Characterisation of Coal Fly Ash for Potential Wastewater Treatment Opportunities

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Abstract
Lakvijaya coal power plant, which is in Norochcholai, Puttalam District, Sri Lanka, is the largest coal power plant in Sri Lanka. It annually produces about 150,000 tonnes of fly ash (FA) as waste, and the management of it is a pressing concern. Various studies have been conducted to valorise FA in a useful manner without simply dumping it into the nearby lands. To this end, we propose the utilisation of FA in wastewater treatments to adsorb heavy metal ions in wastewater to promote environmental sustainability. The direct application of FA for that purpose may be questionable due to the contaminants present in the FA; however, it is reported commercially. Therefore, we attempt to initiate a pre-processed preparation route to ensure the leachate contains fewer contaminants compared to the use of raw FA. Washing is a commonly used preliminary pre-processing step, though it is not studied extensively in the literature with reference to the FA. Herein, we aimed to study the effects of the number of washing cycles and temperature on the characteristics of the FA. With the results, we could conclude that washing is an effective means of pre-processing to alleviate the contaminants of FA, *en route* for wastewater treatment.

Keywords: Preliminary separation, Washing cycles, Particle size distribution

1. Introduction

Coal is a fossil fuel, and it mainly consists of Carbon. There are four coal types: bituminous, sub-bituminous, lignite and anthracite. It is estimated that there are about 1070 billion tonnes of coal worldwide in 2019. Coal is used in power generation, steel production, cement manufacturing, and heating purposes. Coal plays a significant role as a source of power generation. Globally, 41% of all the sources used in power generation is coal [7].

Coal combustion is the burning of coal in the air to liberate thermal energy. This process is used to generate steam in electric power plants. FA, bottom ash, boiler slag, and flue gases are generated as by-products of coal-burning [6]. In this work, we focus on FA, and it constitutes 64% of the total by-product generation in coal combustion [3]. Though there is a utilising amount of FA, the high FA generating rate has become a huge problem in most countries due to the significant gap between the FA generation and utilising amount. The excess production of FA may cause excessive costs, groundwater contamination, air poisoning, and several health issues, especially in the respiratory system. However, the usage of FA in wastewater treatments to adsorb heavy metal ions is a useful application of FA.

SiO_2 and Al_2O_3 are present in the structure of FA as functional oxidised groups. The surface of silica (SiO_2) has a high affinity towards metal ions. The central ion of silicates (Si^{4+}) has a very strong affinity for electrons; therefore, the oxygen atoms that are bound to the silicon ions have low basicity, making the silica surface act as a weak acid. The oxygen atoms on the silica surface are free to react with water, forming surface silanol (SiOH) groups. The acidity of the silanol (SiOH) groups determines the dependence of the charge of the silica surface on pH. At low pH, a positively charged silica surface results, and at high pH values, a negatively charged surface prevails. Alumina and iron also show the same phenomenon of developing positive or negative charges depending on pH [4].

However, the direct application of FA for the adsorption of heavy metal ions may not give sufficient efficiency. When using FA in the adsorption of heavy metal ions, different pre-processing steps have been reported. FA has been subjected to many types of preliminary treatments such as mechanical activation, chemical modification, impregnation, and thermal or heat treatment (calcination at high temperature) for better performance and to get the required formulation for selected wastewater treatment technique [5].

In this study, we aimed to find the effects of the number of washing cycles and temperature of FA, concerning the particle size distribution (PSD) of residue and pH value and conductivity variations in the effluent.

2. Materials and Methodology

2.1 Sample Preparation

The FA samples used in the study were collected from the Lakvijaya coal power plant in Norochcholai, Puttalam District, Sri Lanka. The coal used in the Lakvijaya plant is imported from Indonesia [2]. The type of that coal is bituminous. The FA type which is generated from the burning of bituminous coal type is class F [1].

Table 1: Composition of FA – Sample A

Mineral ash analysis (Dry Basis)	Unit	ASTM Standard	Results
SiO_2	%	D4326	55.38
Al_2O_3	%	D4326	23.96
Fe_2O_3	%	D4326	8.12
CaO	%	D4326	4.96
MgO	%	D4326	1.26
Na_2O	%	D4326	0.38
K_2O	%	D4326	1.26
P_2O_5	%	D4326	0.33
TiO_2	%	D4326	1.18
Mn_2O_4	%	D4326	0.18
SO_3	%	D1757	2.28
Undetermined	%		0.71
Total	%		100

Table 2: Composition of FA – Sample B

Mineral ash analysis (Dry Basis)	Unit	ASTM Standard	Results
SiO_2	%	D4326	49.88
Al_2O_3	%	D4326	29.22
Fe_2O_3	%	D4326	2.83
CaO	%	D4326	8.55
MgO	%	D4326	1.84
Na_2O	%	D4326	0.18
K_2O	%	D4326	0.68
P_2O_5	%	D4326	1.95
TiO_2	%	D4326	1.52
Mn_2O_4	%	D4326	0.05
SO_3	%	D1757	3.10
Undetermined	%		0.2
Total	%		100

FA sampling was carried out according to the D2234 and D7430 standards in ASTM. Two samples were collected during the entire discharging from the vessel. Both FA samples were analysed using X-ray Fluorescence (XRF) equipment to obtain the composition of the FA of the Lakvijaya coal power plant. The XRF analysis results of two FA samples are presented in Table 1 and Table 2.

Furthermore, twenty 200 g FA samples were measured using an electronic mass balance from OHAUS® Discovery.

2.2 FA Pre-processing

Prepared 200 g FA samples were introduced to the pre-processing stage.

200 g FA sample was put into a 1-litre beaker, and the distilled water from the Banstead EASYpure® II water system at room temperature was poured until the 1-litre mark. To complete a one washing cycle, the sample was stirred for 15 minutes using a magnetic stirrer (AM4) from VELP® and kept settling for 15 minutes (at room temperature). After the settling, the first washing cycle was completed. Then the top water layer was removed, and the bottom FA layer was transferred to another 1-litre beaker, and it was filled with distilled water up to the 1-litre mark and kept at room temperature. Likewise, FA washings were conducted for 1, 3, 5, 7, and 10 number washing cycles at room temperature (RT), 50° C, 70° C, and 90° C.

After finishing the respective washing cycles, residue bottom samples were collected and analysed for the size distribution using FRITSCH ANALYSETTE 22 Laser particle sizer. Finally, the effluents of respective washing cycles were tested for the pH and conductivity values using a SensION-1 pH meter from Hach® and an HQ40D digital conductivity meter from Hach®.

3. Results and Discussion

3.1 Variation of pH Value

The results of the pH value of the solution after a respective number of washing cycles at a respective temperature are presented in Table 3.

The results are graphically represented in Figure 1. The maximum pH value has been reported as 12.10 for the sample with one washing cycle at 50° C. The minimum pH value has been reported as 10.79 for the sample with 10 washing cycles at 90° C. So, it can be concluded that the solution always takes an alkali nature throughout all the washing cycles at different temperatures. When the overall trend of the graph is considered, the pH values of the solutions decrease with the increasing number of washing cycles.

Table 3: pH values of the solutions.

WC	RT	50° C	70° C	90° C
1	11.75	12.10	11.71	11.61
3	11.86	11.73	11.48	11.69
5	11.73	11.29	11.16	11.34
7	10.97	10.89	11.20	11.18
10	10.85	10.89	10.88	10.79

*WC – No. of Washing Cycles

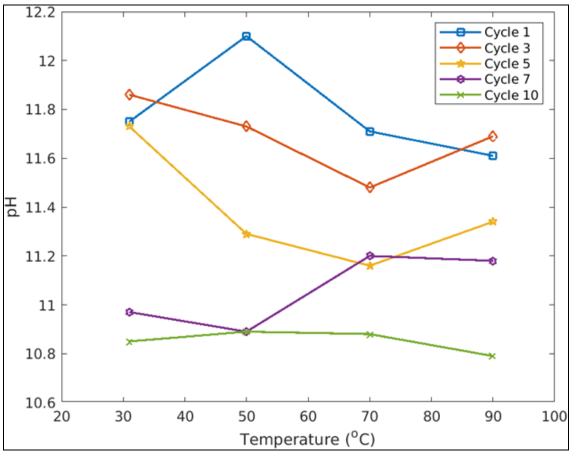

Figure 1: Temperature dependence of the pH of the solution with different washing cycles.

3.2 Variation of Conductivity

The results for the conductivity values of the solution after a respective number of washing cycles at a respective temperature are presented in Table 4.

Table 4: Conductivity values of the solutions.

WC	RT (mS/cm)	50° C (mS/cm)	70° C (mS/cm)	90° C (mS/cm)
1	3.42	6.96	6.40	5.48
3	3.61	4.56	4.34	4.41
5	2.50	2.45	2.30	2.40
7	1.39	1.41	1.89	1.88
10	0.87	0.99	1.83	2.00

The results are graphically represented in Figure 2. The maximum conductivity value has been reported as 6.96 mS/cm for the sample with one washing cycle at 50° C. The minimum conductivity value has been reported as 0.87 mS/cm for the sample with 10 washing cycles at RT. When the overall trend of the graph is considered, the conductivity values of the solutions decrease with the increasing number of washing cycles.

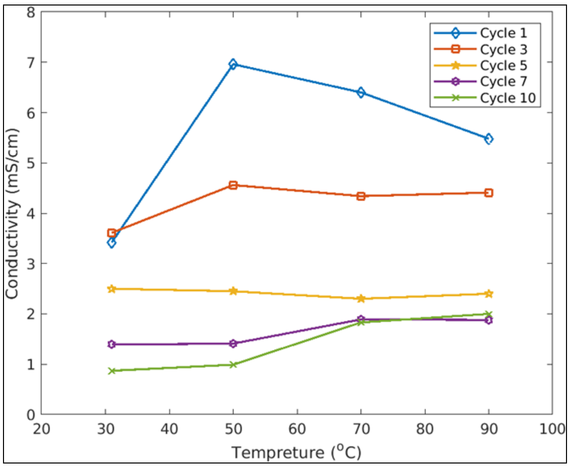

Figure 2: Temperature dependence of the conductivity of the solution with different washing cycles.

3.3 Particle Size Analysis

Table 5: The average mode diameter size of the bottom samples.

Sample name	Average mode diameter of the sample (µm)
Raw FA	31.29
Sample with one washing cycle at RT	24.12
Sample with one washing cycle at 50° C	23.25
Sample with one washing cycle at 70° C	24.47
Sample with one washing cycle at 90° C	20.26
Sample with three washing cycles at RT	25.46
Sample with three washing cycles at 50° C	33.03
Sample with five washing cycles at RT	29.34

A raw FA sample and the bottom samples; the sample with one washing cycle at RT, the sample with one washing cycle at 50° C, the sample with one washing cycle at 70° C, the sample with one washing cycle at 90° C, the sample with three washing cycles at RT, the samples with three washing cycles at 50° C and the sample with five washing cycles at RT were analysed, and the average mode diameter of each sample is tabulated in Table 5.

The result of each sample is graphically presented in Figure 3 to Figure 10. The variation of the average mean diameter of the bottom sample with the number of washing cycles at a similar temperature value is represented in Table 6.

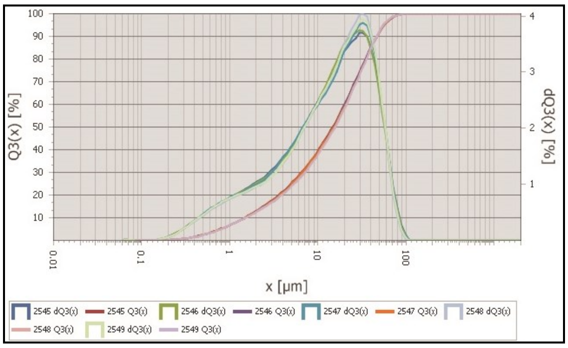

Figure 3: PSD of the raw FA sample.

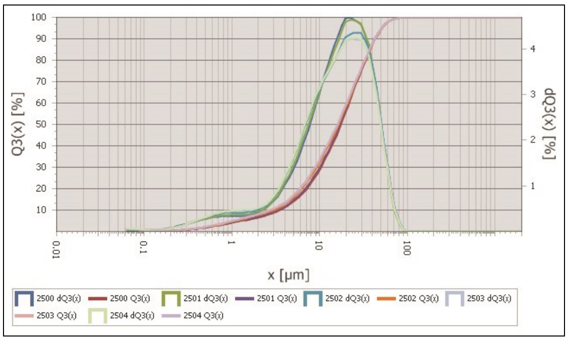

Figure 4: PSD of the bottom sample with one washing cycle at RT.

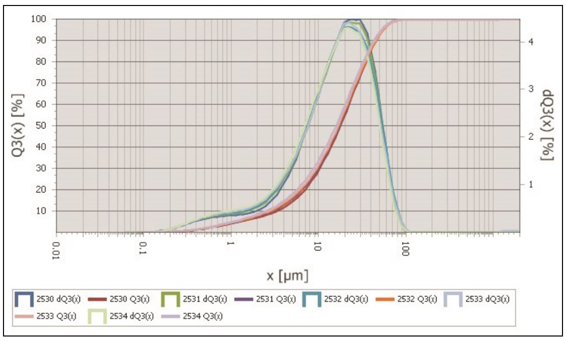

Figure 5: PSD of the bottom sample with one washing cycle at 50° C.

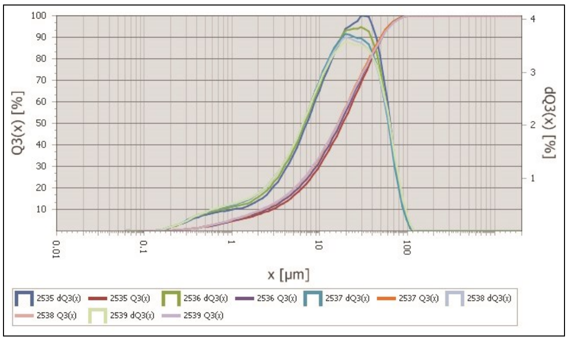

Figure 6: PSD of the bottom sample with one washing cycle at 70° C.

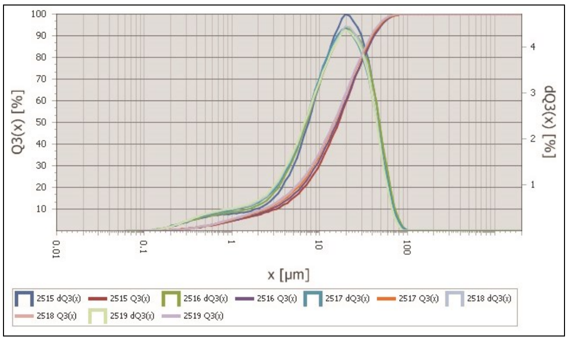

Figure 7: PSD of the bottom sample with one washing cycle at 90° C.

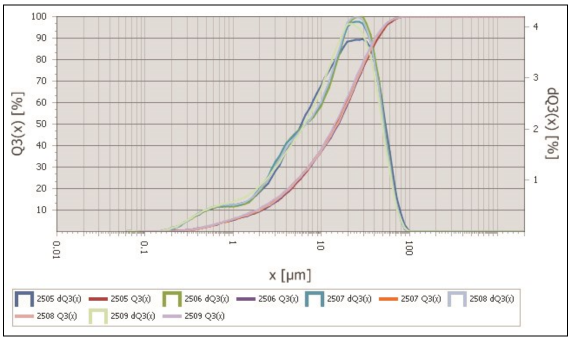

Figure 8: PSD of the bottom sample with three washing cycles at RT.

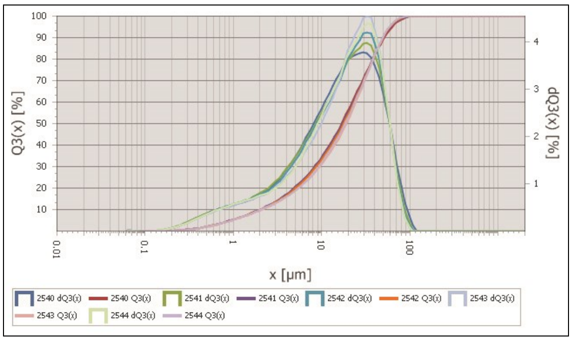

Figure 9: PSD of the bottom sample with three washing cycles at 50° C.

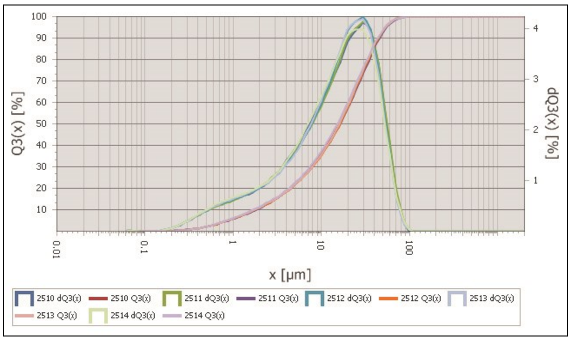

Figure 10: PSD of the bottom sample with five washing cycles at RT

Table 6: Bottom sample particle diameter size variation with the number of washing cycles.

Sample name	**Average mode diameter (µm)**
Sample with one washing cycle at RT	24.12
Sample with three washing cycles at RT	25.46
Sample with five washing cycles at RT	29.34

According to the data of the above table, the mode particle diameter value in the bottom sample is increasing with the increasing number of washing cycles.

The variation of the average mean diameter of the bottom sample with different temperature values at a similar number of washing cycles is presented in Table 7.

Table 7: Bottom sample particle diameter size variation with the temperature

Sample name	**Average mode diameter (µm)**
Sample with one washing cycle at RT	24.12
Sample with one washing cycle at 50° C	23.25
Sample with one washing cycle at 70° C	24.47
Sample with one washing cycle at 90° C	20.26

The highest value for the mode diameter size has been reported to the sample with one washing cycle at 70° C as 24.47 µm. The lowest value has been reported to the sample with one washing cycle at 90° C as 20.26 µm. A visible trend cannot be identified in the available data set for the variation of mode particle diameter in the bottom samples with increasing temperature at a constant number of washing cycles.

4. Conclusions and Recommendations

According to the observed compositions of FA samples, it can be concluded that the raw FA sample shows similar characteristics to class F FA. The pH value of the solution decreases with the increase in the number of washing cycles. But the solution gets an alkali nature throughout all the number of washing cycles. As the ion concentration in the FA sample decreases with the increment of the number of washing cycles, it can be concluded that washing is a good pre-processing method as it can be used to decrease the ion concentration in FA sample, which can be interruptive for the adsorption process of heavy metal ions in wastewater. An AAS analysis can be conducted to identify the types of ions that remain in the solution after the given number of washing cycles. A clear relationship was not observed between the mode particle diameter size in the bottom sample and the temperature value of the water which is used to wash the FA samples. However, further comprehensive experiments are recommended to draw precise conclusions. The mode particle diameter size value in the bottom sample increases when the number of washing cycles is increased.

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