Use of coal ash to restore acid mine drainage in the Moatize mine tete province, Mozambique

Esnaider Rodríguez Suárez
erodriguezsuarez2013@gmail.com
UniTiva University (Mozambique)
Julio Omar Prieto García
omarpg@uclv.edu.cu
Universidad Central de Las Villas (Cuba)
Loide Augusto Furtado
loideafurtado@gmail.com
Higher Institute of Science and Technology of Mozambique (Mozambique)

Abstract: The purpose of this research is to assess the potential of using coal ash for restoring Acid Mine Drainage. For this purpose, we decided to determine the physical-chemical composition of the coal waste, coal ash and effluent, where physical and chemical parameters were assessed. Mineralogical characterization of tailings was carried out, where quartz, kaolinite, siderite, palygorskite, muscovite and dolomite were verified. Geochemical characterization of coal ash was also done, where found Si, Al, Fe, K, Ca, Ti as the main elements and presence of Cu, Cr, Zn, Rb, Ir, Mn, As, Y, Pb, Nb, Th as trace elements, being defined by the X-Ray Diffraction and X-Ray Fluorescence method. The dynamic and the static of Fizz test methods were used, which showed the maximum time of absorption for H^+ ions from the activation of ashes in the effluent. Satisfactory results were obtained after calcination, since the main acid-generating elements contained in the fine residues were converted to trace elements. The pH of the ashes was found to be neutral. It is concluded that coal ashes from fine coal tailings have the power to restore the Acid Mine Drainage.

Keywords: Acid mine drainage; coal ash; fine coal refuse; remediation; static and dynamic methods.

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Utilización de cenizas de carbón para remediar drenajes ácidos de mina en la provincia de tete de la mina Moatize, Mozambique

Resumen: Se evaluó el potencial del uso de cenizas de carbón para remediar el Drenaje Ácido de Mina en la Mina Benga, ubicada en el Distrito de Moatize-Región de Benga. Para satisfacer los objetivos se determinó la composición físico-química de los residuos de carbón, cenizas de carbón y efluentes, donde se evaluaron parámetros físicos y parámetros químicos. Se realizó la caracterización mineralógica de los relaves donde se constató la presencia de cuarzo, caolinita, siderita, paligorskita, moscovita y dolomita, y la caracterización geoquímica de las cenizas de carbón donde se constató la presencia de Si, Al, Fe, K, Ca, Ti como elementos principales y la presencia de Cu, Cr, Zn, Rb, Ir, Mn, As, Y, Pb, Nb, Th como elementos traza, definiéndose por el método de Difracción de Rayos X y Fluorescencia de Rayos X. Se utilizaron los métodos estáticos de Fizz test y los métodos dinámicos los cuales mostraron el tiempo máximo de absorción de iones H+ a partir de la activación de las cenizas en el efluente. Se obtuvieron resultados satisfactorios, como el paso de los principales elementos generadores de acidez contenidos en los residuos finos a oligoelementos después de la calcinación, se comprobó la ventaja de que el pH de las cenizas sea neutro. Se concluye que las cenizas de carbón de los relaves finos de carbón tienen el potencial de remediar el drenaje ácido de Mina.

Palabras clave: drenaje ácido de mina; cenizas de carbón; residuos finos de carbón; remediación; métodos estáticos y dinámicos.

Introduction

Mozambique is a country characterized by a high geological diversity, consisting of magmatic, metamorphic and sedimentary rocks, with large amounts of mineral resources of paramount importance for its development and economic growth. Mining activity is the main economic source of the country, so it is important to carry it out responsibly.

The term Acid Mine Drainage (ADM) is used for describing drainage from the natural oxidation of sulfide minerals that occur in rocks and tailings exposed to oxygen and water, causing the oxidation of pyrite sulfur and releasing polluting metal ions (Kontopoulos, 1998; Glastein & Matías, 2023).

Coal mining is a favorable environment for the AMD formation, as a result of chemical reactions of sulphides, in the presence of O_2 and H_2O. In recent years, methodologies that allow predicting the probability of occurrence of AMD, and assessing its evolution over time (static and dynamic), have been developed (Gray, 2004).

The objective is assessing the potential of using coal ash to restore acid mine drainage in Benga Mine at Mozambique.

Materials and methods

The field activity was carried out at Benga Coal Mine, which allowed observation, sample collection and interviews. It was opposed to a non-systematic and non-participant individual observation, where it is carried out only by an observer, who plays the role of spectator and consists of observing the most relevant aspects for the study in question (Lakatos & Marconi, 2018).

For the work development, the boundaries of the mining concession where the work would be carried out and the coordinates for the collection of samples of fine coal tailings from the processing plant in the tailings AMD and effluent shown in table 1 were analyzed.

Table 1. Coordinates of sampling points

Sampling points	**Coordinates**		
	Latitudes (S)	**Longitudes (E)**	Depth (m)
Point 1	16°12'57.32"S	33°40'44.61"E	1413 m
Point 2	16°13'1.24"S	33°40'41.82"E	1407 m

Laboratory research was carried out in Maputo, at Eduardo Mondlane University (UEM) at the Faculty of Sciences, Chemistry Department, and Analytical Chemistry Laboratory. The laboratory activities, preparations and characterization were carried out through physical chemical, mineralogical and geochemical tests of ashes of the fine coal tailings, as well as static and dynamic tests, and the construction of spectra.

Evaluation criteria for choosing static and dynamic methods

The concepts used to evaluate and choose the methods that best suit the study are based on the weighted numbering criteria, which are taken into account according to the objectives of this work. The following six evaluation criteria were applied: detection limit, snalysis steps, used equipment, time required for analysis, efficiency, costs (MEND, 2009).

Analysis and choice of methods based on the criteria

Based on the evaluation criteria, the static and dynamic methods that best scored and led to answer those that are the objectives of the work were defined.

The first static tests for predicting AMD were developed in the 1970s by Smith and Sobek, at West Virginia University, with studies focused on acid drainage in coal mines (Querol *et al*., 2001).

Static methods determine the acidity generation potential (AP) and the neutralization potential (NP) of a sample, the balance between these two magnitudes allowed analyzing the production of acid mine drainage and the neutralization potential of coal ash (U.S. Environmental Protection Agency, 2009; Leiva, Negrelli & Hidalgo, 2021; Pardavé *et al.,* 2023).

The dynamic tests allow estimating the quality of the drainage effluent over time, as they simulate the evolution (oxidation and dissolution) of the waste. The methodology consists of subjecting the samples to conditions similar to those at the miner's disposal site, with the aim of determining the rates of acidity neutralization and sulphides oxidation, over an extended period of time and at higher costs. Among the main dynamic methods, there is the Leach Column (CL) and the Soxhlet Extractor (U.S. Environmental Protection Agency, 2009). In short, tests were selected: the fizz test, the pulp pH method, the acid-base balance method and the British Columbia initial method and the H^+ ion absorption test in ash by agitation.

Laboratory procedures

The experimental methodology was subdivided into three subsequent procedures from ash preparation, characterization and static and dynamic tests.

Procedure 1. Calcination and ashes preparation

For the preparation in procedure A, eight porcelain canisters with a capacity of 10 ml to 30 ml were removed from the desiccator, where the empty canisters (Cv) were first weighed and the values recorded. The ash was homogenized using a stainless steel spatula and about 20 g of fine waste for each crucible were weighed on the same analytical balance with a maximum capacity of 100 g and precision of 0,0001 g. Ashes were recorded as m-sample for points 1 and 2.

Then the crucibles were placed under mass, temperature, time and atmosphere control in the muffle furnace with automatic oxygen injection at a temperature of 800°C within a period of twelve hours (12h) for complete combustion to occur. After twelve hours, the samples were kept in the muffle until it cooled down (1h). Finally, the samples were mixed and passed through a grinding process until they reached the appearance of ash and were conserved in a beaker.

Procedure 2. Physical-chemical and mineralogical characterization of ash and effluent from acid mine drainage

Physical characterization

The physical characterization of samples, were made using materials and equipment from the laboratory where the following physical parameters were analyzed: Color: determining the color of the waste and ashes was verified from visual observation. Trace or stripe: the trace was determined from the powder of fine coal waste and coal ash, on a white sheet; pH: The pH was determined using an equipment, the pH meter that gave the pH value and its temperature; Conductivity: It was determined by means of a conductivity meter which gave its value and its temperature.

Mineralogical and geochemical characterization

The characterization of tailings was carried out using the DRX equipment and the characterization of the effluent and coal ash was carried out using the XRF equipment, both procedures consisted of placing a sample of each in the sample holder (fine coal tailings; effluent and solids suspended; charcoal ash).

Procedure 3. Tests of static and dynamic methods

Fizz test method

The fizz test indicates the volume and concentration of HCl reagent used in determining the neutralization potential. The purpose of adding HCl was to verify the amount of carbonates present in the sample, which could be recognized by bubbling and/or the intensity of effervescence. The presence of carbonates was indicated by the intensity of effervescence, with an audible fizz test sound, with which the volume and concentration of HCl to be used in the static tests was determined.

Paste pH method

This method makes it possible to instantly identify the degree of alkalinity of the ash; through direct measurement of the pH, value of the paste prepared from the ash itself and distilled water. The value obtained does not identify the occurrence of consumption reactions and acidity production, but it shows indications about the possible acid character of the sample, due to the absence of neutralizing components or its difficulty in solubilizing and acid consumption (Querol *et al.,* 2001; Weber *et al.*, 2004).

Paste pH procedure

The potentiometer was calibrated using pH 4 and 7 standard solutions, and the standard procedure was followed according to the equipment instruction.

- Approximately 10.0 g of ash was weighed in an Erlenmeyer flask, about 9 mL of distilled water was added, and the sample was slightly stirred with a spatula to form a fine paste.

- The potentiometer was carefully inserted into the paste and it was moved to ensure contact between the paste and the electrode.

- pH values were determined with a Eutech Instrument digital pH meter, pH 700, with a combined Ag/AgCl glass electrode.

Acid Balance Method - Standard Base (Standard ABA)

Sample neutralization potential (ton eq.$CaCO_3$/1000ton)

$$NP = \frac{50.a\left[\frac{b}{a}\right].y}{c}$$

Potential for acidity formation of the sample (ton eq.$CaCO_3$/1000ton)

$$AP = \%\, S\ total\ \times 31.25$$

Potential for neutralization (ton eq.$CaCO_3$/1000ton)

$$NNP = PN - PA$$

Ratio between neutralization potential and sample acidity formation potential

$$RNP = \frac{PN}{PA}$$

British Columbia Research initial test method (B.C. Research initial test)

The initial B.C. Research method differs from other methods by expressing the neutralization potential in terms of the amount of H_2SO_4 that can eventually be neutralized by the basic reacting minerals present in the sample instead of the calcium carbonate content.

It was calculated:

Potential acidity consumption (AC) of the sample (kg H_2SO_4/ton)

$$AC = \frac{VH_2SO_4 \times\ 0,049\ \times 1000}{SampleWeight\ (g)}$$

Sample acidification potential (AP) (kg H_2SO_4/ton)

$$AP = \%\, Stotal\ \times 30,6$$

Study of absorption of H^+ ions

Procedure for studying the absorption of H^+ ions

a) Starting from the previously prepared sample of the ash fraction, the activation of 5 g of ash was carried out by adding an amount of 250 mL of the acid effluent. Then, it was subjected to an activation process maintained under constant stirring at 400rpm at 25°C for 1 hour. One hour later, 10ml of the solution was removed with a test tube every 10 minutes (minute - 10, 20, 30, 40, 50, 60, and 70) and filtered d) 5mL of the filtrate was removed with a syringe for the titration process with standard base (NaOH) and methyl red indicator. For titration, 3 drops of indicator were added to 5mL of each filtrate, it was titrated using NaOH, and valuesobtained were recorded.

Results and discussion

Observation at the field, interview and the questionnaire came to complement the relevant aspects for the study. It was found that about 2km from the Benga Mine there is a community (Community of Benga) and a river that supplies it (River Rovubue). This proximity causes the neighboring community to suffer impacts from coal mining in the study area, with greater emphasis on river water pollution that population consumes. It was also verified that the feed per hour is 800 ton/h and the tailings deposited in the dam per hour is 300 m^{3}/h.

Physical characterization of coal waste, ash and effluent samples

The results of the physical parameters evaluated in the waste, ash and effluent samples are shown in table 2.

Table 2. Physical parameters evaluated in samples of gray waste and effluent

Parameters	**Results**	
Reject color	Black	
Ash color	**Rubra (tends to be pink)**	
Trace or stripe of the tailings	Black	
Ash dash or stripe	Light pink color	
Effluent pH	*insitu*- 3	3.1
Condutivity of the effluent	*insitu*- 4ms/cm	3.75 ms/cm

It is understood from the coloration that the coal tailings come from an idiochromatic mineral, because it presents a constant color in any observed sample. The color of red ash with changes to pink shows that it is an all-chromatic ash, presenting a considerable variety of colors.

The tailings and ash traces are black and light pink, and the trace is the color obtained when the sample is reduced to powder. The pH of 2.99 and 3.1 shows that the effluent has acid characteristics, proving the origin of acid mine drainage. The effluent conductivity of 4 ms/cm and 3.7 ms/cm shows that the ionic concentration in the effluent are high, which proves its ionic impurity.

Chemical characterization of the effluent

The chemical analysis of suspended and dissolved particles in the effluent was performed using the XRF technique, with the results shown in table 3.

Table 3. Chemical parameters of the effluent using the XRF method

Chemical Parameters	(mg/L)	Chemical Parameters	(mg/L)
Si	16193.60	Cu	402.312
Fe	5956.298	K	329.722
S	3004.833	Zn	111.094
Ca	1667.798	Ti	64.645
Mg	1507.815		

The presence of non-metals Si and S, the presence of transition metals Fe, Cu, Zn and Ti and the presence of alkali metals (K) and alkaline earth metals (Ca) were verified. Where the presence of high amounts of polluting metals present in the effluent is confirmed, which according to the table of physical-chemical standards established for water quality established by Ministerial Diploma No. 189 (Ministérios dos Recuersos Minerais, 2006), the levels of magnesium and calcium are around more than thirty times above the admissible average.

Analysis, discussion, and interpretation of mineralogical characterization

Mineralogical characterization aims to identify the crystalline phases present in the sample. The results of the analysis of the fine waste by the aforementioned method are described in accordance with graph 1 and table 4.

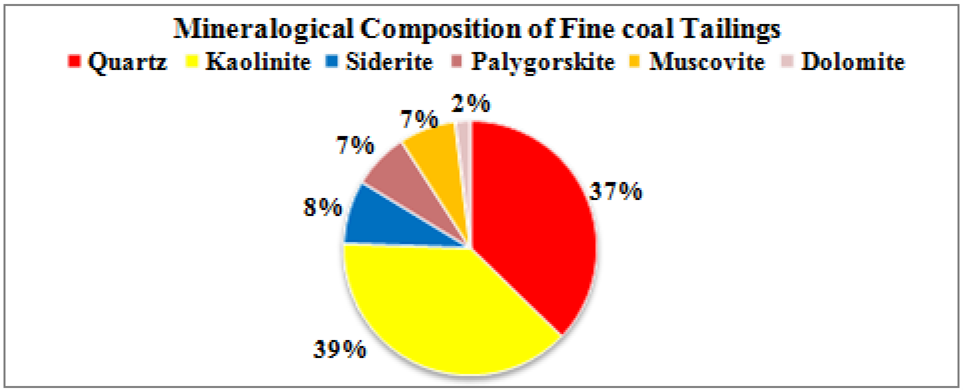

Figure 1. Percentage diagram of mineralogical composition of fine tailings.

In the mineralogical analysis of the fine coal tailings samples, the following minerals and their reactivity and solubility were identified (Table 4).

Table 4. Mineralogical analysis of fine tailings by XRD

Mineral		Mineral behavior	
		Solubility	Reactivity
Quartz (SiO_2)	37,28	Inert	Inert
Kaolinite (Al2Si2O5 $(OH)_4$)	38,31	Low solubility	Low reactivity
Siderite ($FeCO_3$)	8,15	High solubility	High reactivity
Palygorskite ((Mg,Al)2Si4O10(OH)·4(H_2O))	7,18	Low solubility	Low reactivity
Muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$)	7,18	Low solubility	Low reactivity
Dolomite ($CaMg(CO_3)^2$)	1,93	Very soluble	Very reactive

Geochemical characterization of coal ash

The coal ash samples were analyzed using the X-ray fluorescence technique, at the central laboratory of the UEM-Chemistry Department. The results of the analysis are illustrated in qualitative and quantitative terms in tables 5 and 6 and in figures 2 and 3.

Table 5. Results of the geochemical analysis of coal ash from point 1 by XRF

Si	**Al**	**Fe**	**K**	**Ca**	**Ti**	**S**	**P**	**V**	**Zr**	**Sr**
46.04	22.52	14.86	4.57	4.48	3.74	1.61	1.15	0.20	0.18	0.17
Cu	**Cr**	**Zn**	**Rb**	**Ir**	**Mn**	**As**	**Y**	**Pb**	**Nb**	**Th**
0.08	0.06	0.05	0.03	0.03	0.03	0.03	0.02	0.023	0.018	0.007

Table 6. Result of the geochemical analysis of coal ash from point 2 by XRF

Si	**Al**	**Fe**	**Ca**	**K**	**Ti**	**S**	**P**	**V**	**Zr**	**Sr**
46.36	22.12	15.04	4.42	4.27	3.79	1.82	1.18	0.22	0.17	0.15
Cu	**Cr**	**Zn**	**Ir**	**Mn**	**Ga**	**Y**	**As**	**Pb**	**Rb**	**Th**
0.07	0.06	0.05	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.001

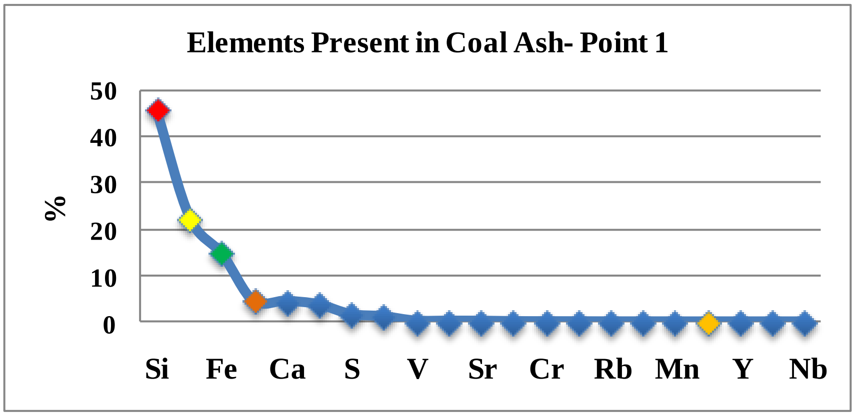

Figure 2. Percentage diagram of the geochemical composition of mineral coal ash from Point 1.

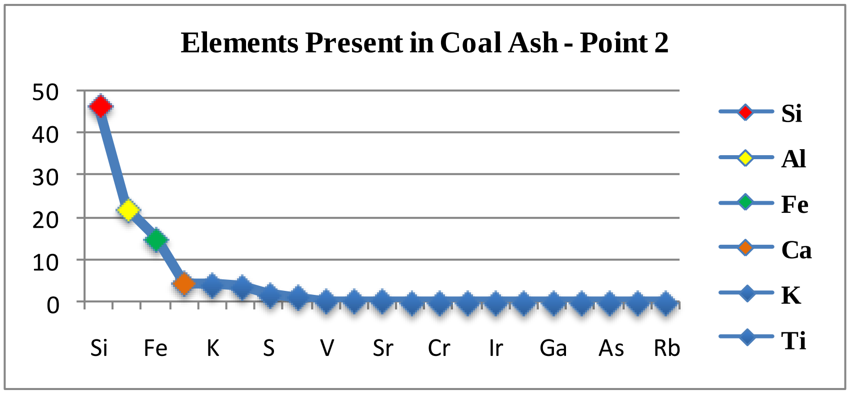

Figure 3. Percentage diagram of the geochemical composition of mineral coal ash from point 2.

In the mineralogical analysis of coal ash samples, the following minerals were identified as major elements: Si, Al, Fe, K, Ca, Ti. Moreover, the following were identified as trace elements: Cu, Cr, Zn, Rb, Ir, Mn, As, Y, Pb, Nb, Th. Although the material (ash) is the same, due to the difference in the place of collection they present a small variability in the percentages of the elements. It is visible that the elements responsible for oxidation such as Sulphur, lead and zinc were reduced to trace elements, changing to oxide and evaporating in the calcination process, losing much of their negative influence.

Analysis, discussion and interpretation of static methods

Fizz test method

In the fizz test, a null (none) effervescence was observed, which corresponds to 20 mL of 0.1N HCl. Indicating the absence of carbonates.

Paste pH method

In the pulp pH test, a pH of 6.23 was observed for the sample from point 1 and a pH of 6.51 for the sample from point 2. Showing that coal ashes tend towards a satisfactory neutral pH.

Acid Balance Method-Standard Base (Standard ABA)

Table 7 presents the neutralization potential, acidity potential, net neutralization potential of the sample, ratio between neutralization potential and potential for the formation of acidity in the sample.

Table 7. Results obtained in the standard ABA test

Method	**PN**	**PA**	**NNP**	**RNP**
Standard ABA	2835.75ton eq.$CaCO_3$/1000ton	50.625 ton eq.$CaCO_3$/1000ton	2785.125ton eq.$CaCO_3$/1000ton	56.015

The standard static ABA methods, presented titration volume with 0.1N NaOH of 5.7ml. The low volume of 0.1N NaOH used in the titration corresponds to the volume of 0.1N HCl, which in turn corresponds to a large amount of soluble neutralizing minerals present in the sample. The calculated values of PN, PA, NNP and RNP are 2835.75ton eq.$CaCO_3$/1000ton, 50.625ton eq.$CaCO_3$/1000ton, 2785125ton eq. $CaCO_3$/1000ton and 56,015 respectively. These values indicate that the sample has a low potential for the formation of ADM and a high potential for neutralization.

British Columbia Research Initial Method (B.C. Research initial test)

Table 8 presents the sample acidity consumption potential and the sample acidification potential.

Table 8. Results obtained in the initial B.C Research test

Method	AC	AP
B.C Reasearch	12.74kg H2SO4/ton	49.592 kg H2SO4/ton

The initial test of the B.C. Research presented the volume of 2.6 mL ± 0.208mL titration with H_2SO_4. This low volume of 1.0N H_2SO_4 a used in the titration is confirmation of the large amount of soluble neutralizing minerals present in the sample. The values of acidity formation potential (AP) and acidity consumption potential (AC) by the sample are 12.74 kg H_2SO_4/ton and 49,592 kg H_2SO_4/ton respectively, that is, the sample does not show acidity formation potential.

Analysis, discussion and interpretation of dynamic methods

Study of absorption of H^+ ions

The absorption capacity of coal ash obtained from the fine tailings of hydrogen ions present in the effluent of the tailings dam was tested. Graphs 4 and 5 below show the behavior of ash (sample from points 1 and 2) as an adsorbent for acid mine drainage effluent containing H^+ ions.

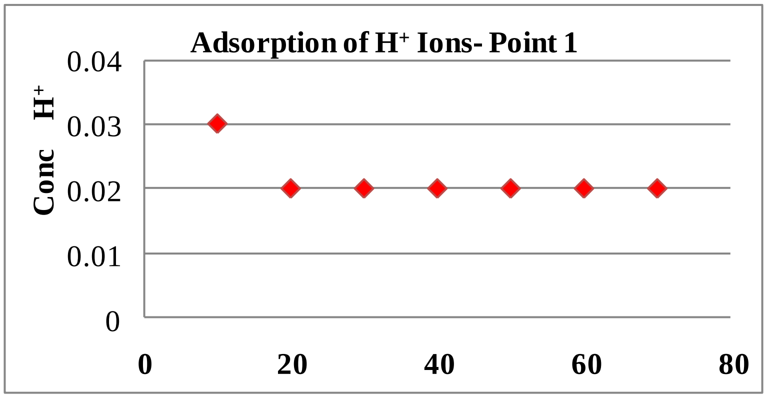

Figure 4. Result of adsorption of H^+ ions over time using ashes from point 1.

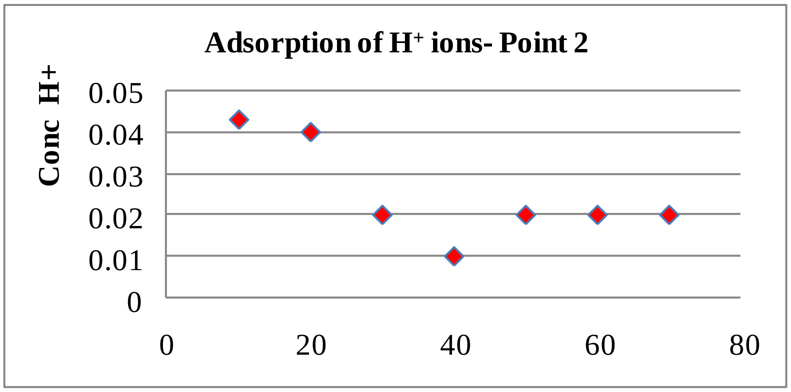

Figure 5. Result of adsorption of H^+ ions over time using ashes from point 2.

The H^+ ion absorption test used two different sample point dynamic models. The behavior of the coal ash reached the absorption peak in the first 10 minutes after the activation of the ash, which shows that the ash does not need a long time of interaction with the effluent to be able to lower its acidity. In turn, figure 4 and figure 5 show that the ash manages to remedy up to minute 30 and minute 50, then entering a stable state where it neither absorbs nor releases H^+ ions (Wang *et al.,* 2006).

Conclusions

The kinetic ion adsorption test confirms that ash does not need a long interaction time to work as a good acid mine drainage restorer, being able to remediate for a considerable time before its saturation

The coal tailings has a constant black color, being considered idiochromatic while the red ash color with changes to pink shows that it is an allochromatic ash.

The mineralogical characterization of the sample of fine coal tailings by XRD verified the presence of quartz, kaolinite, siderite, palygorskite, muscovite and dolomite.

The geochemical characterization of coal ash found the presence of major elements of the following minerals: Si, Al, Fe, K, Ca, Ti and the following trace elements: Cu, Cr, Zn, Rb, Ir, Mn, As, Y, Pb, Nb, and Th. It is possible to verify the similarity between the elements present in the characterized fine waste and the ashes.

The static study shows that the coal ash sample has no presence of carbonates, which is satisfactory because it means that there is no risk of transformation of carbonates to carbon acid.

The pH of the slurry shows that coal ash tends to a neutral pH, so in the case of passing an acid effluent to coal ash, it will lead to acid neutralization leading to the most neutral pH possible.

Static study ABA Standard and B.C show that ash samples have high acid neutralizing potential and very low acid forming potential.

The kinetic test of adsorption of H+ ions manages to remediate about of 40 minutes, with the maximum peak of adsorption in the first hours.

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