. Fly ash (FA) performance for adsorption was tested by varying the ratio of adsorbent with wastewater by 20, 40, 60, and 80 g/L. The adsorbents' performance was then compared between the application of FA directly (without activation) and adsorbents that were previously calcinated in 100 °C and 200 °C. Samples of pulp and paper liquid waste are placed on the erlenmeyer flask and stirred using a jar test with speeds varying by 100, 200, and 300 rpm. The results showed that FA is potential directly used with no thermal treatment as an adsorbent in treating liquid waste in the pulp and paper industry. It was effectively used with a dosage of 20 g/L and a 100 rpm fatigue speed with a contact time of 10 min. The quality changes of several wastewater parameters were found with a 92.5% reduction in TSS, 83.31% in COD, 19.99% in chlorides, 95.41% in NH3, and 19.6% in TDS, 19.6% in EC. Those parameters have successfully complied with the regulation standard of Indonesia (SNI) for wastewater.

1. Introduction

As a result of the strong demand for paper, the pulp and paper industry has become one of the country's leading promising growth industries. The global pulp and paper market is projected to grow from \$351.51 billion in 2021 to \$370.12 billion in 2028 in forecast period, 2021-2028 (Fortune Business Insights, 2021). At once, the center of attention of pulp and paper industries is changing towards the environmentally eco-friendly generation of paper because of the generation of a large amount of waste. The pulp and paper mills produce wastewater and sewage sludge from the beginning of the pulp digestion process to pulp, to the washing process of paper-making machines. At the pulping stage, wood pieces are boiled at a very high temperature and pressure in the presence of chemicals to break up lignin and hemicelluloses. At least 80% of process wastewater from paper manufacturing operations includes chemical bleach, nitrogen, total suspended solids (TSS), heavy metals, organic compounds, color and bacteria (Mazhar et al., 2019).

Pulp and paper industries are now facing challenges to comply with stringent environmental regulations. The pulp and paper mill effluents are highly loaded with corrosive and toxic materials. They contain high organic materials that cause high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), high adsorbable organic halides (AOX), suspended solids (colloids), metal ions, tannins, lignin, and derivatives, fatty acids, and so on (Teng et al., 2014). These compounds can increase COD, BOD, TSS, and trace metals which can reduce water quality and become a threat to various ecosystems. Studies by Brink et al. (2018), Kamalinejad et al. (2018), Mazhar et al. (2019) reported a higher content of salts, turbidity, BOD and COD in paper and pulp wastewater due to the presence of organochlorine compounds produced during different processes of pulping and bleaching processes via the degradation process of lignin. The volume and properties of pulp and paper wastewater and related pollutants depend upon several factors, such as production scale, the raw materials used, and applied production technologies (Kamali and Khodaparast, 2015).

The typical treatment processes have been widely used for pulp and paper mill effluents: the physicochemical, biological, and combined techniques (Kumar et al., 2005; Mandeep et al., 2020). The use of adsorbents to treat pulp and paper liquid waste has also been developed. Today's challenge is finding adsorbents that effectively reduce pollutant

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levels, cheap and easy to obtain, handle and produce, and environmentally friendly. The development of advanced materials to treat waste with modern and effective technology is carried out intensively, which is considered advanced through the development of green materials adsorbents, as reported by several authors (Bin-Dahman and Saleh, 2020; Haile et al., 2021; Kamali and Khodaparast, 2015; Kimura and Wajima, 2017; Novais et al., 2019; Rezaei et al., 2022; Saleh et al., 2022; Vu et al., 2016).

Most of the biomass produced in pulp and paper mills consists of organic residues. Since black liquor is the primary waste, other possible wastes include sawdust, sludge of various types, paper waste and FA. The subsequent development of the pulp and paper mill resulted in the discharge of a large amount of fly ash as a result of combustion processes of waste biomass (Hackett et al., 1999; Haile et al., 2021; Vu et al., 2012). A study by Vu et al. (2012) confirmed that the continual growth of pulp and paper industry has led to the generation of tremendous volume of FA as byproducts of biomass combustion processes, and recycling of lime mud and FA as raw materials of anorthite ceramic is a feasible approach to solve the solid wastes (Pio et al., 2020; Qin et al., 2015). Commonly, a major part of it is landfilled; however, updated environmental regulations have tended to restrict the landfilling of FA due to rising disposal costs and the scarcity of suitable land. The pulp and paper industries are therefore urgently seeking energy-efficient mechanisms and management for the beneficial use of FA in an ecological and economical manner (Cherian and Siddiqua, 2019).

The fly ash generated from biomass combustion contains a substantial number of elements, macronutrients (P, K, S, Ca, and Mg), and micronutrients (Mn, Cu, Zn, Co) considered as being essential for plant growth (Jarosz-Krzemińska and Poluszyńska, 2020). In form of oxides, the main chemical components contained in FA are silica (SiO_2), alumina oxide (Al_2O_3), and iron oxide (Fe_2O_3), the rest are carbon, calcium, magnesium, sulfur and other metals (Cherian and Siddiqua, 2016; Haile et al., 2021; Hu et al., 2020; Zhou et al., 2000). Based on a statistical survey conducted by Cherian and Siddiqua (2019) more than 50% of ash is landfilled, 20–25% is used as a soil amendment (direct application or compost), and less than 20% is used for other beneficial applications such as the construction of embankment fills, the stabilization of pavement layers, and the solidification of wastes.

Fly ash is quite fine (micron size) and almost completely combusted although it contains some residual carbon, sulfur, and many hazardous substances such as heavy metals and toxic organic compounds. The utilization of biomass-based fly ash has been developed for many applications. Due to its compositions, FA mostly known as a potential mineral fertilizer or soil improver in land use. Compare to FA from coal firing, the biomass ash, when properly treated, can easily return to the soil, thus closing the natural biogeochemical cycle (Gao and Fatehi, 2018; Haile et al., 2021). Besides the low price, FA also has several advantages, namely having a quality equivalent to activated carbon so that it has the potential to increase the economic value of FA.

Various studies state that fly ash is a potential raw material that can be used as an adsorbent. Some alternatives have provided regarding methods to increase the adsorption capacity. It is important to lead FA more competitive as adsorbent when compared to activated carbon and zeolite (Kushwah et al., 2021; Novais et al., 2018). Due to it is a solid waste, FA can be more cheaper adsorbent material and it is available in abundant quantities.

Some studies suggest that FA needs to be previously treated in order to activate and increased adsorption capacity. The adsorption capacity of the activated FA carbons will depend on the surface area and porosity of the carbonaceous material as well as the hydrophobicity of the substituent. Chemical activation improves not only the total surface area of the FA carbon materials, but greatly increases the number of micropores in the processed materials as indicated by differences in micro and mew pore volumes.

Biomass-based FA commonly has a heterogeneous surface and each molecule has different absorption potential for adsorption processes.

Table 1
Method of analysis for wastewater parameters.

Parameter	Unit	Standard Method	Analysis Method
TDS	mg/L	SNI 6989.27:2019	gravimetric /conductivity
pH	-	SNI 6989.11-2019	pH analysis
TSS	mg/L	SNI 06-6989.3-2004	gravimetric
COD	mg/L	SNI 6989.73:2019	titrimetric analysis (closed)
Cl	mg/L	SNI 06-6989.19-200	Argentometry
NH3	mg/L	SNI 06-6989.11-2004	spectrophotometric
Electrical Conductivity	μs/cm	SNI 6989.1:2019	Conductivity meter

The purpose of activation is to remove impurities present in FA and to improve the absorption performance of compounds or ions both from solution and air. Otherwise, FA can be pretreated by heating to high temperature (termed as calcination), to prepare a highly porous material with improved contaminant removal ability (Kimura and Wajima, 2017).

The adsorption capacity of Pulp and Paper fly ash increases with carbon content and makes it more suitable for re moving hazardous metal concentrations. It has high acid-neutralizing properties and fast nutrient-releasing capacity, and due to this it can potentially act as a soil conditioner in agriculture and forestry applications (Cherian and Siddiqua, 2019). The affinity of biomass-based FA for reducing lignin concentration, chemical oxygen demand (COD) and turbidity of the bleaching effluents prior to biological treatment process was studied by Gao and Fatehi (2018). Charge neutralization plays a key role at a low FA dosage for removing lignocellulosic flocs. Coagulation and adsorption were the main phenomena for the removals of COD, lignin and turbidity at a higher fly ash dosage and a prolonged treatment time.

Fly ash based geopolymer spheres were used by Kushwah et al. (2021), Novais et al. (2019) to extract methylene blue from synthetic wastewaters. They showed a much faster and higher methylene blue uptake in comparison with the other bulk-type geopolymers. Meanwhile, Jarosz-Krzemińska and Poluszyńska (2020) confirmed that biomass FA amendment to soil does not have any toxic influence on plant germination and growth, despite a very high concentration of chloride anions, which are potentially detrimental to plants. Biomass ash, when properly treated, can easily return to the soil, thus closing the natural biogeochemical cycle.

The wastewater treatment process in pulp and paper industries is often complex, high-cost, and rigid remains another environmental problem. The use of economical but effective adsorbents in processing waste is continued to examine. So far, the maximum utilization of FA has not been optimal because of its complex characteristics and needs further process. It has not been comprehensively applied in industrial waste ponds. Therefore, it is necessary to specify the FA's activation and its direct application effects on the liquid waste treatment. This study will prove that FA can be beneficial in overcoming the problem of solid waste disposal from boilers and can increase economic circularity if it proves effective as an adsorbent to treat liquid waste itself.

2. Materials and method

The liquid waste and fly ash used in this study was taken from one of pulp and paper industry located in Muara Enim, South Sumatera, Indonesia. The company has a production capacity of 1,430 articulated dump trucks (ADT)/day or 450,000ADT/year. The company produces high-quality kraft pulp and bleached hardwood with 100% of the *Acacia mangium* trees grown on plantations. The company's operations in Indonesia are managed to world-class standards, and have ISO 14001, ISO 9001 and SMK3 for diligent compliance with Environmental, Quality and Safety Management. Samples were taken from liquid waste ponds and fly ash stocks. The fly ash shape taken is in the form of dark

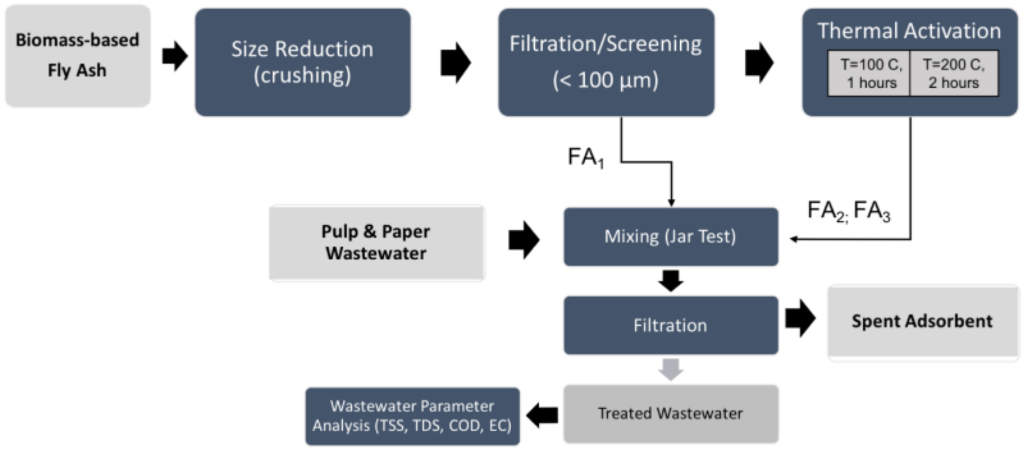

Fig1. Scheme of biomass-based fly ash experiments on pulp and paper wastewater treatment.

Table 2
Experimental sample data and process variable.

Adsorbent Type	FA_1, FA_2, FA_3
Description	FA_1: fly ash with no treatment (directly use as adsorbents) FA_2: fly ash activated by calcination of 100 °C, 1 h FA3: fly ash activated by calcination of 100 °C, 1 h
Temperature (°C)	26-30 °C (room temperature)
Contact Time (minute)	10; 20; 30
Stirring Speed (rpm)	100; 200
Adsorbent Dosage (gr/mL)	10; 20; 30
Analysis	Wastewater Quality Parameters (Table 2) Adsorbent Elemental Compositions (XRF)

gray solids and rough with various sizes. While the sample of liquid waste is brownish yellow. Pulp and paper mills liquid waste parameters were analyzed using a number of methods according to standards set by the ministry of environment in Indonesia, as presented in Table 1.

In this study, most of the boilers in the pulp and paper mill were operated by utilizing acacia wood waste as biomass fuel. Fly ash is taken from the boiler in the form of a dark gray solid. Boiler ash is usually removed periodically from the boiler and laid in the open field. The size of the ash particles tends to be irregular and, in minor amounts, still contains other impurities. For this study, 30 kg of boiler ash was prepared and placed in a metal drum.

In the initial stage, the boiler ash is separated from impurities, then mashed with a grinder machine, then filtered until it meets a size below 100 µm. Furthermore, the activation process for fly ash to become an adsorbent is conducted using a thermal, electrical fiber furnace or burnout oven with a working temperature of 100-210°C. In each treatment of PPILW, it required an average of 1500 g of fly ash, where 60 g of each sample was set aside for solid analysis purposes. The biomass-based fly ash experiments on pulp and paper wastewater treatment are described in Fig. 1.

Each of the samples are taken for characterization purposes. The 3 (three) kind of FA adsorbent, can be defined based on the pre-treatment applied as FA_1, FA_2 and FA_3, respectively. The details of each adsorbents were described in Table 2. FA_2 and FA_3 are distinguished based on the temperature and time of calcination. The calcination is intended to remove the water contained in the FA and open the FA pores to absorb more pollutants in the pulp and paper industry's liquid waste

X-Ray Fluorescence (XRF) is used to analyze the elemental composition in the fly ash. It works based on X-rays reacting with atoms in the sample with a general detection ability of about 0.01%. The elements tested on XRF are Si, Al, Fe, Mn, Mg, Ca, Na, K, P, etc. The test sample on XRF is usually in the form of a powder and will be detected more effectively if the sample is homogeneous.

The adsorbent effectiveness tests for pulp and paper waste treatment were conducted on a laboratory scale by adding adsorbents in dose variations of 100g, 200g, and 300g to an Erlenmeyer flask containing 1000 mL of liquid waste with the support of jar tests. The performance of each adsorbent prepared is tested and compared between FA_1, FA_2, and FA_3. Variations in process conditions include adsorbent dose, contact time, and stirring speed. The mixing of the adsorbents in liquid waste was using a magnetic stirrer with speed variations of 100 and 200 rpm. All stages of this process were carried out at room temperature without heating. The contact time between the adsorbent and the liquid waste varied from 10 to 30 min, with interval of 10 min.

After the treatment process, the mixture was separated using filter

Table 3
The water quality measurement after treatment.

Mixing Speed (rpm)	Time(min)	Wastewater Quality Measurement								
		pH			TDS (ppm)			EC (µs/cm)		
		FA_1	FA_2	FA_3	FA_1	FA_2	FA_3	FA_1	FA_2	FA_3
100	10'	10,5	9,7	10,9	1785	2636	2840	2816	5272	5272
	20'	10,1	9,7	11,1	2022	2636	2840	3096	5272	5272
	30'	10,4	9,6	11	2022	2840	2840	3002	5272	5680
200	10'	10,2	8,6	10,5	1501	2840	2840	3002	4864	5680
	20'	10,1	8,5	10,7	1785	2432	2636	3002	6088	5680
	30'	10,5	8,4	10,8	2022	2228	2840	4044	6080	5680
300	10'	10,3	8,5	10	1785	2432	2226	2910	6088	4456
	20'	10,5	8,5	10,4	1785	2636	2022	3002	6964	3570
	30'	10,6	8,3	10,3	2022	2228	2432	3002	6964	4864

Table 4
Fly ash performance in adsorption process (without activation).

SampleCode	FA weight (gr)	RPM	Time (min)	pH	TDS (ppm)	EC(µs/cm)
F_0	-	-	-	6.9	1435	2870
F_1	20	100	10	8.10	1160	2320
F2	40	100	10	9.80	1357	3186
F3	60	100	10	9.90	1828	3342
F4	80	100	10	9.90	2064	3655
Quality Standards for Minister of Environment Regulation No. 5 of 2014 and National Environmental Quality Standards (NEQS, 2000).				6.0-9.0	3500	2665

Table 5
Water quality characteristics of adsorption process.

Sample	TSS (mg/L)	COD (mg/L)	Chloride (mg/L)	N-NH_3 (mg/L)	pH	TDS (ppm)	EC (µs/cm)
Initial waste	80	893	66,47	21,8	6,9	1435	2870
Treated Waste*	6	149	53,18	1,0	8,1	1160	2320
Adsorbent efficiency (%)	(-) 92.5	(-) 83.33	(-)13.29	(-) 95.41	(+) 14.8	(-) 19.61	(-) 19.16

(*) adsorbent: FA1, dosage 20 g/L, 100 rpm, 10 min.

paper. The parameter of treated wastewater observed is hardness (TDS), electrical conductivity (EC), pH, TSS, COD, Chloride, and N-NH_3. The solids retained on the filter paper were then analyzed using XRF to obtain their elemental composition. It will compare the arrangement of the elements on the adsorbent before and after the adsorption process.

3. Results and discussion

3.1. Fly ash adsorbent performance comparison

Before using adsorbents, liquid waste initially showed pH = 7.1, TDS = 1455 ppm, and EC = 2816 µs /cm. The condition of this liquid waste will be compared to the condition after treatment with the adsorbents. Especially at this stage, the dose of FA adsorbent fed into the flask was 100g in 1000 mL of wastewater. The water quality measurement data obtained from the wastewater treatment process using all kind of FA are presented in Table 3.

The addition of all types of adsorbents causes an increase in pH, TDS, and EC. Physically, the wastewater color seems better, but the extreme increase in TDS and EC may indicate an excessive adsorbent dose. TDS value and its conductivity increase with the increase in the heating temperature of the FA adsorbent. This is because the chemical composition of FA is generally composed of silicate compounds SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, SO_3. At the time of stirring and heating, these compounds will be released from the FA surface and decay to form solids in solution so that the TDS increases and the conductivity also increases because these compounds are generally charged alkali metals.

The components contained in pulp and paper wastewater are inorganic and organic components such as calcium, magnesium, sodium, potassium carbonate, hydrogen carbonate, chloride, sulfate, and nitrate ions. These compounds interact to form dissolved solids which are recorded as total dissolved solids (TDS), and suspended solids provide a level of turbidity in pulp and paper wastewater which can be explained by analysis of Total suspended solids (TSS) in pulp and paper wastewater. The higher the concentration of suspended solids, the higher the turbidity level.

Boiler's FA from a paper mill which undergoes combustion at high temperatures, the alkali will melt and the alkali position is replaced by air, thus forming pores in the FA particles. This is because the alumina and silicates contained in FA are reactive, so they are easy to change into the structural form of the adsorbent materials.

From the experimental data as presented in Table 3, almost all adsorbents showed the same tendency to have the same effect on wastewater quality. It may conclude that FA without activation could be considered to have performance equivalent to FA treated with calcination, and the wastewater quality has already met the local environmental standards. It will be very beneficial for the pulp and paper industry in treating the wastewater with solid waste FA directly *in situ*. The boiler's FA can be used *in situ* on the liquid waste without thermal treatment. The addition of processing time and increasing the stirring speed did not significantly affect changes in wastewater quality. Hence, the next test of the effectiveness of the adsorbent will be focused on variations in lower doses (low doses) with the conditions of the sewage treatment process at room temperature, stirring speed of 100 rpm, and contact time of 10 min.

3.2. The effectiveness test of fly ash adsorbent (without calcination)

In this section, the FA adsorbent effectiveness test (without thermal activation) was carried out on the same process apparatus and procedure but limited to 100 rpm stirring conditions and 10 min contact time. The dosage variation of FA1 adsorbent was 20; 40; 60; 80 g. The results of the adsorption process were compared with the initial wastewater condition F0. The experimental results are the wastewater quality as presented in Table 4.

The best results from the adsorption process carried out were obtained at a weight of 20 g of FA capable of increasing pH 8.1 and lowering TDS to 1160 ppm and EC reduce to 2320 µs/cm, where the water quality value obtained met the standard environmental quality, the liquid pH is 6-9 and TDS 3500 ppm. This proves that FA has the ability as an adsorbent that is able to absorb pollutants in pulp and paper industrial liquid waste (PPILW) in accordance with study by Novais et al. (2019) which stated that FA waste produced by pulp and paper factories has great potential to absorb metal ions because it has high porosity.

The process with adsorbents has a tendency to attract other molecules such as liquid and gas molecules. To see the characteristics of the treated water, what compounds were successfully absorbed by the pulp and paper industry FA adsorbent in the liquid waste, then an analysis of the parameters of TSS, COD, Cl-, N-NH_3, TDS, pH and EC was carried out for the most efficient FA weight, which is considered in 20 g.

3.3. Characteristics of adsorption processed water

The results of the adsorption process with 20 g FA adsorbent without heating, speed of 100 RPM, process time of 10 min were sampled then the parameters TSS, COD, Cl-, N-NH_3, TDS, pH and EC were analyzed by their respective methods and the results of the analysis can be seen in the Table 5.

This research proves that boiler's fly ash has good characteristics to act as an adsorbent. Furthermore, the jar test method with stirring of 100 rpm and a contact time of 10 min was effectively applied in treating waste with the low adsorbent dose, which is 20 g FA per liter of liquid waste. The maximum decrease in wastewater quality parameters occurred in the N-NH_3 and TSS parameters. The results can be compared with a study by Mazhar et al. (2019) which manages pulp and paper wastewater with anaerobic and aerobic methods. They have reached reduction of 81% COD, 65% TSS, and 60 TDS.

The removal of COD and TSS using FA as adsorbent is higher than the biological method. This is because fly ash is able to absorb pollutants greater than the performance of microorganisms that are able to absorb finer solids dissolved in wastewater. All of the above parameter values are included in the quality standards for pulp and paper industrial

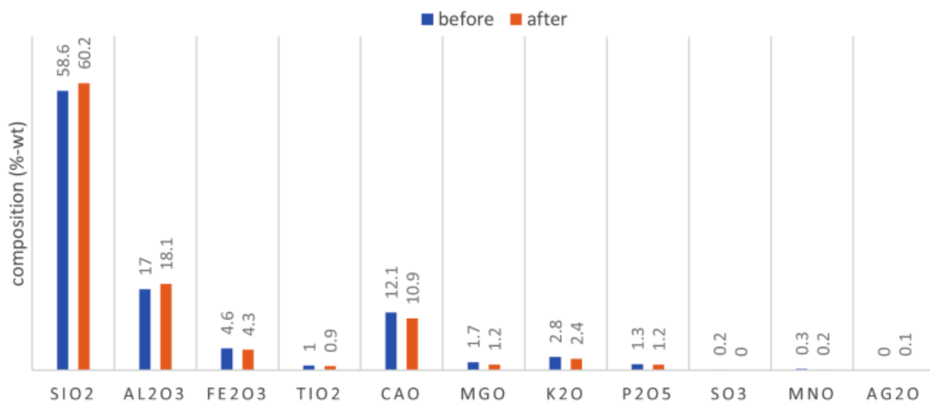

Fig.2. The chemical composition of FA before and after adsorption process.

wastewater according to the Regulation of the Minister of the Environment of the Republic of Indonesia.

The reduction in N-NH_3 content in PPILW is up to 95.41%. The value is highly dependent on the pH value of the wastewater and the alkaline nature of the FA adsorbent which contains a lot of alkali metals. This rapid increase in pH value is associated with the formation of different hydroxides when the pH of the solution increases. This indicates that only in its ionic form can ammonium be removed from solution by ion exchange. At pH 8 and below, most of the ammonium exists in its ionic form. Therefore, it is very possible to assume that these conditions are very good for the ammonium ion removal process so that the pH value of the FA adsorbent has a low ammonia value with a high pH compared to the liquid waste.

Many researchers have proven that fly ash will perform better if it is previously activated before the adsorption process. There are several methods used to activate adsorbents, including dealumination, ion exchange, and calcination methods. However, from the results of this work, when FA adsorbents are implemented directly in PPILW with no thermal activation, the efficiency results are very high, and this will reduce the cost of wastewater treatment processes for the pulp and paper industry if the wastewater will be managed using adsorption technology with FA as adsorbent.

3.4. *Elemental analysis of the fly ash adsorbent*

After being used in the waste treatment, the fly ash adsorbents (then called spent adsorbents) are separated by filtration from the liquid waste after the adsorption process. The composition of compounds in the FA adsorbent before and after the adsorption process is compared. The changes made can show a strong adsorption capacity of the materials in the treatment process. The results of the analysis can provide an overview of the effect of pollutant absorption from the wastewater on the characteristics of FA used as an adsorbent as seen in Fig. 2.

The largest compounds in the form of oxide in FA are Al_2O_3, SiO_2, CaO and Fe_2O_3. As seen in Fig. 2., after the adsorption process, the changes in the elemental composition in the FA were not too significant. This shows that in the adsorption process with FA adsorbent, the release of heavy metals into wastewater is low, but FA is still effective in adsorbing the ammonia compounds, reducing TDS and COD, and increasing pH, as shown in Table 5.

The content of aluminum (Al) and iron (Fe) oxides in FA has the potential to be used as a coagulant. Al and Fe-based coagulants have been widely known and used in water or wastewater treatment processes because they are able to bind colloidal particles, organic substances and impurities in the water (Nurul Ajeng Susilo, 2019).

The content of Fe in waters is one of the heavy metals that can harm living things that live in water if the content exceeds the specified threshold. According to Toczylowska-Mamińska (2020), Fe is an essential heavy metal, where its presence in certain amounts is needed by living organisms, but in excessive amounts it can cause toxic effects.

4. Conclusions

Solid waste of wood chips from the pulp and paper processing industry is generally used as boiler fuel. Boiler fly ash is produced in large quantities and has been tested for its performance in treating liquid waste from the internal mill. From this study, the boiler's fly ash can be directly used as an adsorbent without requiring thermal treatment/calcination. The performance shown by the FA adsorbent has been able to make most of the quality parameters of the pulp and paper industry liquid waste meet environmental quality standards. The effectiveness of treated and untreated FA adsorbents (with calcination) showed the same trend of good results. The removal efficiency achieved is TSS 92.5%, COD 83.31%, Chloride 19.99%, NH3 95.41%, TDS 19.6% and EC 19.6%. The best efficiency for reducing pollutant levels is in the adsorption process using a jar test with a dosage of 20 g of FA/L liquid waste and a stirring speed of 100 RPM for 10 min. Most of the water quality parameters after using *in situ* adsorbents have been met according to the National Environmental Quality Standard 2000 and the Indonesian Minister of Environment Regulation No. 14 of 2014.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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