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Methylene Blue Removal Using Microwave Activated Method of Solid Boiler Waste

Sofia Anita [1,*], Ganis Fia Kartika [1], Elvi Yenie [1], Itnawita [1], T. Abu Hanifah [1]

[1] Chemistry Department, Universitas Riau, Indonesia; sofia.anita@lecturer.unri.ac.id; ganis.kartika@lecturer.unri.ac.id (G.F.K.); elviyenie@yahoo.co.id (E.Y.); itnawita@lecturer.unri.ac.id (I.);
* Correspondence: sofia.anita@lecturer.unri.ac.id;

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Abstract: Bottom ash and fly ash are hazardous solid waste. They are produced from burning palm oil shells and fiber at a temperature of 900°C in palm oil mills. This study aims to characterize and utilize both types of ash boilers as an adsorbent for methylene blue dye. Adsorbent from boiler ashes was prepared using the microwave activation method at 100 watts with varying times (1; 2; 3; 4, and 5 minutes) to get the optimum efficiency of methylene blue dye. The non-activated and microwave-activated functional groups of ash were compared and analyzed using the Fourier Transform. Infrared, surface morphology, and elemental composition were analyzed and compared using Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy. The results showed that the optimum adsorption efficiency for 3-minute activation for bottom ash using methylene blue was 93.45% and fly ash was 99.94%, respectively. The activation process causes changes in the content of the adsorbent elements, i.e., loss of Fe element and increase in the percentage of elements of O, Si, P, K, and Al for bottom ash. Then, O, Mg, Al, Si, P, K, and Ca elements increased, and the loss of Fe and Cu for fly ash. The functional groups for both are unchanged due to the activated process.

Keywords: bottom ash; functional group; surface morphology; palm oil shell; adsorption efficiency.

1. Introduction

Based on statistical data [1], Indonesia is the world's largest palm oil production area, at about 48.3 million tons per year. The solid waste produced from crude palm oil mills was empty fruit bunches. Usually, it is used as fuel or composting material, and then, after combustion, it becomes hazardous ash. Empty fresh fruit bunches are now thought to have higher economic value [2]. The combustion process in the boiler produces waste in the form of ash. It is divided into fly ash with a lighter mass and bottom ash with a heavier mass. The combustion results in the boiler producing bottom ash waste of about 20 % of bottom ash and 80% of fly ash, which became an environmental concern [3]. Handling ash waste by landfilling also impacted the environment and surrounding communities, such as the dissolution of the chemical content in the ash so that it flew into the water [4]. Based on studies by [5], boiler ash was solid waste from biomass combustion of palm oil. It was used as a building material and adsorption material for wastewater treatment. Boiler ash contains lots of carbon and silica [6] found that boiler ash consists of silica, alumina, ferric oxide, and other oxides such as cenospheres [7] reported that boiler ash contained SiO_2, CaO, and MgO. As an adsorbent, boiler ash is processed. Methylene blue dye, for example [8]. The activation methods using chemical activators were costly and sometimes associated with secondary contamination. Currently, microwaves' activation method is more environmentally friendly because it reduces reaction time, side reactions, and less solvent and improves purity [9]. The principle of the microwave was due to dipole interactions. It caused the water molecules to interact with other molecules under an electrical field. Dipole-dipole interactions of polar molecules with electromagnetic radiation cause thermal effects [10,11] conducted microwave activation of pine sawdust using a power varying from 100 to 800 W. Under these conditions, the results showed that microwave activation increased the yields. The most important physical properties of the adsorbent were porous, and porosity [12] showed that the adsorbent surface area and pore volume of microwave heating were higher than conventional heating. Due to the quick heating and efficient method, the development of activation using microwaves was conducted by [13], using a microwave with an optimum time of exposure of 6.9 minutes and a power of 600 W to get the biochar yield of 36.98%. Coal bottom ash based on geopolymer had high compressive strength, and water adsorption by the additional use of microwave energy [14,15] found that coconut shells using a microwave at a low power of 100 W for 5 minutes produced 95% of color removal. The objectives of this work were to characterize bottom ash and fly ash boilers and measure the adsorption ability of boiler ash applied to methylene blue dye. According to [16], silica gel could absorb methylene blue up to 80% after 80 minutes at pH 5, higher than fly ash [17] discovered that coal bottom ash could be used to replace cement [18] also reported that coal fly ash-derived mesoporous silica material removed methylene blue at an optimum pH of 10.

2. Materials and Methods

Materials used in this research were bottom ash and fly ash boiler, methylene blue (Sigma-Aldrich), aqua DM and Whatman No. 42. Equipment used in this work were Analytical Balance (Mettler tipe AE200), Japan; Microwave (Panasonic convection microwave oven), Japan; Oven (Gallenkamp Hotbox Oven Size 1), Indonesia; Spektrofotometer UV-VIS (Shimadzu UV-1800 UV Spectrophotometer), Japan; Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy (SEM/EDS HITACHI FLEXSEM 1000, WD = 10 mm (T.O.A = 30°), ultra variable-pressure detector), Japan; Spectrophotometer FTIR (IRPrestige-21 Spectrophotometer Shimadzu, Japan, Single beam optics, DLATGS detector, Tungsten light source, Scan range 7800-350 cm^{-1}); 100 dan 200 mesh Sieves, pH meter (Horiba LAQUA act D-71), Japan and glasswares (Pyrex, Japan). In terms of the data analysis, the ANOVA statistic method was used for the preliminary treatment of data.

The sample used in this study was boiler ash in the form of bottom ash and boiler fly ash collected from one of the palm oil mills in Rokan Hulu Riau, which used boiler fuel in the form of palm shells and fiber. The type of boiler used at this mill was the Takuma N750 Water Tube with a combustion temperature of 900°C and a pressure of 23 bar.

Samples were sieved using 100 and 200 mesh and washed using aqua DM until neutral pH. Then, samples were dried in an oven at a temperature of 100 5°C for 24 hours and stored in a desiccator. The activation of bottom ash and fly ash boilers is irradiated using microwaves. Last, samples were activated for 1; 2 ; 3; 4, and 5 minutes. Activated samples were heated in an oven at a temperature of 100 5^{o}C for 1 hour and then cooled in a desiccator for 30 minutes. 0.1 g of samples were put into a 25 mL Erlenmeyer of 50 mg L^{-1} of bottom ash, and 30 mg L^{-1} of methylene blue was added to each sample, then stirred with a magnetic stirrer for 10 minutes. Then, the mixture was centrifuged at 3600 rpm for 5 minutes. The absorbance was measured at the optimum wavelength of 664 nm and control.

3. Results and Discussion

3.1. Adsorptivity analysis of bottom ash and fly ash boiler toward methylene blue.

The best microwave activation time in bottom ash and fly ash boilers was determined based on their adsorption power to methylene blue with a concentration of 50 mg L^{-1} for bottom ash and 30 mg L^{-1} for fly ash. At first, the initial concentration of methylene blue was the same, but then, the bottom ash remained minus concentration, so it concentrated to 50 mg/L. The results of the adsorption of methylene blue by bottom ash and fly ash boilers without activation and activated by microwave with a variation of activation time of 1; 2; 3; 4, and 5 minutes were shown in Table 1.

Table 1. Optimum methylene blue adsorption of bottom ash and fly ash boiler.

Microwave Activated time (minutes)	Bottom Ash			Fly Ash		
	Init. Conc (mg L^{-1})	**Adsorbed Conc./ remained (mg L^{-1})**	**Efficiency (%)**	**Init. Conc. (mg L^{-1})**	**Adsorbed Conc./ remained (mg L^{-1})**	**Efficiency (%)**
0	50.47	4.271	91.54	22.846	0.150	99.34
1	50.47	3.817	92.44	22.846	0.134	99.41
2	50.47	3.609	92.85	22.846	0.099	99.57
3	50.47	3.304	93.45	22.846	0.012	99.94
4	50.47	3.571	92.92	22.846	0.031	99.86
5	50.47	3.686	92.70	22.846	0.051	99.78

The result showed that fly ash boilers activated by microwave could adsorb methylene blue better than bottom ash. The percentage of optimum adsorption efficiency shown in bottom ash and fly ash boilers activated by microwave for 3 minutes was 93.45% and 99.94%, respectively. Bottom ash also acts as a low-cost adsorbent used to remove Malachite green (MG), Methylene blue (MB), and Crystal Violet (CV) dye in binary systems [19]. The washing process was carried out until the pH of the filtrate was close to neutral. It means that pH did not affect the adsorption process when the boiler ash adsorbent contacted the adsorbate. The filtrate of boiler ash in this study had a pH of 9.45 for bottom ash and 9.13 for fly ash. The brown filtrate indicated that the boiler ash was more alkaline in nature due to the metal oxide content. The final color of the filtrate was clear, and the final pH was 7.6 for bottom ash and 7.99 for fly ash, respectively. Methylene blue dye has a positive charge that can interact through electrostatic bonds with the negative charge of the adsorbent of the two types of boiler ash. The negative charge contained in the boiler ash was proportional to the amount of methylene blue adsorbed, so a high adsorption efficiency was obtained. Methylene blue removal decreased with an increase in initial concentration, particle size, and ionic strength [20].

3.2. Surface morphology.

Figure 1 and Figure 2 showed that Scanning Electron Microscope analyses for non-activated and activated surface morphology of bottom ash and fly ash. Bottom ash and fly ash that activated for 3 minutes had more pores than non-activated.

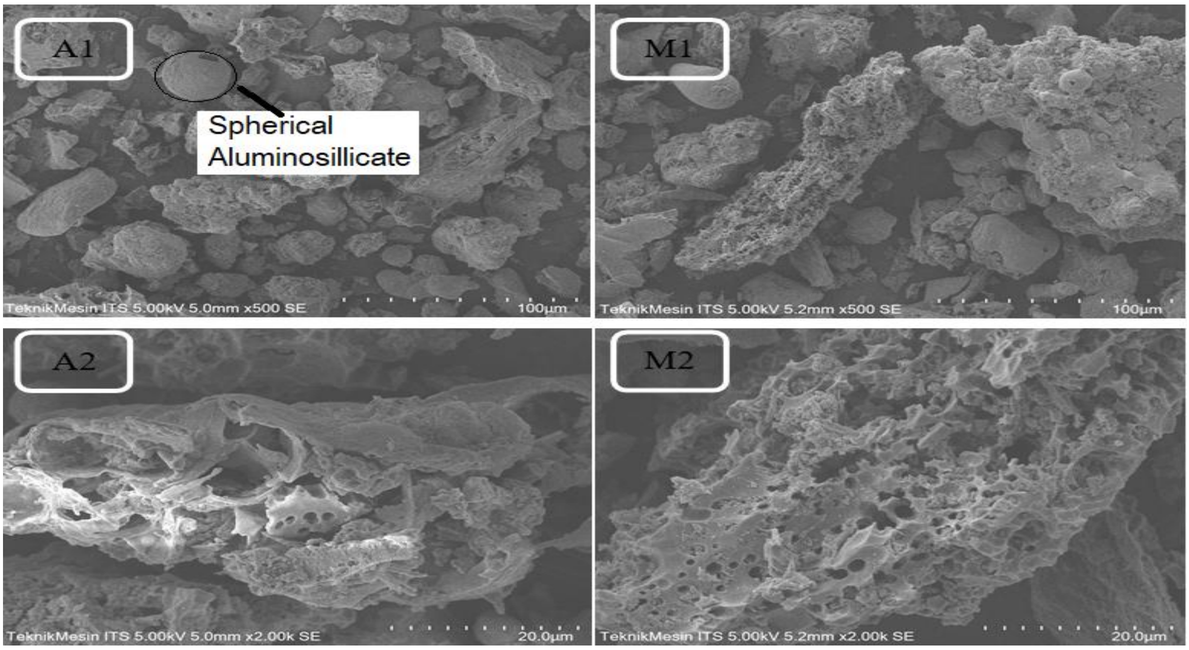

Figure 1. Surface morphology: non-activated bottom ash 500x enlarged (A1) and 2,000x enlarged (A2) and activated bottom ash 3 minutes 500x enlarged (M1) and 2,000x enlarged (M2).

It indicates that the activation process affected the number of pores in both boiler ash. Boiler ash and fly ash had a spherical microstructure morphology, indicating spherical aluminosilicate content. Non-activated bottom ash (B1) and fly ash (A1 and A2) had impurities on the surface because the pores were covered and clogged, meaning heterogeneous adsorbent.

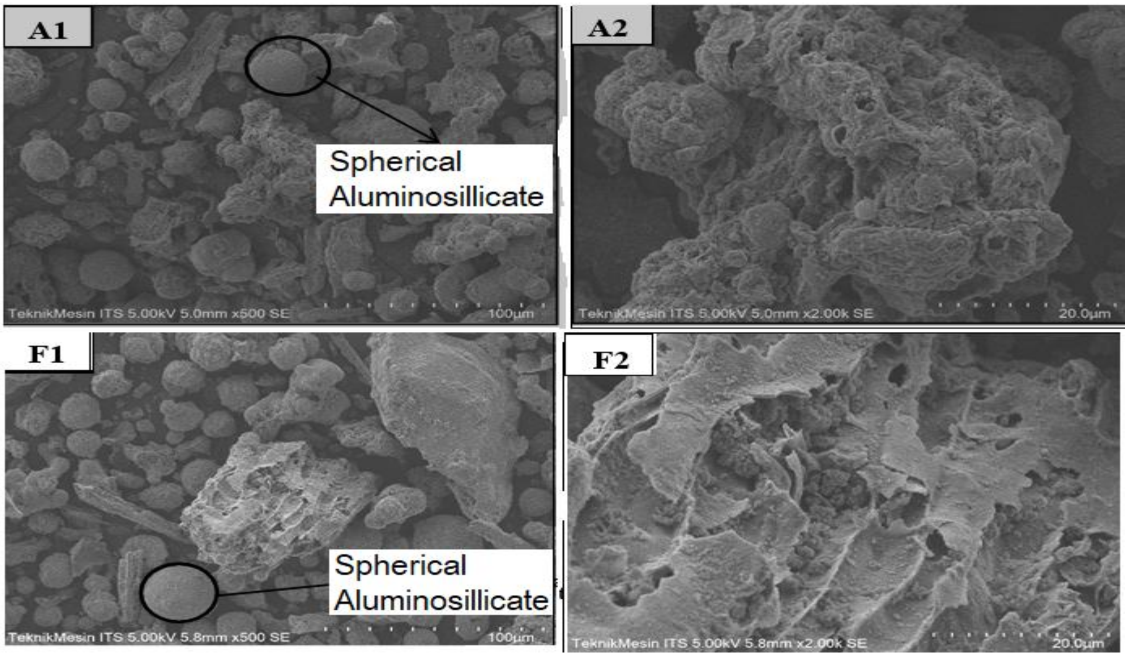

Figure 2. Surface morphology: non-activated fly ash 500x enlarged (A1) and 2,000x enlarged (A2) & activated fly ash 3 minutes 500x enlarged (M1) and 2,000x enlarged (M2).

3.3. Bottom ash dan fly ash boiler content.

Characterization of surface morphology and boiler ash content carried out using SEM-EDS. The spectra of the non-activated bottom ash EDS analysis and the 3-minute microwave irradiation showed in Figure 3 and Figure 4. The EDS spectra of non-activated fly ash and 3-

minute microwave activation showed in Figure 5. The elements contained in both boiler ash were O, Mg, Al, Si, P, K, Ca, Fe, and Cu.

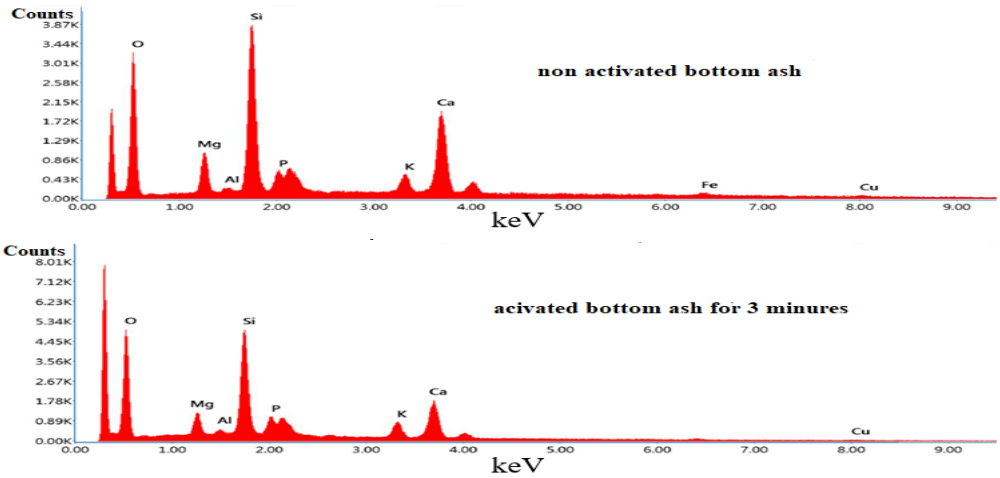

Figure 3. EDS Spectra of bottom ash.

The activation process causes increased content of several elements in the bottom ash and fly ash boiler. The composition of an element in the bottom ash was O, Mg, Al, Si, P, K, Ca, Fe and Cu. Activated bottom ash caused loss of Fe element, and the elements increased were O, Mg, Si, and Ca.

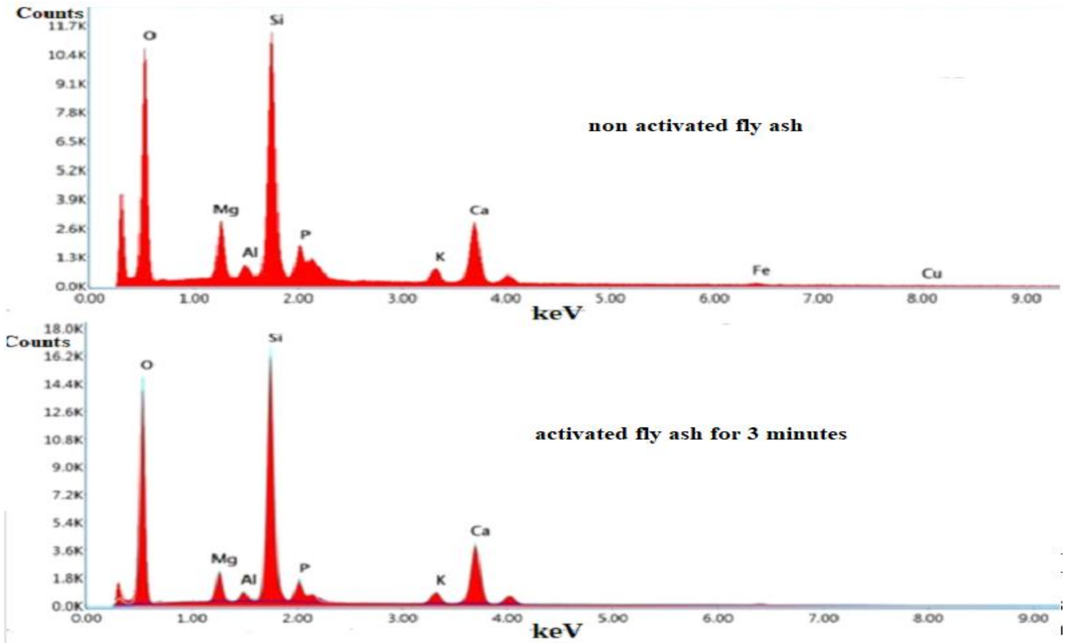

Figure 4. EDS spectra of fly ash non-activated and activated for 3 minutes.

Meanwhile, EDS data showed that non-activated fly ash also has O, Mg, Al, Si, P, K, Ca, Fe, and Cu elements, and activated samples loss of Fe and Cu elements. Activation at 3 minutes of microwave irradiation increased the content of O, Si, and Ca elements. Oxygen and Si were the most abundant elements. The spherical aluminosilicate might be degraded as Al, Si, and O elements. The other elements contained in the boiler ash were in the form of oxides. Microwave irradiation affected some elements to oxidize and evaporate. It explained by [7] that microwaves' activation process caused the evaporation of volatile substances, and an oxidation process occurred.

3.4. Functional groups of bottom ash dan fly ash boiler adsorbent.

The results obtained in this study, FTIR spectra produced on fly ash before and after activation, did not show any significant changes, as seen in Figures 5 and 6. There was only a slight shift in wavenumber and transmittance difference. Many silanol groups (Si-OH) were present on the surface of deprotonated silica in the form of Si-O-. In addition, the silanol group on the surface of the adsorbent interacted with the amine group through hydrogen bonds. This silicon dioxide compound was an active site that could act as an adsorbent because of the slightly reactive oxygen atoms. Silicon dioxide had a giant covalent bond structure that accommodated large amounts of the adsorbate. The atoms are linked to each other.

Table 2. Change of functional group of bottom ash and non-activated fly ash and microwave irradiated for 3 minutes.

Vibration	**Wavenumber (cm^{-1})**	
	Non-activated bottom ash	**3 minutes activated *bottom ash***
Si-O-Si	472.15	470.22
Si-O-Al	526.45	527.53
Mg-O	560.13	562.34
Si-O bending	784.10	784.10
Ca-O	875.72	874.76
Al-O	1000.37	1000.13
Si-O stretching	1037.75	1040.64
Vibration	**Wavenumber (cm^{-1})**	
	Non-activated bottom ash	**3 minutes *activated bottom ash***
Si-O-Si	365.53	364.50
Si-O-Al	492.83	434.00
Mg-O	514.05	562.34
Si-O bending	787.96	712.73
Ca-O	875.72	874.49
Al-O	1010.74	1000.13
Si-O streching	1350.75	1021.35

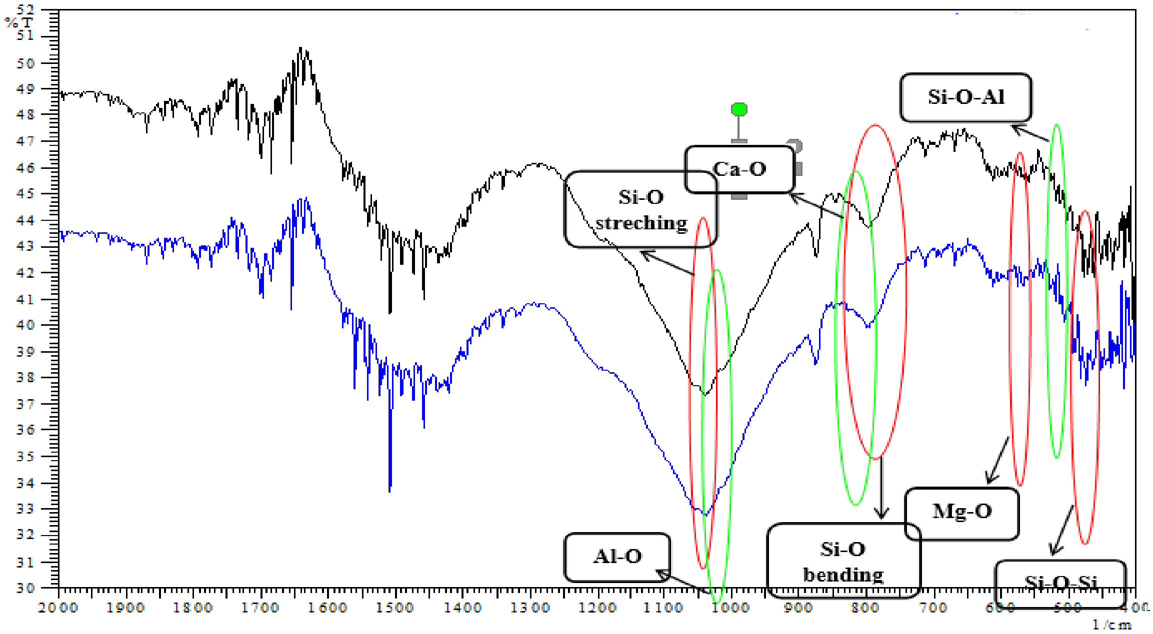

Figure 5. Functional groups of non-activated (blue line) and 3 minutes microwave irradiated (black line) bottom ash.

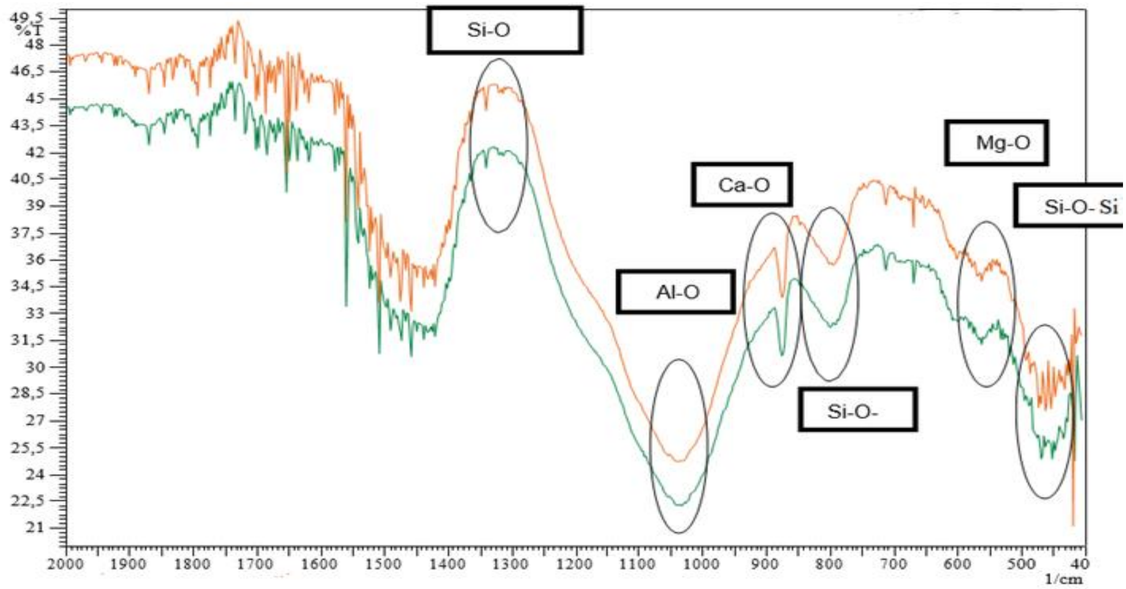

Figure 6. Functional groups of non-activated (blue line) and 3 minutes microwave irradiated (black line) fly ash.

3.5. Statistical analysis of the adsorption efficiency of the boiler ash.

Statistical determination using the ANOVA test proved that there was no difference in the variation of activation time on the adsorption ability of boiler ash, both without activation and activated by microwave at variations time. ANOVA test has a significant value of 0.000 (<0.05) for bottom ash and 0,008 for fly ash. These results were followed by Duncan's test, which showed that adsorption efficiency values have significantly different activation for each activated time. Based on these results, it concluded that activation with microwave radiation affects boiler ash.

4. Conclusions

The optimum time of microwave irradiation on the adsorption ability of methylene blue was 3 minutes at a power of 100 W for both boiler ash. The Methylene blue optimum concentration adsorbed was 3.304 mg L^{-1} for bottom ash and 0.012 mg L^{-1} for fly ash. This proved that the activation of fly ash had better adsorption ability than methylene blue. The adsorption efficiency of boiler ash on methylene blue dye increased with increasing activation time from 1 minute to 3 minutes and decreased adsorption efficiency with activation times of 4 and 5 minutes. The optimum activated time of boiler ash for 3 minutes was 93.45% for bottom ash and 99.94% for fly ash. Boiler ash consists of O, Mg, Al, Si, P, K, Ca, Fe, and Cu. Some elements change microwave irradiation due to evaporation and oxidation processes. It concluded that boiler waste as hazardous waste is used as an adsorbent to solve macromolecule dye pollution.

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Conflicts of Interest

The authors declare no conflict of interest.

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