
Evaluation of Ultrasound-assisted Modified Fly Ash for Treatment of Acid Mine Drainage

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Abstract

The aim of this chapter is to assess the suitability of utilizing fly ash (FA) and modified fly ash (MFA) in the treatment of acid mine drainage (AMD). The effects of various experimental conditions such as mixing speed, fly ash dosage, contact time, and pH on the efficiency of metal removal from AMD was studied in batch experiments. For modification of FA, ultrasound (US) process was conducted at low frequency (20 kHz) to activate surface area and decrease particle size of FA at 90 W for 30 minutes. Chemical, physical and mineralogical compositions of FA, MFA and solid residues (SR) were determined using arrays of X-ray fluorescence (XRF), Brunauer-Emmett-Teller (BET), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) techniques and particle size analysis. The removal efficiency of Al, Fe, Mn, Ni, Zn and SO_4^{2-} from AMD was compared using FA and MFA. According to the obtained results, ultrasound-assisted MFA provided successful results for metal removal in a shorter reaction time and with smaller dosage than FA. As the pH of the solution (ash:AMD) increased, the metal and SO_4^{2-} concentrations in SR increased mainly due to precipitation; this data was verified with XRD and XRF analysis. Preliminary treatment of AMD from Etili coal mine (NW Turkey) indicates that MFA could be an effective and low-cost adsorbent for the treatment of AMD.

Keywords: acid mine drainage, modified fly ash, ultrasound, metal, sulphate, solid residue

1. Introduction

The Can coal basin (Canakkale province, NW Turkey) is rich in lignite (100 Mt); though these reserves, known as Can coals, cannot be described as quality coals due to low calorific value and high sulphur content (max: 14.36 wt%) [1]. In the Can coal basin, the Etili mine has

operated as open pit since the 1980s [2]. When mining activities ceased without any accompanying remediation methods, these depressions filled with surface and ground waters. During the time, artificial lakes formed and showed typical characteristics of acid mine lakes (AML) with low pH (min: 2.59) and high electrical conductivity values (max: 6430 $\mu\text{S}/\text{cm}$), in addition to high SO_4^{2-} (max: 5370 mg/L) and metal (Al, Fe, Mn, etc.) concentrations [3]. Acid mine lakes are located upstream of the Kocabas stream, which passes through the Can coal basin before flowing into the Sea of Marmara. Along this stream, drinking water for several residential areas is supplied from boreholes [4]. The pH value of creeks around the mine lakes varies between 2.85 and 5.75 [5], with these creeks passing close to settlement areas. Soil and groundwater quality has been affected along these creeks. These conditions prohibit discharge of untreated acid mine drainage (AMD) into public streams, as they have a detrimental effect on environment. So, for removal of metals from AMD, suitable physical or chemical treatment processes such as chemical precipitation, adsorption, oxidation-reduction, ion exchange, etc. must be performed [6–12]. Adsorption refers to a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions [13]. Activated alumina, activated carbon, silica gel, fly ash, saw dust and zeolite are different adsorbent materials reported in the literature [10–16] for removal of pollutants from water with the adsorption process.

Fly ash (FA), which is a low cost and abundant industrial by-product, has been known for its effectiveness in the remediation of different kinds of industrial wastes in Europe and USA since 1960s [14]. In Turkey, 13 million tons of FA is produced annually and this amount is expected to reach 50 million tons per year by 2020 [17, 18]. But only a small amount of FA in Turkey (approximately 1%) is reused in the construction industry (particularly cement industry) [19, 20] and the rest is disposed of in ash dumps or landfill which is an inconvenient solution both from environmental and economical points of view [21]. Recent studies have demonstrated that treatment of AMD with FA is an effective adsorption process for metal uptake from water [16, 22–28]. Ultrasound (US) has been used recently as one of the most successful means of activating adsorbate surfaces [29, 30]. The US technology works according to the principle of cavitation and the adsorbent surface modification is achieved by means of pyrolysis and $\bullet\text{OH}$ radicals which burst in the water under high temperature and pressure and this results in continuity of use of the adsorbent for purification purposes [30–33]. High power US produces a permanent chemical or physical change in a material and $\bullet\text{H}$, $\bullet\text{OH}$ and $\bullet\text{OH}_2$ radicals when water is liquid irradiated with US [34–36]. High intensity shear forces and radicals formed during the US mechanical effect create pits and cracks on adsorbate surfaces resulting in larger specific surface area, higher pore volume and lower particle diameter [37]. The use of US cavitation with adsorption for water treatment has been reported in the literature [38–40]. This chapter is a site-specific research carried out to assess the suitability of utilizing FA and modified fly ash (MFA) in the treatment of AMD from Etili coal mine. Within this chapter, an AML that is one of the largest mine lakes in Etili coal mine 1 km Southwest of Keciagili village with 29.41 decar area in July 2016 not drained since the 1990s was chosen (**Figure 1a** and **b**). Fly ash was collected directly from the fluidized bed combustion thermal power plant precipitator, which is a coal-fired 135 MW generating facility, located in Northwestern Turkey. In this chapter, FA, a coal combustion by-product, was US-assisted modified with the aim of activating the surface area and decreasing particle size. Removal of metal and SO_4^{2-} using FA and MFA was determined under various conditions such as mixing speed, ash

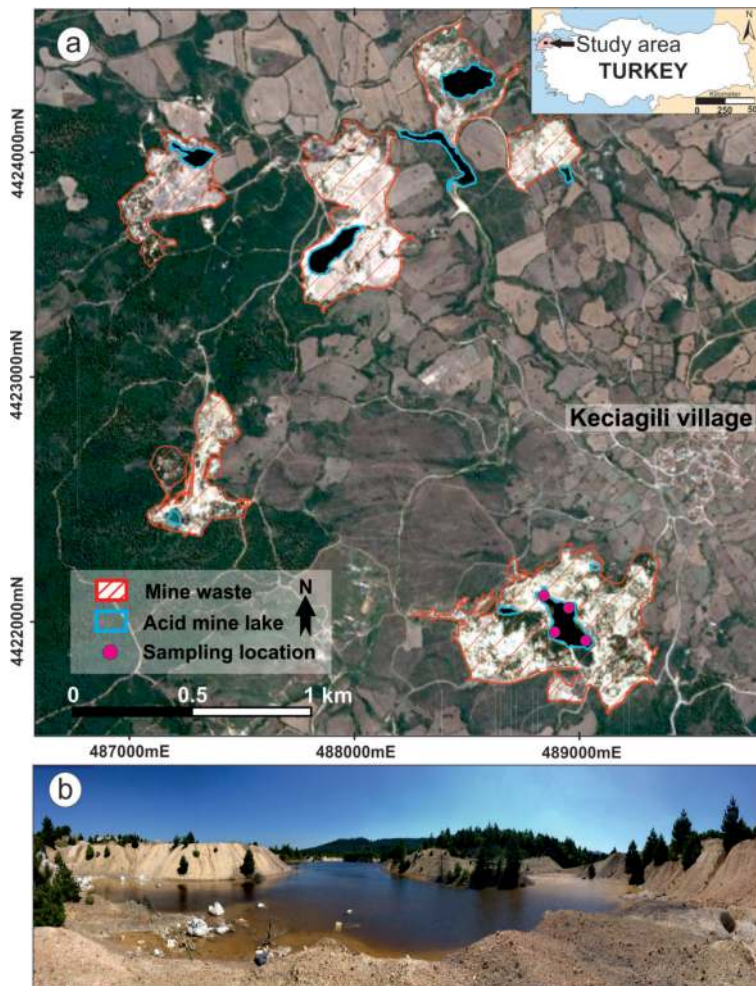


Figure 1. (a) Location map of Etili coal mine (b) snapshot from sampling AML.

dosage, contact time and pH in batch experiments. The possibility of utilizing FA and MFA to remove selected metals and SO_4^{2-} from AMD is evaluated.

2. Materials and methods

2.1. Acid mine lake characterization

Four different sampling points were selected and water samples were taken from 0.5 to 1 m depths in the lake using a bailer sampler (Eijkelkamp). Physicochemical parameters of AML

were measured in the field, including pH, oxidation-reduction potential (ORP, mV), temperature (T, °C), electrical conductivity (EC, $\mu\text{S}/\text{cm}$), dissolved oxygen (DO, mg/L), total dissolved solids (TDS, mg/L) and salinity (Sal, %), using a multi-parameter measurement device (WTW 3410). All water samples were stored in 500-mL polyethylene bottles and refrigerated at 4°C until further analysis. Water samples were analysed for major and trace elements using an inductively coupled plasma-mass spectrometer (ICP-MS) at AcmeLabs (Canada). Acidity was measured as methyl orange acidity with digital titrator (APHA 2310 titration method), and Fe(II) was determined by ferrozine spectrophotometric method using a Hach Lange DR 2800 spectrophotometer. Fe(III) was calculated as the difference between Fe(t) and Fe(II). Sulphate was measured by Hach Lange DR 2800 using SulfaVer 4 method.

2.2. Fly ash modification

The FA modification was achieved using US technology. The US system was equipped with a titanium probe having diameter of 19 mm, connected to a horn-transducer of 20 kHz supported with a booster and eventually plugged to a power supply of 500 W with a cable (VibraCell 505, Sonics&Materials) (Figure 2). The batch reactor had a cooling jacket through which tap water was circulated to absorb the heat generated by US treatment. Each 200 mL pure water sample initially containing 10 g of FA was placed in the cooling-jacket reactor, and then modified with US (20 kHz) at 90 W for 10, 30 and 60 minutes. Modified FA was dried in the oven at 80°C for 12 hours. The variations in particle size of MFA at 10, 30 and 60 minutes were determined to identify optimum modification time according to particle size analysis

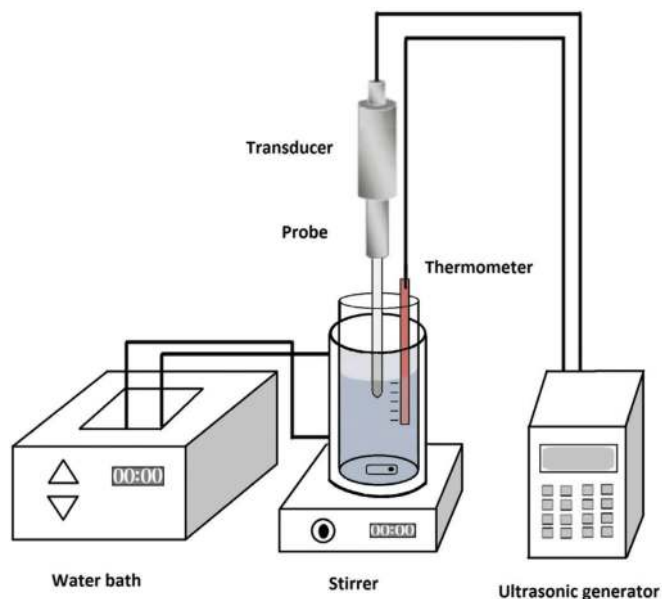


Figure 2. Low frequency ultrasonic system (20 kHz).

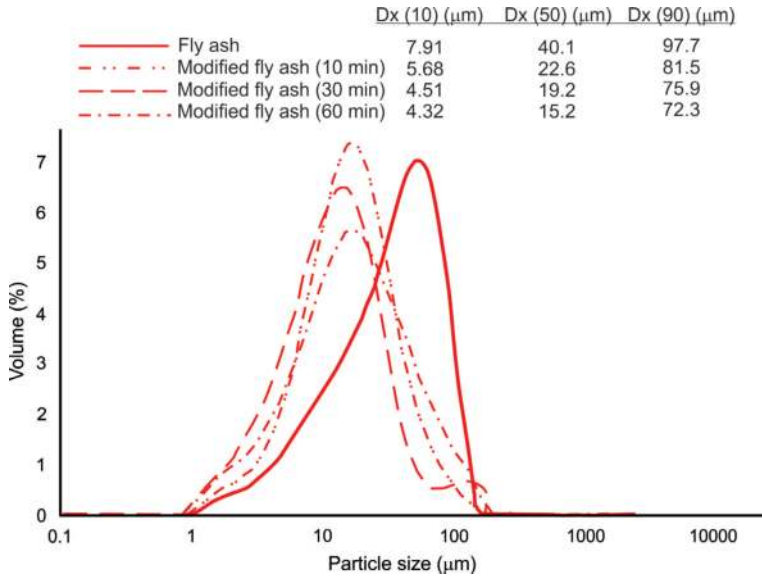


Figure 3. Particle size distribution of FA and MFA.

(Figure 3). The particle size diameter of FA was decreased and surface area was increased by US mechanical effects. The obtained particle size distribution resulted for 30 minutes had similar Dx (10, 50 and 90) values compared to 60 minutes. Therefore, 30 minutes was chosen as optimum time for modification of FA due to reduce US energy, cost and time.

2.3. Batch experiments

Batch experiments were conducted to determine various parameters such as (1) mixing speed (rpm), (2) ash dosage (g), (3) contact time (hour) and (4) pH that affect the removal of metal and sulphate (SO_4^{2-}) from AMD using FA and MFA at ambient temperature. (1) Twenty grams of FA and MFA was mixed with 100 mL AMD samples and was agitated under different mixing speeds (60, 120 and 180 rpm) using an orbital shaker (GFL®3005) to determine optimum mixing speed for 0–6 hours contact time. It was found that removal of metal increased with increasing mixing speed. Thus, 180 rpm was selected for optimum mixing speed. (2) FA and MFA were weighed at 5, 10 and 20 g dosage and subsequently added to AMD of 100 mL volume in a conical flask. The mixed sample was agitated using an orbital shaker at 180 rpm for 0–6 hours to determine optimum adsorbent dosage for Fe removal. (3) The effect of contact time on the adsorption of metal (Al, Fe, Mn, Ni and Zn) and SO_4^{2-} from AMD using 10 and 20 g FA and MFA dosage was evaluated with various contact times (0.2, 0.5, 1, 2, 3, 4, 5 and 6 hours) at 180 rpm. (4) The pH of the AMD was adjusted to 3, 5, 7 and 9 using 1 N NaOH before the tests. All experiments were conducted according to optimum mixing speed (180 rpm), 20 g adsorbent dosage, 6 hour contact time and various pH values to determine Al, Fe, Mn, Ni, Zn and SO_4^{2-} removal from the solution. At the end of mixing, FA and MFA were separated from

suspension by filtration through a 0.45 μm membrane filter. pH and EC values of the suspension were measured with a multi-parameter device. The residual concentrations of the metal ions in the supernatant were determined using ICP-MS technique. The amount of metal ions adsorbed by FA and MFA was taken as the difference between the initial and residual concentration of the metal ions. Each test was repeated at least three times. In each case, the percentage error for the experiment was lower than $\pm 5\%$. The solid residues (SR) including FA:AMD and MFA:AMD determined for optimum Fe removal results could settle for 5 minutes and separated from water. Then, SR was dried in the oven at 80°C for 12 hours to determine SR characterization.

2.4. Fly ash and modified fly ash characterization

The physical, mineralogical and chemical composition of FA, MFA and SR were identified with particle size, Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) analyses. The particle size distribution of FA, MFA and SR were measured using a laser-based particle size analyser (PSA), namely a Malvern Mastersizer 3000 PSA, in the Polymer Laboratory at Chemistry Department in Canakkale Onsekiz Mart University. Morphology, particle shape and mineralogical components of FA, MFA and SR were examined through micro-graphs taken by SEM (JEOL SEM-7100-EDX) coupled with EDX performed at the Centre for Material Science in Canakkale Onsekiz Mart University. Specific surface area of FA and MFA was identified by BET (Quantachrome, Quadrasorb SI) analyses at the Centre for Material Science in Canakkale Onsekiz Mart University. Mineralogical compositions of FA, MFA and SR were identified by XRD using Philips PW 1830 instrument at the General Directorate of Mineral Research and Exploration Analysis Laboratories in Ankara, Turkey. Both major and minor element concentrations of FA, MFA and SR were obtained using an XRF spectrometer (PANalytical, Axios) at the General Directorate of Mineral Research and Exploration Analysis Laboratories. The chemical compounds of FA, MFA and SR were identified using a single-beam FTIR-PerkinElmer spectrum 100 spectrometer, equipped with a diamond crystal in the Chemistry Laboratory in Canakkale Onsekiz Mart University. IR spectra were recorded as changes in absorption as a function of wave number ranging from 600 to 4000 cm^{-1} .

3. Results and discussions

3.1. Hydrochemical characteristics of acid mine lake

The pH value of the mine lake was strongly acidic (2.66). Low pH value of the lake increases the dissolution of numerous elements. Electrical conductivity value of the mine lake was measured as 5.2 mS/cm (**Table 1**). Electrical conductivity is related to the concentration of TDS and major ions. Total dissolved solids may be obtained by multiplying the conductance by a factor, which is commonly between 0.55 and 0.75, and generally multiplication factor is approximately 0.67 [41]. Total dissolved solids were measured and calculated as 2720 and

Parameter	Unit	Concentration
T	°C	26.3
pH	-	2.66
ORP	mV	355
EC	mS/cm	5.2
Sal	%	2.7
TDS	mg/L	2720
DO		5.7
Acidity		2000
Ca ²⁺		496
Mg ²⁺		267
Na ⁺		156
K ⁺		3
SO ₄ ²⁻		3600
Cl ⁻		65
Al		249.9
Fe(t)		199.7
Fe ²⁺		37
Fe ³⁺		162.7
Mn		114.74
Zn		6.21
Co		2.29
Ni		1.11
Cu		0.23

Table 1. Hydrochemical characteristics of AML.

3484 mg/L, respectively. Temperature of the lake (26.3°C) was related to climatic fluctuations (e.g. season and different times of day and depth of water body). Oxidation-reduction potential and DO values were measured as 355 mV and 5.7 mg/L, respectively. Oxidation-reduction potential influences the mobility of most metals, which can exist in several oxidation states. Typically, high ORP values correspond to the presence of oxidizing agents. Thus, ORP values are typically found to be high when DO levels are high [42]. Acidity values based on titrations performed in the laboratory were quite high, 2000 mgCaCO₃/L. The titrated values are slightly lower than acidity values (2128 mgCaCO₃/L) calculated using the formula of [43]. Major cation order is Ca²⁺ (496 mg/L) > Mg²⁺ (267 mg/L) > Na⁺ (156 mg/L) > K⁺ (3 mg/L), and major anion order is SO₄²⁻ (3600 mg/L) > Cl⁻ (65 mg/L). Therefore, lake water is best classified as Ca-SO₄ water. The concentrations of Fe and Al in the mine lake are in most cases greater than those of the common ions Na⁺ and K⁺. The dominant dissolved metals in the lake water,

in order of average abundance, are Al (249.9 mg/L) > Fe (199.7 mg/L) > Mn (111.74 mg/L) > Zn (6.21 mg/L) > Co (2.29 mg/L) > Ni (1.11 mg/L) > Cu (0.23 mg/L). Most the dissolved Fe in the lake water is Fe^{3+} (162.7 mg/L). According to the Turkish inland water quality regulations [44], the mine lake had pH, SO_4^{2-} , Al, Fe, Mn, Zn, Co, Ni and Cu values in class IV, and were classified as highly polluted waters.

3.2. Mineralogical, physical and chemical characterization of original and modified fly ash

The mineralogical, physical and chemical properties of fly ash depend on the nature of the parent coal, conditions of combustion, type of emission control devices, storage and handling methods [45, 46]. Fly ash (pH = 10.95) and MFA (pH = 11.58) have alkaline character when added to deionized water 1:2 (solid:solution ratio) at the end of 24 hours (**Table 2**). Electrical conductivity value of MFA (2.24 mS/cm) is slightly lower than EC value of FA (2.35 mS/cm). The chemical composition of the FA was determined by XRF analyses to contain 50.75% SiO_2 + 19.98% Al_2O_3 + 5.37% MgO + 5.35% Fe_2O_3 + 2.15% Na_2O and 1.81% CaO and 10.9% LOI. According to the American Society for Testing Materials [47], the ash is classified as 'F-class fly ashes', the sum of SiO_2 + Al_2O_3 + Fe_2O_3 > 70% and CaO content is less than 5%. The combustion of bituminous or anthracite coal produces F-class FA and F-class FA is pozzolanic [48]. The chemical composition of MFA contains 50.48% SiO_2 + 19.59% Al_2O_3 + 5.58% MgO + 5.39% Fe_2O_3 + 2.05% Na_2O and 1.74% CaO and 11.65% LOI. Specific surface area (BET) of FA is increased with US-assisted modification from 3.21 to

Parameter	Unit	FA	MFA
pH	-	10.95	11.58
EC	mS/cm	2.35	2.24
Specific surface area	m ² /g	3.21	4.54
SiO_2	wt%	50.75	50.48
Al_2O_3		19.98	19.59
MgO		5.37	5.58
Fe_2O_3		5.35	5.39
Na_2O		2.15	2.05
CaO		1.81	1.74
K_2O		1.75	1.72
MnO		0.052	0.051
ZnO		0.017	0.017
NiO		0.008	0.008
CuO		0.006	0.006
LOI		10.90	11.65

Table 2. Chemical composition of FA and MFA.

4.54 m²/g. The MFA contains lower amounts of Si and Al and has a higher surface area, LOI and pH than the FA. The results for the mineralogical composition of FA and MFA remained the same as obtained by XRD analysis. Mineralogical composition of FA includes quartz (42%), amorphous phase (23%), mullite (13%), plagioclase (12%), hematite (6%), magnetite (2%), mica (1%) and K-feldspar (1%). Modified FA contains quartz (37%), amorphous phase (31%), mullite (10%), plagioclase (10%), mica (5%), K-feldspar (4%), hematite (2%) and magnetite (1%). Ultrasound-assisted modification decreased particle size diameter of FA and so the percentages of mineral composition changed. Particle size characterization of FA is important for metal adsorption. Adsorption capacity of the smallest particles is better as they are more reactive, and in addition trace elements tend to concentrate in the finest particles. The mean particle size distribution of the FA and MFA is presented in **Figure 3**. The results show that the particle size distribution of the FA and MFA ranges between 1 and 144 μm and 0.9 and 116 μm, respectively. From the cumulative distributions, the following values for Dx (10, 50 and 90) of FA and MFA were observed 7.91, 40.1 and 97.7 μm and 4.51, 19.2 and 75.9 μm, respectively. The size and shape of the FA were scanned with SEM-EDX as shown in **Figure 4a–d**. Generally, FA particles have an irregular and porous microscopic structure. Most of the FA particles exhibit irregular shapes, primarily because most minerals in the coal do not undergo melting but soften only, under the relatively low boiler temperature of 850–900°C [49–51]. Irregularly shaped unburned carbon particles tended to be in the upper end of the size distribution. The occurrence of hematite results from oxidation of pyrite in the combustion units. Fly ash and MFA contain small pores, which range between 0.6 and 11.2 μm. Ultrasound mechanical effect created pits and cracks on FA surface and part of ash particles filled inside the pores (**Figure 5a–d**).

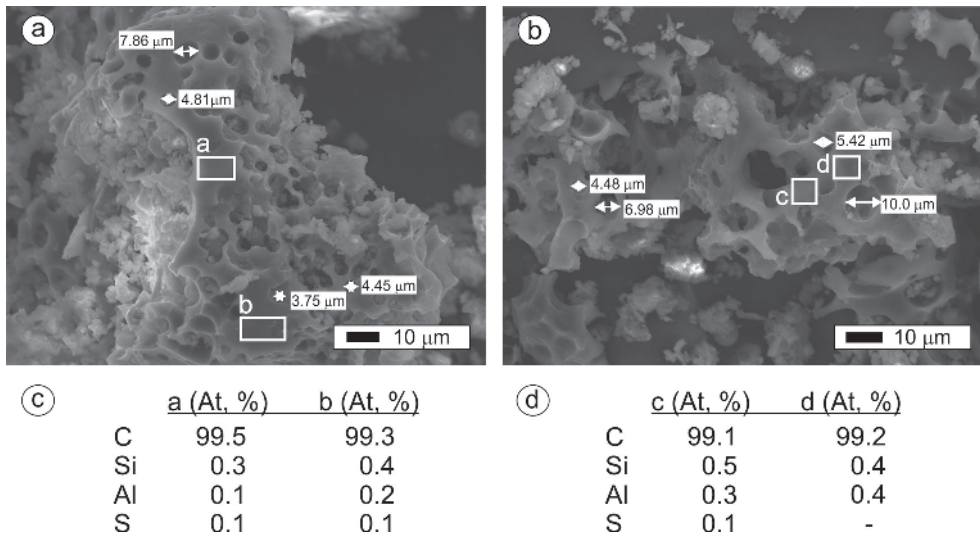


Figure 4. (a, b) SEM images of FA, (c, d) EDX results of FA.

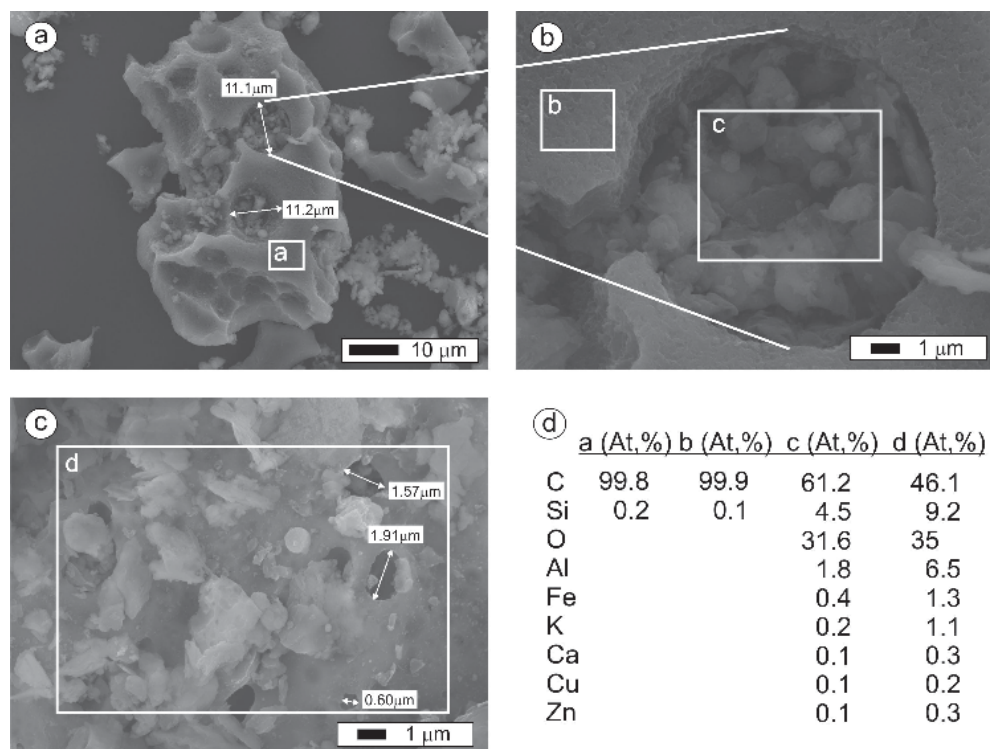


Figure 5. (a-c) SEM images of MFA, (d) EDX results of MFA.

3.3. Metal removal from acid mine drainage using fly ash and modified fly ash

3.3.1. Effect of agitation

At higher agitation speeds, the mass transfer resistance related to ion diffusion through the liquid film surrounding the FA is reduced as the film thickness reduces due to agitation, resulting in greater metal uptake [52]. To determine the effect of agitation on the removal of Fe (t), AMD (100 mL) was homogeneous mixed with FA and MFA (20 g) at 60, 120 and 180 rpm for 0–6 hours. The results of the Fe concentration vs. contact time are shown in **Figure 6a** and **b**. According to the obtained results, the speed of agitation is an important factor for removal of Fe from solution. The maximum removal of Fe increased with increasing mixing speed and the optimum mixing speed was determined as 180 rpm at least time. The Fe concentration of the solution was measured 4.6, 0.38 and 0.1 mg/L; 4.5, 0.30 and 0.05 mg/L for 60, 120 and 180 rpm at the end of 6 hours for FA:AMD and MFA:AMD, respectively.

3.3.2. Effect of adsorbent dosage

Neutralization is generally the first step in AMD treatment [11]. The kinetics of the neutralization reactions was investigated by monitoring the pH and EC values of FA:AMD and

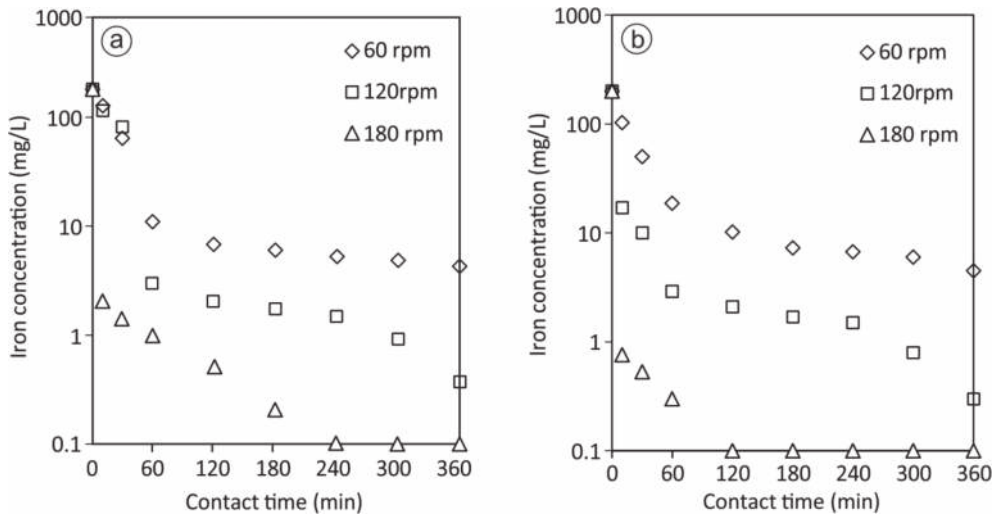


Figure 6. Effect of agitation on Fe concentration of AMD mixing with (a) FA and (b) MFA.

MFA:AMD ratio (1:20, 1:10 and 1:5) over a period of 6 hours. Initial pH (2.66) of the FA:AMD increased within the first 30 minutes for all ash dosages, indicating that soluble material dissolved quickly resulting in the solution. pH values reached 4.28, 4.43 and 5.18 for 5, 10 and 20 g FA dosage at the end of 6 hours, respectively (Figure 7a). Electrical conductivity values ranged from 5.2 to 4.8 mS/cm, 5.2 to 4.81 mS/cm and 5.2 to 4.51 mS/cm were measured for the 5, 10 and 20 g FA dosage at 0–6 hours, respectively (Figure 7b). pH value of the solution reached 5.51, 7.3 and 7.9 for 5, 10 and 20 g MFA dosage at the end of 6 hours (Figure 7c). Low pH value with a minimum of 2.66 was measured in initial, and the highest pH value was measured ash dosage of 20 g at 6 hours, which compared well with the adsorbent dosage and contact time. Alkaline pH value of solution indicates that modification of FA affects the alkalinity. Acid mine drainage reacted with MFA in 6 hours using 1:5 and 1:10 MFA:AMD ratios by weight produces neutral and alkaline process waters. Electrical conductivity values ranged between 5.2 and 4.85 mS/cm, 5.2 and 4.8 mS/cm, 5.2 and 4.2 mS/cm were measured for MFA dosage of 5, 10 and 20 g at 0–6 hours, respectively (Figure 7d). A sudden increase in EC was observed during the first 10 minutes for all MFA dosages, indicating that soluble material dissolved into the solution resulting in a rapid and irregular increase in EC value. Adsorbent dosage is effective parameter for metal removal [53]. In order to determine the effect of adsorbent dosage on the removal of Fe, AMD (100 mL) was homogeneously mixed with FA and MFA (5, 10 and 20 g) at 180 rpm for 0–6 hours. According to FA, various adsorbent dosages (5, 10 and 20 g), Fe concentration were determined 1.43 mg/L at pH = 4.28, 1.03 mg/L at pH = 4.43, 0.1 mg/L at pH = 5.18 at the end of 6 hours, respectively (Figure 8a). According to Turkish inland water quality regulations [44], Fe concentration must be lower than 0.3 mg/L for unpolluted water classification (Class I). Considering this regulation, optimum FA dosage for Fe removal from AMD was determined as 20 g in this chapter. Fe concentration shows approximately 99.9% removal at pH = 5.18 attained by the FA:AMD ratio of 1:5. According to various adsorbent dosages (5, 10 and 20 g) for MFA,

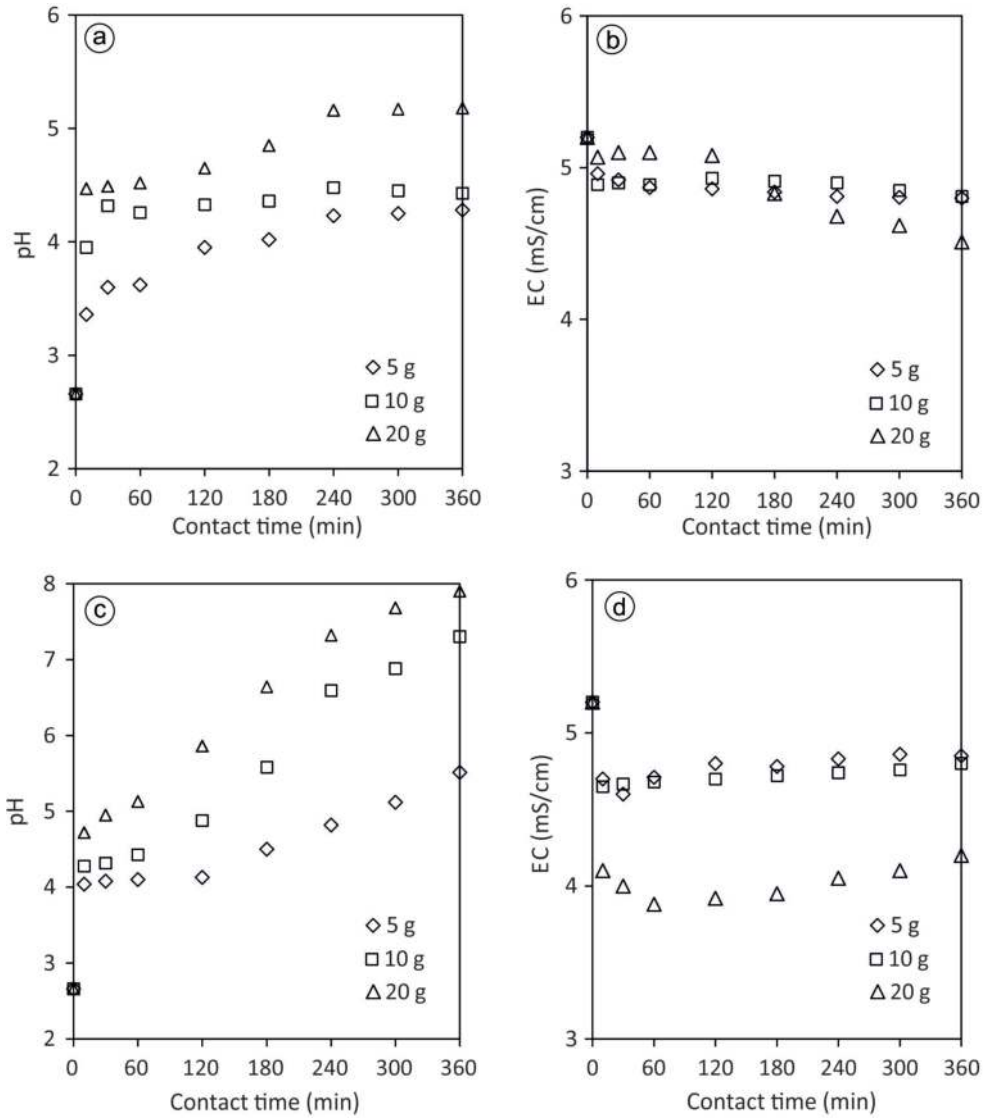


Figure 7. pH and EC vs. contact time as a function of adsorbent dosage, (a, b) FA, (c, d). MFA ($pH_{initial} = 2.66$; $EC_{initial} = 5.2$ mS/cm).

Fe concentration was determined 0.5 mg/L at pH = 5.51, 0.1 mg/L at pH = 7.3 and 0.05 mg/L at pH = 7.9 at the end of 6 hours, respectively (**Figure 8b**). It was observed that the adsorbent dosage is an effective parameter for Fe removal using FA and MFA into AMD. Previous studies reported that higher adsorption capacity and larger surface area of FA is related to

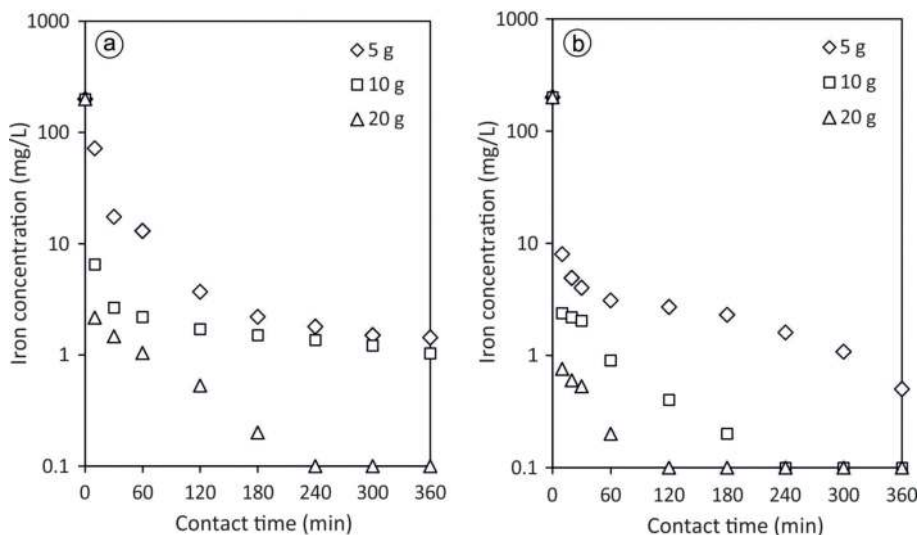


Figure 8. Effect of adsorbent dosage on the Fe concentration vs. contact time (a) FA and (b) MFA.

the efficiency of pollutant removal [54–58]. In this chapter, attempt was made to improve the efficiency of metal removal from AMD with modified FA using US mechanical effect. Modification of FA was provided to increase surface area and decrease diameter range of adsorbent and so, adsorbent dosage reduced by half using MFA. Iron concentration shows approximately 99.9% removal at pH = 7.3 attained by the MFA:AMD ratio of 1:10.

3.3.3. Effect of contact time

In order to determine the effect of contact time on the removal of Al, Fe and SO_4^{2-} , AMD (100 mL) was homogeneously mixed with FA (20 g) and MFA (10 g) at 180 rpm for 0–6 hours. Figure 9a and b shows the effect of contact time on Al, Fe and SO_4^{2-} removal from AMD. The pH of the solution (FA:AMD) ranged between 2.66 and 5.18. It is shown from Figure 9a that the removal percentage of Iron from solution increased rapidly for 20 g FA dosage and reached up to 99% at the end of 2 hours. A further increase in the contact time has a negligible effect on the rate of adsorption of Fe. Therefore, the optimum contact time of 2 hour for 20 g FA dosage could be considered for the adsorption of Fe on FA for entire batch studies. The pH of the solution (MFA:AMD) ranged between 2.66 and 7.3. The adsorb Fe on MFA increased with an increase of contact time in particular of the first 1 hour with 99% removal percentage. Iron concentration was successfully reduced below 0.3 mg/L at the end of 1 hour. Therefore, the optimum contact time of 1 hour for dosage of 10 g MFA could be considered for the adsorption of Fe on MFA for entire batch studies. Aluminium precipitates from AMD when they are diluted or neutralized to a pH of ≥ 4.5 –5 [59] because $\text{pK}_1 = 5$ for Al^{3+} hydrolysis, a necessary condition for onset of precipitation [60]. Removal percentage of Al from solution was calculated 85% (pH = 5.18) for dosage of 20 g FA at the end of 6 hours. Aluminium removal from solution was obtained as 86%

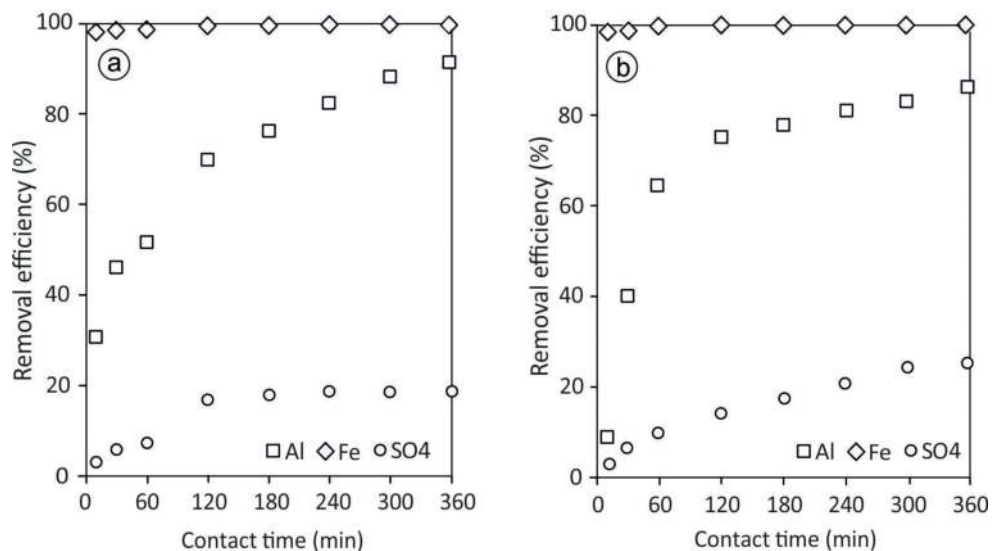


Figure 9. Effect of contact time on the removal of Al, Fe and SO₄²⁻ from AMD using (a) FA (20 g), (b) MFA (10 g).

(pH = 7.3) using 10 g MFA dosage at the end of 6 hours. Modification of FA was provided to reduce adsorbent dosage to half. Initial SO₄²⁻ concentration of AMD was measured 3600 mg/L. The maximum removal efficiency of SO₄²⁻ was obtained 18 and 25% for FA and MFA, respectively. According to the obtained results, the effectiveness of SO₄²⁻ removal from solution using FA and MFA by US enhanced with increasing ash dosage and contact time.

3.3.4. Effect of pH

pH is a major control on the solubility of most metal compounds [61]. The dependence of metal adsorption on pH is different for each metal [62]. Effect of various pH_{initial} (3, 5, 7 and 9) on removal of selected metals (Al, Fe, Mn, Ni and Zn) and SO₄²⁻ from AMD were determined using 20 g dosage of FA and MFA for 6 hours contact time. The removal efficiency of Al, Fe, Mn, Ni and Zn was obtained 85.5, 99.9, 23.4, 67.5 and 51.2% for FA and 90.7, 99.9, 71.6, 93.8 and 99.4% for MFA at pH = 3, respectively (Figure 10a and b). The removal efficiency of Al, Fe, Mn, Ni and Zn was obtained 98.3, 99.9, 49.3, 83.7 and 99.3% for FA and 99.9, 99.9, 88.4, 97.8 and 99.7% for MFA at pH = 5, respectively. Ultrasound process can also accelerate chemical reactions [38]. The removal efficiency of metals increased in pH (7 and 9) reached over 97% removal. The obtained results showed that metal removal from AMD using FA and MFA depends on the final pH of solution. Sulphate removal as a function of different solutions and pH is shown in Figure 10. Approximately 39% of SO₄²⁻ can be removed from the solution (MFA:AMD) when the pH increased from 2.66 to 8.03.

3.4. Discussion

The AMD in Etili coal mine is highly acidic (pH of 2.66) because of intensive sulphide oxidation and ineffective neutralization processes. The abundance of pyrite in the volcanic rocks,

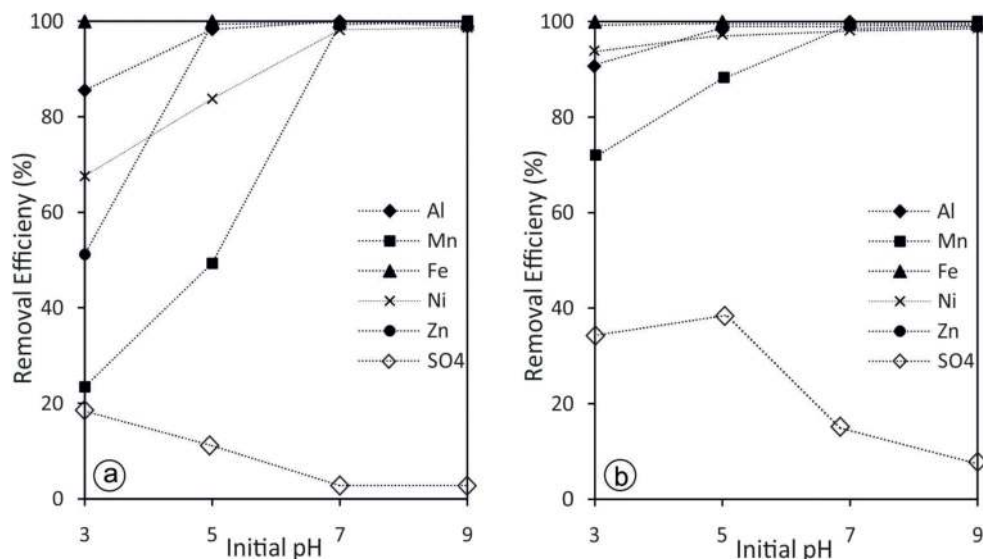


Figure 10. Effect of pH on removal efficiency at various metal and SO_4^{2-} from AMD using (a) FA (20 g) (b) MFA (20 g).

coal, mine wastes and sediments of mine lakes, as evidenced by XRD, SEM/EDX and isotope analyses of SO_4^{2-} , indicates that this mineral is the main sulphide mineral undergoing oxidation [3]. Sulphate is the predominant anion and Fe and Al are the most predominant metal species in AMD. Two anthropogenic pollutants (i.e. AMD and FA), usually formed in close proximity to each other, were reacted together in this chapter. Fly ash collected from the thermal power plant was modified with US process with the aim of activating surface area and decreasing particle size. The pH value of the ash-water system depends mainly on the Ca/S molar ratio in FA, although other minor alkalis or alkaline earth cations may also contribute to the balance [51, 63, 64]. Based on the Ca/S ratio and pH value, FA can be classified into three main groups: strongly alkaline ash (pH 11–13), mildly alkaline ash (pH 8–9) and acidic ash [51]. Fly ash is strongly alkaline, and its surface is negatively charged at high pH (see **Table 2**). Hence, it can be expected to remove metal ions from solutions by precipitation or electrostatic adsorption [62]. Besides, it contains a certain volume of unburnt carbon, which has a high adsorption capacity. The major inorganic species Al, Fe, Mn and SO_4^{2-} seem to be mainly removed through precipitation of amorphous oxides, (oxy)hydroxides and basic hydroxyl sulphates [16]. The AMD was characterized by high concentrations of Fe^{3+} as compared to Fe^{2+} (**Table 1**). The initial decrease in concentration for both ratios at pH 4–4.5 indicates removal of Fe^{3+} in the form of hydroxides or (oxy)hydroxysulphates [16]. Aluminium and Fe mobility at mining sites is related to pH and SO_4^{2-} concentration [65]. Saturation of iron-hydroxysulphate minerals generally occurs around pH = 4 and so, at pH > 4, Fe precipitates as a solid and is no longer mobile [61, 65]. Dissolution of FA and MFA components is confirmed through the decrease of Fe in the Fe-oxide fraction at pH 4.5–4.7. It is often suggested that the tendency of metal cations to adsorb on the oxide surfaces is highly related to their pH of hydrolysis [62, 66]. At pH greater than 7, 90.7% of the Al was removed from solution at 20 g MFA dosage and significant proportion of Al from AMD was hydrolysed to form amorphous (oxy)hydroxides. It was observed that the maximum removal

efficiency for Zn and Ni was achieved using FA and MFA at pH of 8. The leaching of Ca and Mg can be assumed to be controlled by the dissolution of Ca and Mg-bearing silicates [67, 68]. According to ICP-MS results, Ca, Mg, Na and K concentrations were observed to increase from 496 to 645 and 802 mg/L; 267 to 335 and 311 mg/L; 156 to 221 and 166 mg/L; 3 to 36 and 16 mg/L for FA:AMD and MFA:AMD, respectively. Calcium, Mg, Na and K concentrations decreased in SR 0.2, 0.5, 0.11 and 0.02% for FA:AMD; 0.22, 0.14, 0.02 and 0.07% for MFA:AMD, respectively, in XRF analysis results (**Table 3**). The removal of SO_4^{2-} depends on CaO containing FA. Soluble CaO (1.74–1.81%) in FA and MFA increased the pH value of AMD. According to particle size analysis, the particle size distribution of SR (FA:AMD) increased 31, 18 and 12% for Dx (10, 50 and 90), respectively. The particle size distribution of SR (MFA:AMD) increased 5, 6 and 12% for Dx (10, 50 and 90), respectively (**Figure 11**). Fly ash and MFA reacted with AMD were explained based on the particle morphology, shape and mineralogical components. These interpretations from the particle surface analysis were supported with SEM images. **Figure 12a** and **b** shows the SEM images of SR (MFA:AMD). Modified fly ash particles viewed in a predominantly irregular-shaped and have pores and creeks. These results confirm that the surfaces of FA particles were disrupted with US shear forces. According to EDX analysis results, Al, Fe, Mn and Zn concentrations in SR accumulated and precipitated on adsorbent surface. The XRD analysis of the sonicated and unsonicated FA showed no mineral phase change (**Table 4**). Gypsum was the only new mineral phase after treatment of AMD with FA and MFA was identified by XRD analysis in the SR. Gypsum was also detected by SEM-EDX analysis (**Figure 12c**). Gypsum crystals are containing 83.1% O, 8% S and 6.7% Ca, as quantified by EDX analysis (**Figure 12d**). As the final pH of solution increased, more CaO is available and more Ca^{2+} ions are resulting in enhanced removal of SO_4^{2-} as gypsum. The FTIR spectra of the FA, MFA and SR are illustrated in **Figure 13**. The FTIR data validate the observations made through XRD. The main band, due

Major component (wt%)	FA:AMD	MFA:AMD
SiO ₂	49.5	49.28
Al ₂ O ₃	20.17	19.99
MgO	5.28	5.36
Fe ₂ O ₃	5.60	5.67
Na ₂ O	2.01	2.03
CaO	1.68	1.45
K ₂ O	1.70	1.64
MnO	0.072	0.07
ZnO	0.018	0.019
NiO	0.008	0.008
CuO	0.007	0.007
S	0.43	0.40
LOI	11.92	13.41

Table 3. Chemical composition of SR.

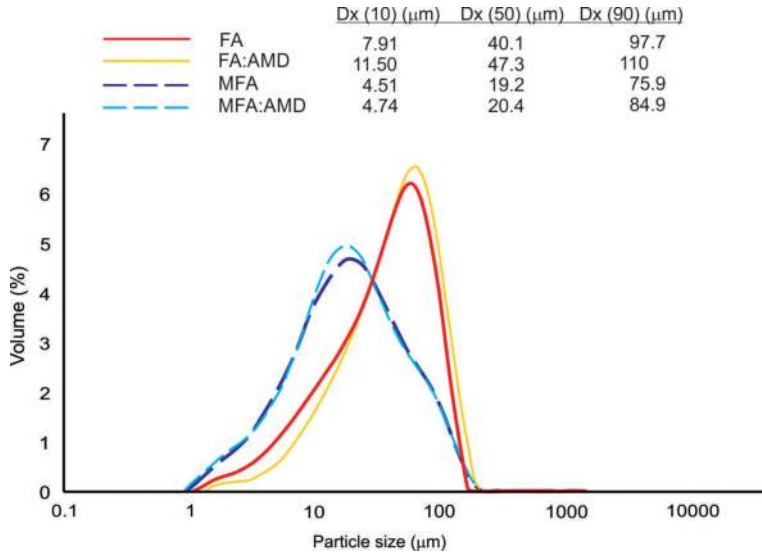


Figure 11. Particle size distribution of FA, MFA and SR.

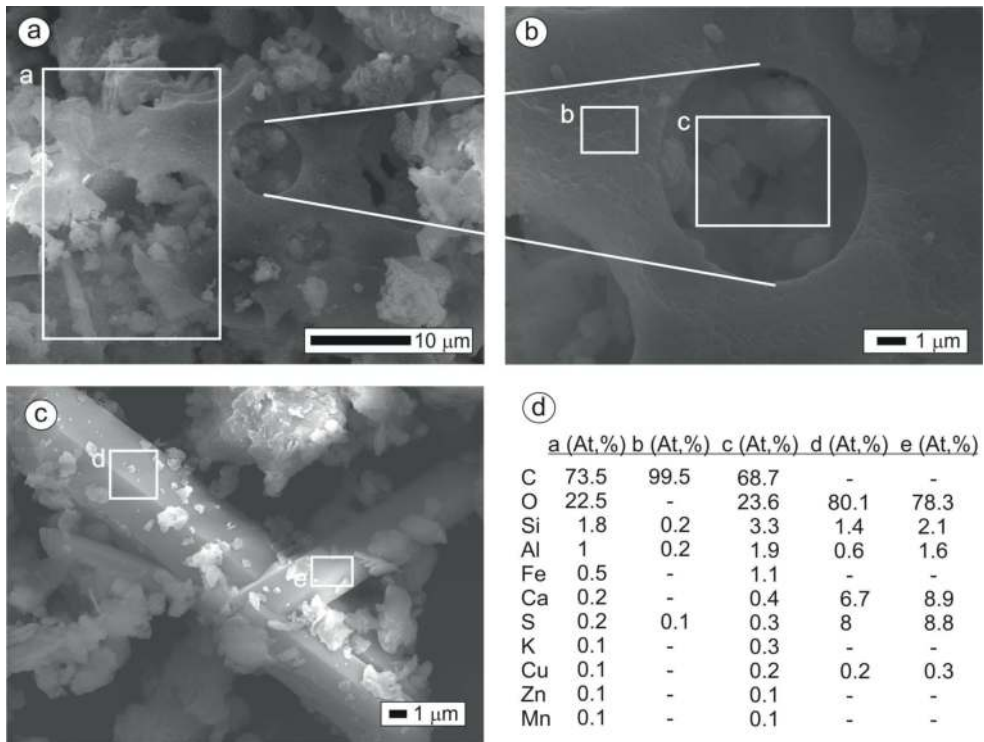


Figure 12. SEM results of: (a, b) SR (MFA:AMD), (c) gypsum and (d) EDX results of SR.

Mineral phases	FA	MFA	FA:AMD	MFA:AMD
	%			
Quartz	42	37	40	33
Amorphous phase	23	31	28	29
Mullite	13	10	7	9
Plagioclase	12	10	8	9
Gypsum	-	-	8	12
Hematite	6	2	4	3
Magnetite	2	1	1	1
Mica	1	5	2	3
K-feldspar	1	4	2	1

Table 4. Mineral phases in FA, MFA and SR.

to Si-O and Al-O vibrations, which is located at 1046 cm⁻¹ in FA, moves towards lower frequencies when those are activated [69]. Ultrasound energy strengthens the bond at the solid particle phase interface [38]. Band at about 1000 cm⁻¹, corresponding either to the stretching vibrations of Si-O bonds in SiO₄ or to the skeleton of bonded SiO₄ tetrahedra, shows the greatest change during crystallization [38, 70, 71]. The FTIR spectrum of the FA and MFA of crystallization contains a number of characteristic vibration bands in the regions 1100–900 and 850–650 cm⁻¹.

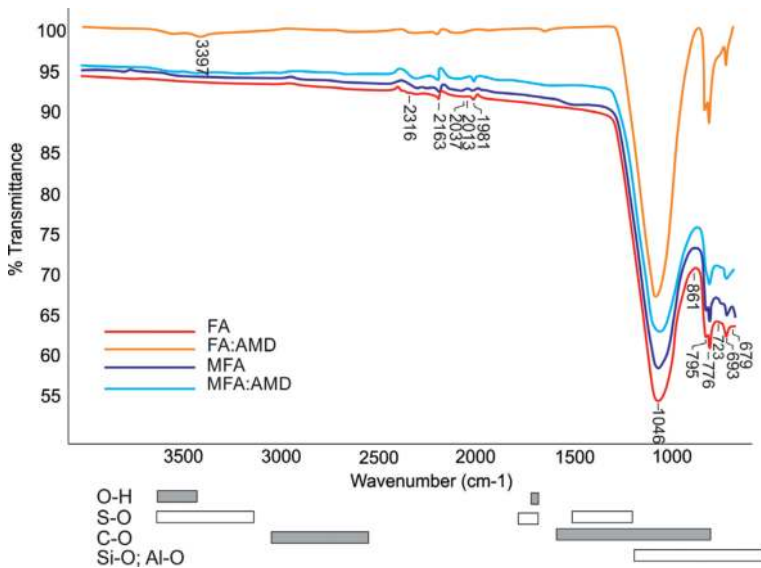


Figure 13. FTIR spectra of FA, MFA and SR.

4. Conclusion

Due to unique properties of the all mines, AMD may display variable hydrogeochemical characteristics; special studies are required for each mine site, though the general approach remains the same. In this chapter, treatment of AMD using FA and MFA under various conditions was investigated. The effect of US on the surface of FA was ensured adsorbent surface activation by ultrasonic cavitation. The physical changes on the surface of the FA caused by the US-assisted modification were identified using arrays of XRF, BET, SEM-EDX, XRD, FTIR techniques and particle size analysis. It was observed that due to the ultrasound-assisted modification, beside the physical properties of FA, the morphological and mineralogical characteristics are varied as well. The MFA has a lower Si and Al concentrations and higher surface area and pH than the FA. The chemical results imply that it is possible to use FA and MFA in order to neutralize AMD followed by precipitation and adsorption of metals. The 99.9% Fe removal was determined using FA with optimum 2 hours contact time and 1:5 (FA:AMD) ratio and using MFA with optimum 1 hour contact time and 1:10 (MFA:AMD) ratio under the same experimental conditions. Modified fly ash provides more successful results in a shorter reaction time and with smaller FA dosage for metal and SO_4^{2-} removal from AMD when compared to FA. Acid mine drainage reacted with MFA resulted in neutral pH after a longer reaction time was accompanied by 39% SO_4^{2-} removal. The five factors that dictate the nature of the final solution in neutralization reactions and metal removal are modification, mixing speed, pH, adsorbent dosage and contact time. Preliminary treatment of AMD revealed that the MFA has the potential to be used as an effective adsorbent to treat AMD. Additionally, this chapter provides an example for other areas with AMD environmental problems.

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