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Investigation of the use of Botswana coal fly ash as a material for the adsorption of arsenic from fortified water

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Abstract: The main objective of the study was to characterize raw (RFA), water-washed (WFA) and iron-modified (Fe-WFA) Botswana coal fly ash to determine the physical and chemical properties as well as investigate its potential use as adsorbents for the removal of arsenic(III) ((As(III))) from fortified water. Scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS) showed particles with irregular size and shape for all the materials and porous iron oxide flakes for Fe-WFA. The SEM-EDS, X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS) showed the main constituents of RFA, WFA and Fe-WFA to be SiO₂, Fe₂O₃, Al₂O₃ and CaO. The XPS further showed the surface composition of Fe-WFA with higher Fe content at 19.7% compared to 0.8% and 1.2% for RFA and WFA respectively. The XRF and XRD results confirmed the successful modification of WFA with iron by showing the Fe₂O₃ composition increasing from 12.6% of WFA to 25.5% for Fe-WFA. The inductively coupled plasma-mass spectrometry (ICP-MS) results showed continuous reduction of metal concentrations for WFA and Fe-WFA from the first to the sixth wash. The adsorption of As(III) on the adsorbents followed the Freundlich adsorption model. The maximum adsorption capacities of 0.85, 0.02 and 2.26 mgg⁻¹ were obtained for RFA, WFA and Fe-WFA respectively.

Keywords: coal fly ash; iron oxide; water; characterization; arsenic

1. Introduction

Coal fly ash is one of the major waste byproducts from the coal combustion process in thermal power plants. It is produced in large quantities by thermal power plants and usually disposed in landfills, that results in pollution of the environment due to its high content of toxic metals [1]. Botswana's energy source is mainly electricity obtained through thermal combustion of coal. Morupule coal mine, situated in the outskirts of Palapye in the central district of Botswana, is the main supplier of coal to Morupule power station. Morupule power station is a coal fired power plant responsible for the main supply of electricity in the country. The power station produces about 350 tonnes of fly ash per day [2], thus poses a challenge in its disposal. Continued growth in demand for power means there will also be growth in the production of fly ash therefore, there is a need to find ways of recycling coal fly ash to reduce landfill disposal. The current applications of fly ash include use in the construction industry, ceramic industry, catalysis, depth separation such as the recovery of unburnt carbon, zeolite synthesis, soil amendment, agricultural use and limited use in water purification [1]. The main constituents of coal fly ash are silica, alumina, ferrous oxide, calcium oxide and varying amounts of carbon [3]. The fly ash

composition, unburned carbon content, distribution of elements, and particle size are influenced by the combustion temperature, air-to-fuel ratio, coal particle size, and combustion rate [4]. The characterization of the particle size, porosity, morphology, surface area, chemical structure, functional groups, chemical composition, and surface composition provide the physical and chemical properties that determine the suitability of coal fly ash for use as an adsorbent [5].

Botswana is a land-locked semi-arid country that experiences long periods of drought resulting in limited available surface water. The limited surface water also undergoes high evaporation rate due to high temperatures that can go up to 40 °C [6]. Recently, water rationing exercises have been carried out in the country to manage the limited water resources. Although it appears the whole of Botswana is covered with aquifers, the amount of extractable water resources in most aquifers is limited due to their generally low transmissivities, storage and recharge rates [7]. The high total dissolved solids, nitrates, iron, manganese, arsenic and fluoride content make some of the extractable ground water resources unsuitable for human and livestock consumption [7]. Metals and metalloids are natural components of the earth's crust and have bioaccumulation tendencies causing environmental pollution and can enter the body through food, drinking water and air. They may be solubilized in ground water through natural processes or by change in soil pH. The landfill leachate, sewage and leachate from mine tailings are also sources of contamination for ground water with metals [8]. Some of the elements are useful to the body at lower quantities but very toxic at high quantities. Factors that contribute to the presence of metals in surface water include adsorption from sediments, organic and inorganic matter, pH and temperature [9]. Arsenic (As) is known to cause diseases such as hyperkeratosis, black foot disease, skin, lung and bladder cancers, diabetes, anemia, and disorders of the immune nervous and reproductive systems [10]. It occurs in ground water in the inorganic form, as either arsenate or arsenite oxyanions. There have been reports of elevated arsenic in groundwater of the Okavango Delta and Maun [7]. This was discovered during the second phase of the Maun groundwater development project. The characterization of arsenic occurrence in the water and sediments of the Okavango Delta was carried out in boreholes drilled to enhance water supply in Maun and neighboring villages. It was discovered that 6 out of 20 boreholes drilled were found to have arsenic values exceeding 10 µg/L, the highest value obtained being 116.6 µg/L [7]. The results of the arsenic analysis of the water reported by Huntsman-Mapila et al. from the Okavango Delta indicated that As(III) is slightly more predominant than As(V) [7] and As(III) exist as uncharged therefore the most difficult to remove. The study is therefore focused on the removal of As(III) to determine if the RFA, WFA and Fe-WFA are able to remove As(III). World Health Organization (WHO) has the guideline value of arsenic in drinking water to be 10 µg/L and designated as provisional [11]. The United States (US) Environmental Protection Agency (EPA) lowered the maximum contaminant level from 50 µg/L to 10 µg/L in public water supplies [12]. Consequently, there is a need for the development of low-cost remediation methods for removal of arsenic and other trace metals in water for enhanced supply of potable water. Reusing coal fly ash to eliminate pollutants from water would solve both the waste management problems and water quality issues in Botswana and elsewhere [13].

Most of literature available focuses on the conversion of fly ash to zeolite before modification which makes the material expensive due to use of heat/electricity and excessive amount of sodium hydroxide therefore, the study focuses on exploring a cheaper, simple and energy saving route of utilization of the coal fly ash. Currently in Botswana, fly ash is mainly utilized for production of cement and there is limited literature about its characterization to examine its applicability in water treatment applications. Therefore, the main aim of this study was to (1) add to knowledge by comprehensively characterizing Botswana coal fly ash (2) determine its potential application in removal of As(III) from water. Furthermore, the study highlights the first application of Botswana coal fly ash (raw, washed and iron-modified) as materials for removal of As(III) from water without following expensive route of converting fly ash to zeolites before modification.

2. Materials and methods

2.1. Sample collection and preparation

The coal fly ash was collected from Morupule B power station located in Palapye (Botswana). The sampling was carried out by the Building Materials Science division of (BITRI) and sub-sampling for water treatment project was carried out by collecting 20 L bucket full of fly ash from 1 bag. The fly ash was stored in a bucket with a lid in the preparation laboratory at room temperature.

2.2. Fly ash pre-treatment with water

About 100 g of RFA powder was placed in a 500 mL conical flask followed by addition of 450 mL deionized water. The mixture was shaken using the automatic shaker set at 150 rpm for 1 h followed by resting the solution on the table for about 30 min. The liquid was then decanted, and the washing processes were repeated about 9 times. The WFA was then dried at room temperature.

2.3. Modification of fly ash with iron salts

About 20 g of WFA was added into 200 mL deionized water and stirred for about 10 min. A 1 M Fe_2SO_4 solution was prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Puriss, 99.5%–104% assay) purchased from Sigma Aldrich from Republic of South Africa by adding 7 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ into 25 mL deionized water. The 1 M Fe_2SO_4 was then used because it gave iron oxide content like what the coal fly ash had before washing pre-treatment. The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was added into the fly ash and continuously stirred for 30 min. About 25 mL of 1 M sodium hydroxide (NaOH) was prepared by dissolving the Reagent grade ($\geq 98\%$) NaOH pellets purchased from Sigma Aldrich Republic of South Africa in deionized water. 1 M NaOH was then added to the coal fly ash and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ mixture followed by stirring for 30 min. The product was filtered and washed with 500 mL deionized water and was left to dry at room temperature.

2.4. Characterization of the fly ash

The RFA, WFA and Fe-WFA were characterized with a Carl Zeiss Gemini scanning electron microscopy coupled with energy dispersive X-ray spectrometer

(SEM-EDX) to highlight the morphology and composition. The powdered samples were pre mounted on the SEM stub by spreading them thinly on the double-sided adhesive tape. The secondary electron imaging mode (SEI) was used for imaging and the EDX to determine the chemical composition of the fly ash. The surface area, pore size and total pore volume were determined with the Micromeritics Brunauer, Emmett and Teller (BET) 3Flex version 5.02 using N₂ adsorption-desorption at analysis temperature of 76.5 K. Fourier-transform infrared spectroscopy (FT-IR) characterization was carried out with a Thermo Scientific Nicolet Is50 FT-IR at a wavelength range of 4000–400 cm⁻¹. A Kratos Axis Supra X-ray Photo Spectroscopy (XPS) with the ESCApe software and S8 Tiger Bruker X-ray Fluorescence Spectrometer (XRF) with spectra plus v3.0.2.1 software, using quant-express measurement mode, were used to study the surface composition of the materials. An Empyrean PANalytical: X-ray diffractometer (XRD) with High Score Plus V4.8 software was used to determine the crystalline mineral phases of the RFA, WFA and Fe-WFA. Sample preparation involved pressing the RFA, WFA and Fe-WFA into pellets, crushing with a mortar and pestle followed by mounting in a sample holder before analysis and mounting the sample as received on sticky tabs with double sided C tape for XRF, XRD and XPS analysis respectively. A Mettler Toledo Thermogravimetric Analyzer (TGA), model TGA/DSC 3+ and STARe software was used for the determination of loss of ignition by a two atmosphere TGA analysis technique using the powders as received with temperature range of 25–950 °C and gas flow rate of 75 mL/min. The Speedwave Xpert microwave digester (model SW-X (EXPERT)) was used for acid digestion of RFA, WFA, Fe-WFA before analysis by the ICPMS for metals with lower concentrations and microwave plasma-atomic emission spectrometer (MP-AES) for metals with concentration at ppm levels.

2.5. Metal content determination

About 0.1 g of RFA, WFA, Fe-WFA were weighed into a conical flask in 5 replicates. Sample digestion was carried out by adding 6 mL of 37% HCl purchased from Sigma-Aldrich, Republic of South Africa (37%, purris, ACS grade) and 2 mL of 70% EMSURE nitric acid (HNO₃) purchased from Merk (ACS grade) and the digestion was allowed to occur overnight at room temperature. Sample digestion was completed with a steam bath for 2 h (temperature was not measured but boiling water was used to produce steam for steam bath).

The samples were then removed from the steam bath and left in a fume hood to cool to room temperature. The samples were then filtered with a Whatman qualitative filter paper with 150 mm diameter into a 25 mL volumetric flask and filled to the mark with water (18.2 MΩ·cm, TOC = 3 ppb) obtained from a Milli-Q water purification system. A multi element standard stock solution with varying concentrations was used to prepare calibration standards. A Thermo Scientific Inductively coupled plasma-mass spectrometry (iCAP-Q ICP-MS) was used for quantification of trace elements using the QTegra software.

2.6. Leaching behavior of metals from fly ash

The ASTM D-3987 Standard Practice for Shake Extraction of Solid Waste with

Water method was used to study the leaching behavior of RFA, WFA and Fe-WFA. About 2.4 g was weighed into 50 mL centrifuge tubes and 48 mL deionized water was added to make a solid-to-liquid ratio of 1:20, prepared in 6 replicates. A Lenton automatic shaker of model 262, bought from Republic of South Africa was used to agitate the samples at 200 rpm for 18 h. The samples were then allowed to stand for 5 min followed by centrifugation at 3000 rpm, for 15 min at 25 °C. A Whatman (grade 1:11 µm) qualitative filter paper was used to filter the samples followed analysis with the ICP-MS. The washing process was repeated 6 times.

2.7. Removal of As(III) from water

Batch adsorption experiments were carried out for RFA, WFA, and Fe-WFA. About 2 g of the powder was weighed separately into 50 mL centrifuge tubes in 6 replicates of each material. Ultra-pure water was spiked with As(III) standard to make it 500 ppb as the preliminary concentration and 25 mL was added into each centrifuge tube containing the powders. Only As(III) was used for this experiment as it is the form that is most difficult to remove compared to As(V). The samples were then shaken for 2 h at 200 rpm with an automatic shaker. The samples were centrifuged at 3000 rpm for 10 min with the temperature set at 20 °C to avoid deterioration of analyte by high temperatures followed by filtering with the Whatmann filter paper. Analysis was carried out with the ICP-MS with a calibration range of 125 ppb–1000 ppb.

2.8. Adsorption isotherms and kinetic parameters

About 2 g of RFA, WFA, Fe-WFA ash was weighed in triplicates into 50 mL centrifuge tubes. A 25 mL aliquot of the 10 ppm As(III) standard was added and the mixture agitated in the automatic shaker set at 160 rpm. Time was varied at 15 min intervals from 15 min to 2 h. The resultant solution was then decanted, filtered, and analyzed with the ICP-MS. The results obtained were used to model adsorption kinetic parameters. Maximum adsorption time was obtained from the kinetic experiments and was used as a constant time for adsorption isotherm experiments. The adsorption isotherm experiments were carried out by weighing about 2 g of the RFA, WFA and Fe-WFA s in triplicates into 50 mL centrifuge tubes. A 25 mL aliquot of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ppm As(III) standard was added and the mixture agitated using the automatic shaker at 160 rpm, for 75 min. The spiked solutions were then decanted, filtered with 0.45 µm syringe filters and analysed with an ICP-MS.

3. Results and discussions

3.1. Characterization of RFA, WFA and Fe-WFA

3.1.1. FT-IR

Figure 1 shows the FT-IR spectra of RFA, WFA and Fe-WFA at a range of 4000–400 cm^{-1} . The bands at 675 and 667 cm^{-1} correspond to Si-O-Al stretching vibration for RFA and Fe-WFA respectively. The valence oscillation of Al/Si-O-Al/Si is shown at 1094 and 1096 cm^{-1} for RFA and Fe-WFA respectively while the peak shifted to 1046 cm^{-1} for WFA. A peak is also observed at 3396 cm^{-1} for Fe-WFA and is attributed to –OH associated with iron oxyhydroxide. The results of RFA and Fe-WFA

are comparable to the one reported by Chen et al. [14].

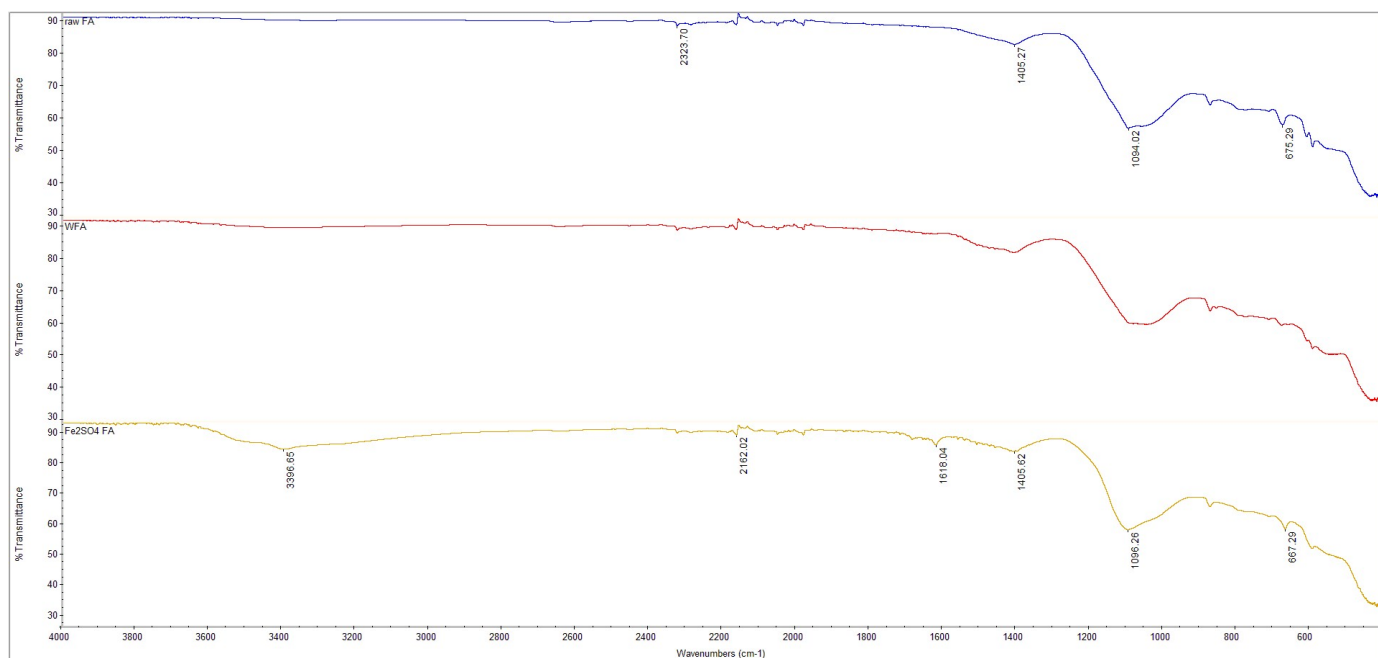
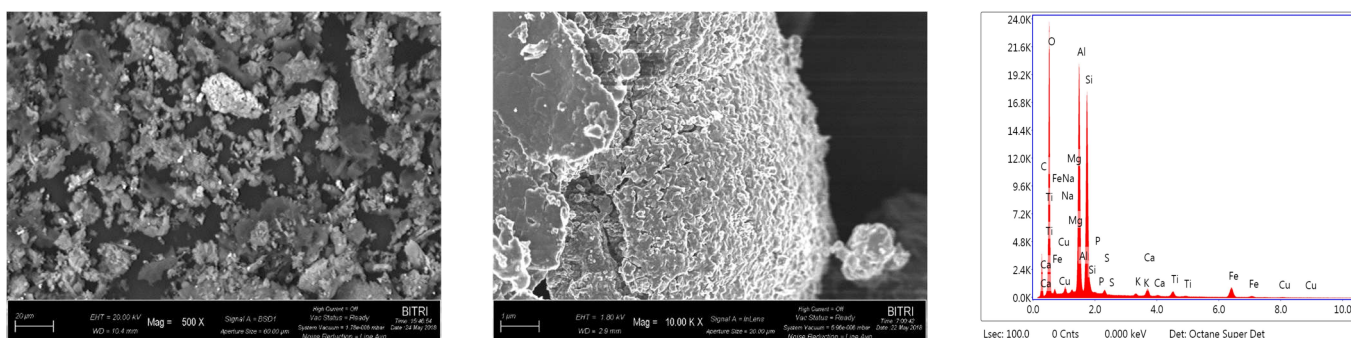


Figure 1. FT-IR spectra of RFA, WFA and Fe-WFA with a range of 4000–400 cm^{-1} .

3.1.2. SEM-EDX characterization

Figure 2a–c shows SEM images of RFA, WFA and Fe-WFA at 500 X and 10.00 kX magnifications. Loose, fine, irregular size and shape particles with rough surface are observed in the raw RFA. The irregular shapes may be due to unburnt carbon, amorphous particles that have undergone diffusion in contact with other particles or rapid cooling, magnetic iron oxide particles and mineral [15]. **Figure 2b** highlights the morphology of WFA showing a porous structure compared to RFA. Mulder explains that the increase in porosity maybe due to the leaching of soluble materials like chlorides [16]. **Figure 2c** is the morphology after WFA was modified with Fe_2SO_4 showing iron oxide flakes that have grown on the surface of the WFA. The EDS results show that there is no significant difference between the RFA and the WFA. More pronounced peak for Fe was highlighted for both the RFA and the Fe-WFA and similar results were reported by Chen et al. [14].



(a)

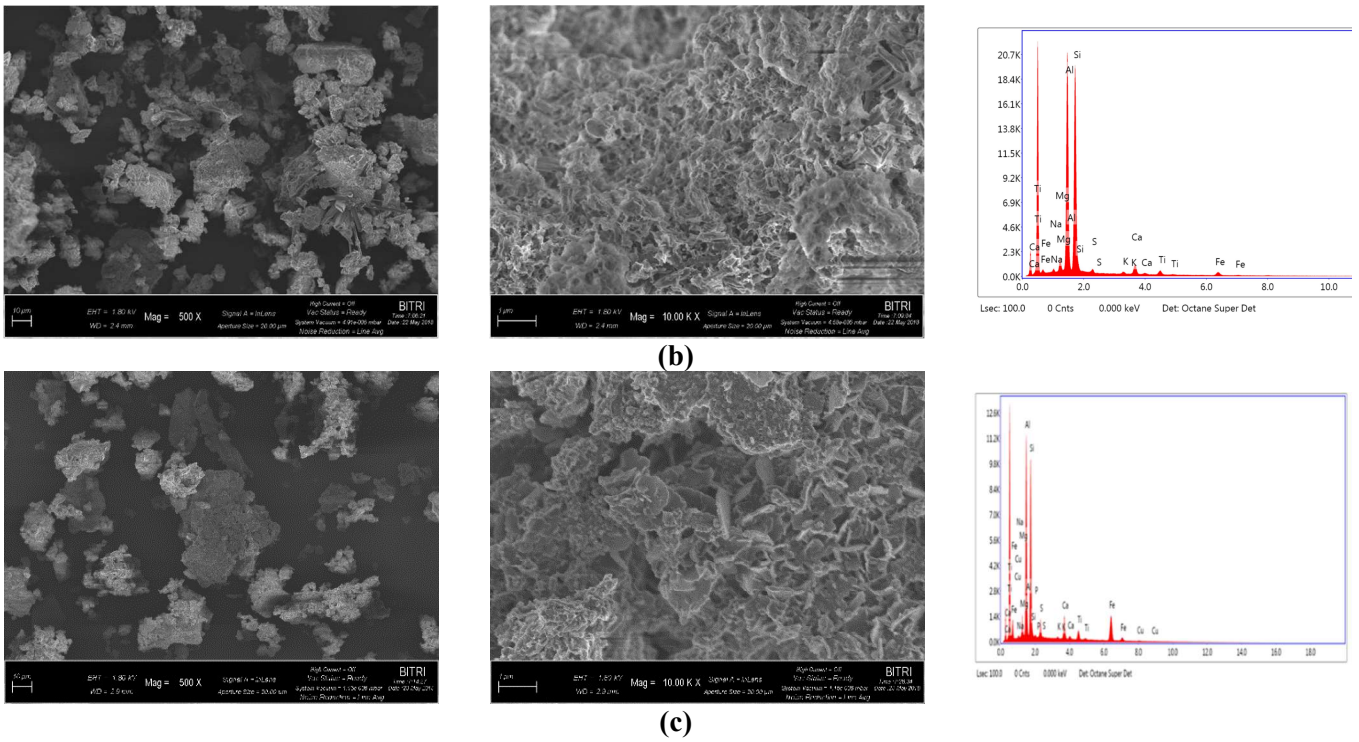
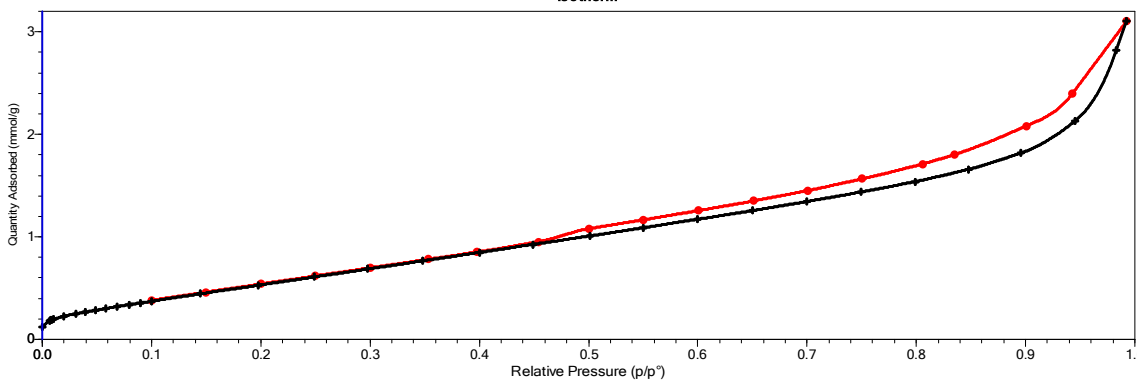
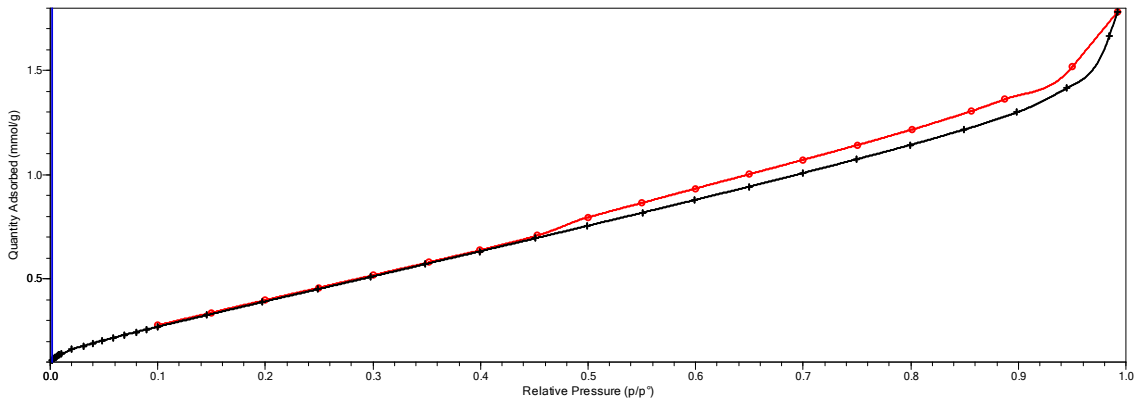
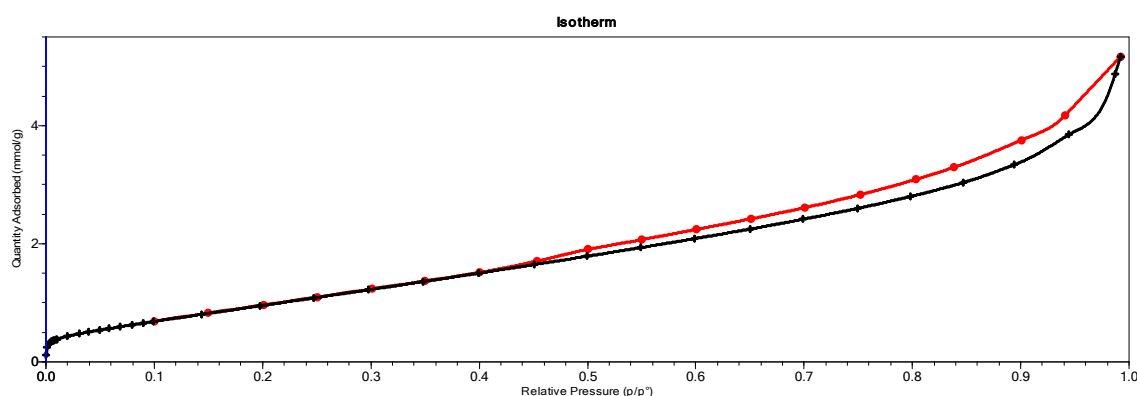


Figure 2. SEM images (500 X and 1000 kX magnification) and EDS results of (a) RFA; (b) WFA; (c) Fe-WFA.

3.1.3. BET characterization





(c)

Figure 3. N₂ adsorption-desorption isotherms of (a) RFA; (b) WFA; (c) Fe-WFA.

Figure 3 shows the N₂ adsorption-desorption isotherms for RFA, WFA and Fe-WFA. The isotherms assume the type IV classification that is common in mesoporous material.

The BET surface area, pore size and total pore volume for RFA, WFA and Fe-WFA are shown in **Table 1**. The surface area, pore size and pore volume increased with WFA that may be due to the dissolution of soluble materials during the washing process. The surface area and total pore volume further increased when WFA was modified with FeSO₄·7H₂O but the pore size decreased. The results indicate that the iron modification increased the adsorption capacity of Fe-WFA by increasing its surface area. The same pattern of results was obtained by Praipipat et al. after modification of zeolites with iron oxide [17].

Table 1. BET surface area, pore size and total pore volume results for RFA, WFA and Fe-WFA.

Material	BET surface area (m ² g ⁻¹)	Adsorption average pore width (nm)	Total pore volume (m ³ g ⁻¹)
RFA	43.7	5.7	0.06
WFA	58.0	7.4	0.11
WFA-Fe ₂ SO ₄	93.4	7.0	0.18

3.1.4. XRF characterization

Table 2 shows the oxides present in RFA, WFA and Fe-WFA. Washing the coal fly ash with water is expected to reduce some alkali and alkaline earth elements like K₂O, Na₂O, CaO and MgO from RFA together with some trace metals that may leach into the water [18]. There is no significant difference in the content of CaO and K₂O, and significant reduction of elements in the WFA is only observed for Fe₂O₃ and Na₂O. The unexpected results of no reduction in CaO, K₂O and MgO may be due to use of cold water instead of hot water to wash the RFA.

Table 2. XRF analysis for raw and water washed fly ash and iron modified fly ash.

Chemical composition	RAW FA (Weight %)	Washed fly ash (Weight %)	FeSO ₄ -fly ash (Weight %)
SiO ₂	34.9	39.1	33.7
Fe ₂ O ₃	25.7	12.6	25.5
Al ₂ O ₃	15.8	28.4	24.5

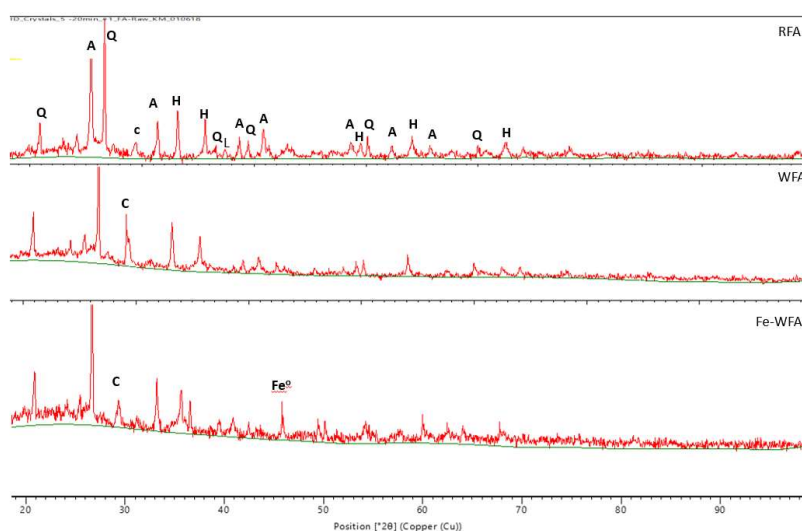
Table 2. (Continued).

Chemical composition	RAW FA (Weight %)	Washed fly ash (Weight %)	FeSO ₄ -fly ash (Weight %)
CaO	8.8	9.1	6.7
Na ₂ O	5.0	0.6	2.8
TiO ₂	1.7	2.8	2.6
MgO	1.3	2.8	2.4
K ₂ O	0.2	0.4	0.6
SO ₃	0.2	3.4	0.4
MnO	0.2	0.2	0.2
LOI	6.0	nd	nd

nd = not determined.

3.1.5. XRD characterization

XRD analysis shows that the main crystalline mineral phases are quartz (SiO₂) and hematite (Fe₂O₃) for RFA, WFA and Fe-WFA (see **Figure 4**) that is further confirmed by XRF and EDS analysis. The anhydrite (CaSO₄) peak is greatly reduced in the WFA and the Fe-WFA, the Ca peak is also observed in the EDS results. The other present phase is the calcite (CaCO₃) in both materials. A pronounced peak is observed at $2\theta = 46^\circ$ for Fe-WFA which is attributed to be FeOOH according to interpretation by Chen et al. [14] and Li et al. [19]. The peak was not assigned to any crystalline phase in our analysis. The presence of iron is important in immobilisation of As [14].

**Figure 4.** XRD diffractogram of RFA, WFA and Fe-WFA.

Q—quartz, A—anhydrite, C—calcite, H—hematite and L—lime.

3.1.6. XPS characterization

The XPS spectra overlay of wide scans in **Figure 5** and **Table 3** shows the surface composition of RFA, WFA, Fe-WFA. The main constituents of RFA were found to be O, Si, C, Al, Ca, Ti, S and Ti. The minor constituents (less than 1%) were found to be Fe, Na and Mg. The results obtained are almost similar to the ones reported by Fu et al. with the absence of Ti only [20]. Few constituents were observed on the WFA

being O, Si, C, Al, Ca, Fe and Na, Ti, S, Ti, Ni and Mg were not identified. The constituents of Fe-WFA were found to be similar to RFA with the absence of Ti and Mg and additional element observed was Ni which was not found in the RFA and WFA. The Ni addition may have occurred due to chemicals used during modification process. A significant surface enrichment of Fe is observed on Fe-WFA with mass % of 19.7% compared to 0.8% and 1.2% of RFA and Fe-WFA respectively. The Fe present on the surface may play an important role in immobilization of As from water [20]. The main constituent in the XPS results give similar main oxides observed in XRF analysis being SiO₂, Fe₂O₃, Al₂O₃ and CaO.

Table 3. Semi quantitative data of the elements present on the surface of the RFA, WFA and Fe-WFA samples.

Peak	RFA-mass conc. [%]	WFA-mass conc. [%]	Fe-WFA-mass conc. [%]
O 1s	44.8	49.5	33.9
Si 2p	15.2	28.2	7.2
C 1s	13.0	18.7	12.0
Al 2s	12.0	2.0	1.8
Ca 2p	5.5	0.1	3.4
Ti 4f	3.0	nd	nd
S 2p	2.2	nd	2.0
Ti 2p	1.8	nd	6.0
Fe 2p	0.8	1.2	19.7
Na 1s	0.9	0.3	0.8
Ni 2p	nd	nd	7.43
Mg 2p	0.8	nd	nd

nd = not determined.

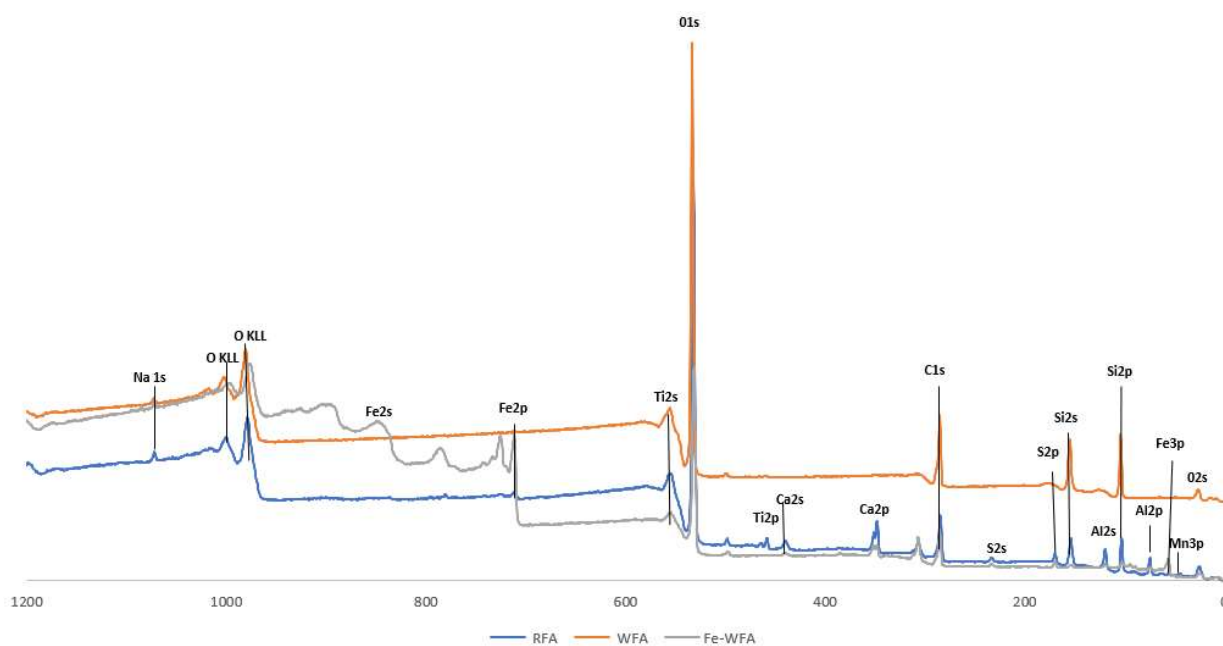


Figure 5. XPS spectra overlaid for RFA, WFA and Fe-WFA samples.

3.1.7. Analysis for metals

Figure 6b shows that the main metal components (>400 ppb) found in RFA, WFA and Fe-WFA were Mn, Sr, Ba, Ni and Mn. The other metals detected were Li, Be, B, Cr, Co, Zn, Ga, As, Se, Mo, Pb and U (see **Figure 6a**). Most metals show a reduction in concentration in WFA and Fe-WFA with exception of Ga, Ni and Ba showing increase in concentration. The RFA results are similar to those reported by Ferrarini et al., which showed the same main elements except for Ni which they reported as a minor element. They also reported similar minor elements with the absence of Mo [15].

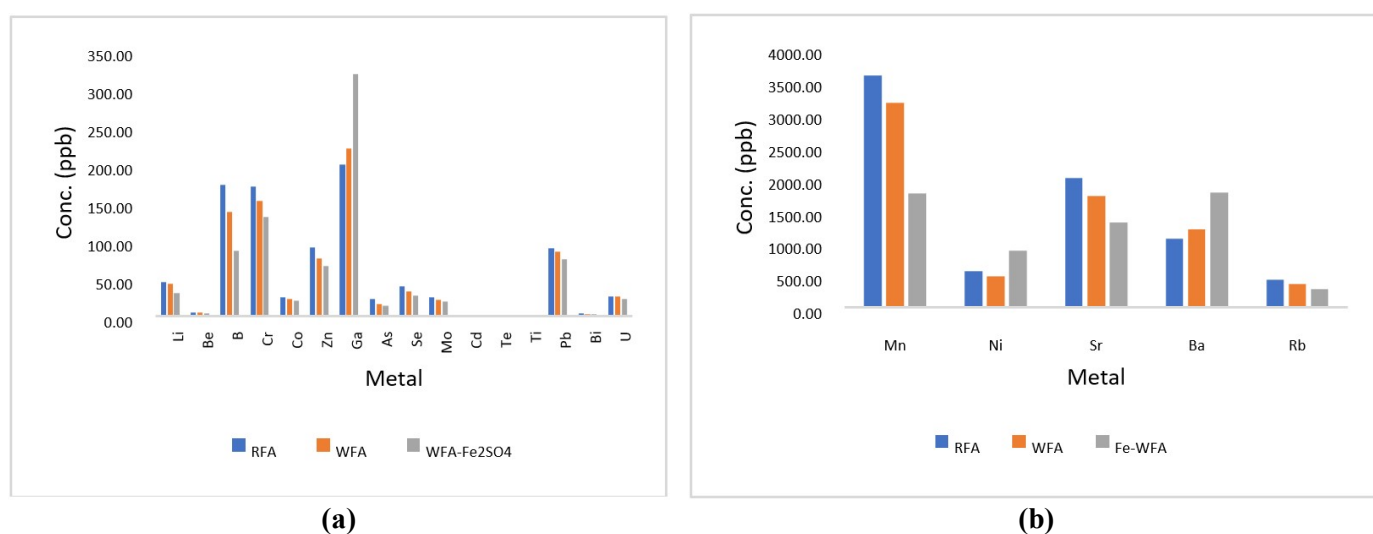


Figure 6. (a) ICP-MS; (b) MP-AES analysis for trace metals in RFA, WFA and Fe-WFA samples.

3.1.8. Leaching of metals

A multi-element analysis of metals was carried out on the leachates collected in 6 washing cycles and the results are shown in **Figure 7**. Most of the elements showed reduction of metal concentration over repeated washing cycles for RFA, WFA, and Fe-WFA. Al, B, Ga and Ba showed the opposite trend with an increase in concentration on repeated washing. The same trends were observed for both WFA and Fe-WFA. Ca was found to be the most abundant in the leachate followed by Sr, Al and Mg. Silva et al. [21] also reported Ca as the most abundant element in the leachate and Al as the slightly higher concentration, Sr and Mg were also reported but not at high concentrations. The reduction in concentration of leachable elements depicts that simple washing of RFA with water is applicable as a pretreatment method before it is used as a sorbent. Although the leaching results show most of the concentrations of metals in water greatly reduced by washing, the effect of large-scale applications of the WFA on the environment was not yet studied.

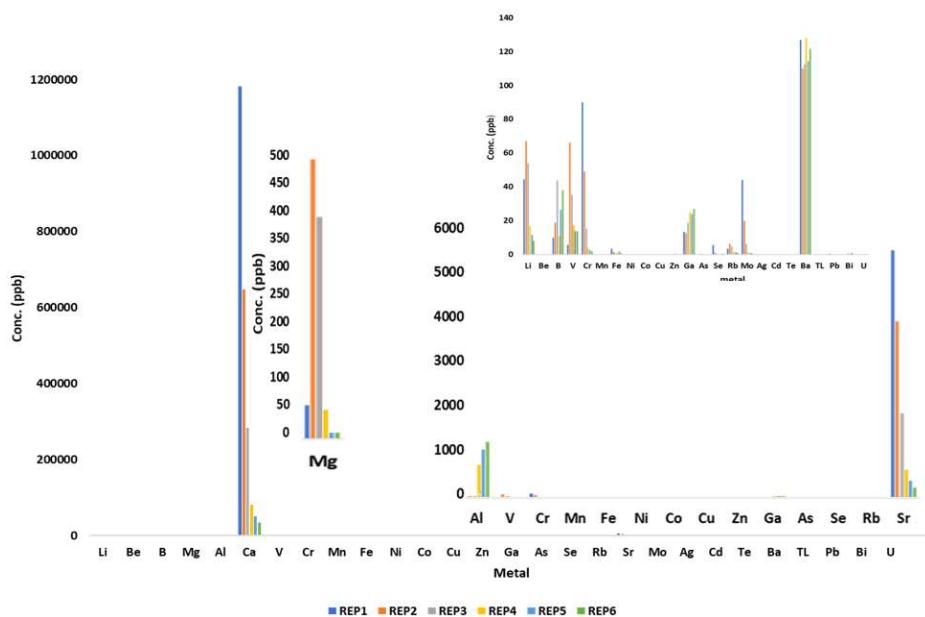


Figure 7. The reduction in concentration of RFA after 6 wash cycles with water.

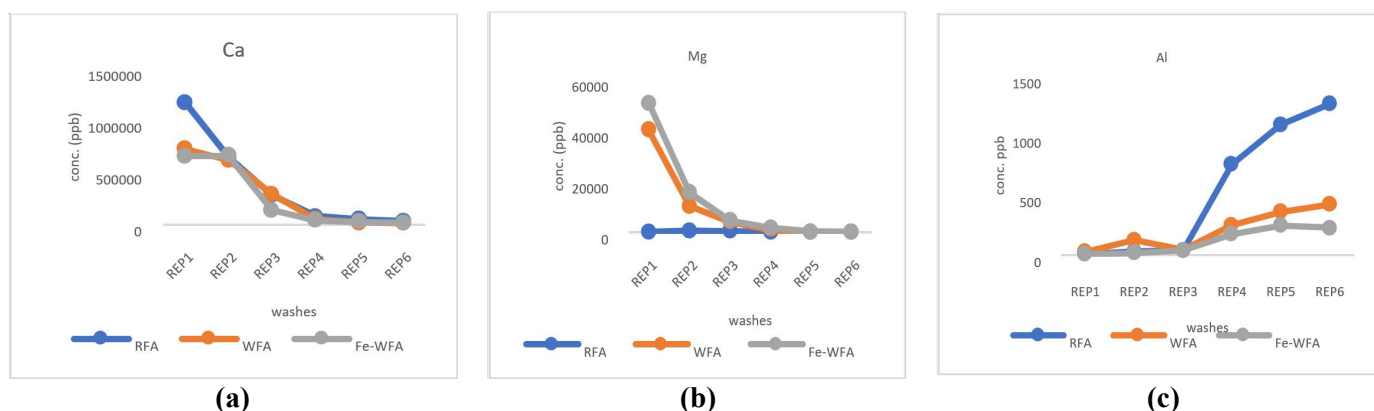


Figure 8. The reduction in concentration of metals in RFA, WFA and Fe-WFA leachates after 6 washes with water.

The comparison of leaching between RFA, WFA, Fe-WFA showed the trends in **Figure 8a–c**. Ca, Li, V, Cr, Fe, Se, Rb, Sr and Mo showed the trend as depicted in **Figure 8a** with reduction of concentration of metals with repeated cycle of washing. The trend in **Figure 8b** was observed for Mg and Mn showing that WFA and Fe-WFA leachates for the first 2 wash cycles had higher concentrations of the elements compared to RFA. Al, Ga and Ba showed increase in concentration with increase in wash cycles as shown in **Figure 8c**.

3.1.9. Arsenic removal

The arsenic removal experiment was carried out with the RFA, WFA and Fe-WFA. **Table 4** summarises results of the adsorption experiments of As(III) of the 3 adsorbents. RFA and Fe-WFA were able to remove 499 ppb whereas WFA removed 388 ppb of the 500 ppb As(III) in water. The inability of the washed fly ash to remove all the As(III) maybe due to the reduced iron oxide content as shown by the XRF data, therefore the surface modification of fly ash with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ produced desirable results for removal of As(III) from water [22].

Table 4. As(III) adsorption studies with RFA, WFA and Fe-WFA.

Adsorbent	Removed conc. (ppb)	Spiking conc. (ppb)	% removal
RFA	499.39	500	99.9
WFA	387.96	500	77.6
Fe-WFA	499.40	500	99.9

3.1.10. Effect of contact time on adsorption of As(III)

Although the results showed lower adsorption for WFA, the difference in adsorption between the RFA and the Fe-WFA was not shown thus further experiments were carried out with the 10 ppm As(III) standard to determine if there is any difference at higher concentration. The percentage removal of 10 ppm As(III) ranged from 97.5%–99.2%, 47.3%–88.6% and 99.6%–99.8% for RFA, WFA, Fe-WFA respectively from 15 min to 150 min. **Figure 9** shows that almost all the As(III) was removed after 15 min with a percentage removal of 99.6%.

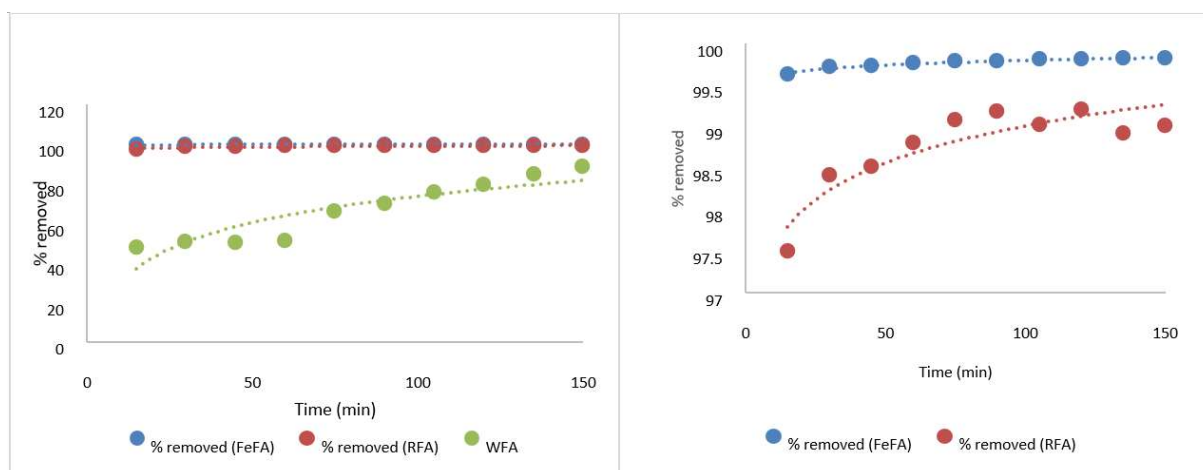


Figure 9. Effect of contact time on percentage removal of 10 ppm As(III) using RFA, WFA and Fe-WFA.

3.1.11. Adsorption isotherms

Langmuir and Freundlich adsorption isotherms were studied to determine the one that best described the adsorption of As(III) on the RFA, WFA and Fe-WFA (see **Figure 10**). The model that best suited the adsorption was found to be the Freundlich with R^2 values of 0.98, 0.98 and 1.0 for RFA, WFA and Fe-WFA respectively. The Freundlich model suggested that the adsorption occurred in a heterogeneous surface of the adsorbent materials.

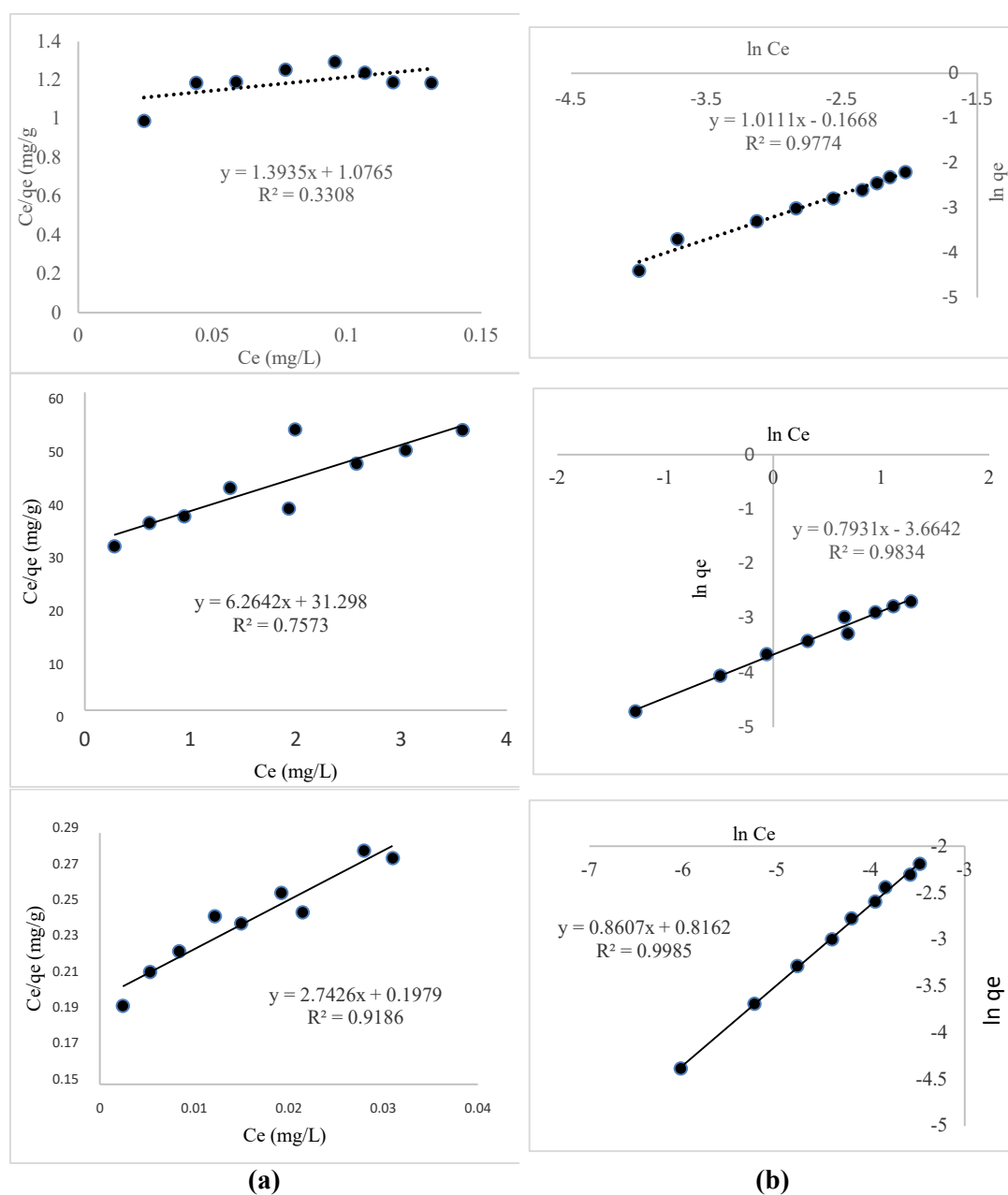


Figure 10. (a) Langmuir; (b) Freundlich adsorption isotherms for adsorption of As(III) on RFA, WFA and Fe-WFA samples.

Table 5 shows the maximum adsorption capacities to be 0.85 mg/g, 0.02 mg/g and 2.26 mg/g for RFA, WFA and Fe-WFA respectively. Therefore, Fe-WFA had the highest adsorption capacity compared to the unmodified WFA. The adsorption capacities 0.075 mg/g and 0.21 mg/g reported by Ochedi et al. [23] for RFA are lower than the 0.85 mg/g obtained in this work although they were for wastewater and ground water and not for spiked deionized water. The 2.26 mg/g obtained for the modified fly ash Fe-WFA was found to be lower than most of the modified fly ash reported with exception of four out of 13 reported by Ochedi et al. [23]. Although the Fe-WFA had lower maximum adsorption capacity compared to most modified fly ash, it had a simple method of preparation. The fly ash was not first converted to zeolites or geopolymer which requires heating or using excessive amount of sodium

hydroxide.

Table 5. As(III) adsorption isotherm parameters for Langmuir and Freundlich model.

	Langmuir		Freundlich	
	R^2	$Q_0 \text{ mg g}^{-1}$	R^2	K_F
RFA	0.33	0.93	0.98	0.85
WFA	R^2	0.75	R^2	0.98
	$Q_0 \text{ mg g}^{-1}$	0.03	K_F	0.02
Fe-WFA	R^2	0.92	R^2	1.0
	$Q_0 \text{ mg g}^{-1}$	5.05	K_F	2.26

4. Conclusion

The Botswana coal fly ash was found to have Fe_2O_3 as the second highest constituent after silica, The high Fe_2O_3 content is vital in removal of As(III) as shown by reduction in efficiency when the Fe_2O_3 content was reduced on the WFA. Although the coal fly ash has a significant amount of trace metals, only lower concentrations leach into the water as shown by the leaching results. Washing the coal fly ash with deionized water reduced the leaching of trace metals into the water. The unexpected results in this study were the increase in concentration of some metals (Al, Ga and Be) in leachates of washing cycles instead of reduction in concentration. Further leaching studies need to be carried out to determine the optimum washing conditions that will reduce their concentrations. Washing pretreatment also reduced the adsorption capacity for As(III) due to reduction in Fe_2O_3 content. The simple and cheap process of washing and modification of the RFA with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ yielded a material that gave the benefits of both reduced leaching and higher adsorption capacity. The arsenic removal assumed the Freundlich adsorption isotherm model, for both RFA, WFA and Fe-WFA. Although the Botswana fly ash shows promising results in removal of arsenic from water, it was difficult to separate it from the water after adsorption experiments. Thus, there is a need to make fly ash into formats such as fly ash-polymer composites, the example being electrospun fibers or granules that can improve its usability. The polymers will be utilized as support material that host the fly ash making it easier to remove after adsorption takes place (i.e., is to be considered for future or further work). The limitations related to this study include; re-usability of the material was not carried out, the study only focused on metals being potential leachates to water and other compounds like polynuclear aromatic hydrocarbons were not analysed.

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Abbreviations

As(III)	Arsenic(III)
ASTM D-3987	Standard Practice for Shake Extraction of Solid Waste with Water method
BET	Brunauer, Emmett and Teller
EPA	Environmental Protection Agency
Fe-WFA	Iron modified water washed fly ash
FT-IR	Fourier-transform infrared spectroscopy
ICP-MS	Inductively coupled plasma-mass spectrometer
MP-AES	Microwave plasma-atomic emission spectrometer
RFA	Raw fly ash
SEM-EDS	Scanning electron microscopy with an energy dispersive spectrometer
TGA	Thermogravimetric Analyzer
WFA	Water washed raw fly ash
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray Fluorescence Spectrometer

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