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Research Article

REMOVAL OF HEAVY METALS FROM SYNTHETIC ACIDIC MINE WATER USING RECYCLED AGGREGATES

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Abstract: *Acid mine drainage (AMD), a highly acidic and sulfate (SO_4^{2-})-rich solution, is an environmental concern related to the release of metal-containing wastewater from mining areas into the environment. In this study, recycled aggregates (RA) produced from concrete debris were used in the treatment of acidic mine water contaminated with heavy metals. For a model synthetic acidic mine water with a pH of 2.31, SO_4^{2-} and iron (Fe) concentrations of 5200 mg L^{-1} and 700 mg L^{-1}, respectively, RA increased the pH value to 11.18 and reduced the SO_4^{2-} and Fe concentrations by 90.51% and 100%, respectively, at RA/AMD ratio of 100 mg L^{-1} after 300 minutes of shaking at room temperature in batch experiments. The test results also showed that 100% of copper (Cu), zinc (Zn), manganese (Mn), silver (Pb), and cobalt (Co) concentrations were removed at this ratio and shaking time. This study demonstrates that RA has significant potential to neutralize acidity and remove heavy metals from AMD, a serious problem for ecological systems and health.*

Keywords: *Acid mine drainage, Heavy metals, Recycled aggregates, Batch experiment.*

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1. Introduction

Acid mine drainage (AMD) is a significant environmental problem caused by sulfide mining operations. AMD process starts when sulfide minerals react with oxygen and water [1-5]. Acidic mine waters have low pH because of the oxidation of sulfide minerals to produce sulfuric acid (1) and contain elevated concentrations of SO_4^{2-}, Fe, and other dissolved metals [6-9].

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \tag{1}$$

Heavy metal contamination in the aqueous environment is a serious problem for ecological systems and health. If AMD is not controlled, its formation can continue for hundreds of years even after the mine is closed [10-13]. AMD with low pH and high concentrations of heavy metals can be remedied using a process such as adsorption, ion exchange, membrane separation, electrochemical approach, or precipitation [14]. These acidic waters are generally treated with alkaline materials such as recycled aggregates (RA), which increase the pH of aqueous systems and precipitate heavy metals [15, 17].

The concrete industry is one of the leading sectors using the natural resource in the world. The demolition process produces very large quantities of concrete debris and causes great concern for the environment and the economy. Concrete contains 70% aggregates and the industry consumes about 7 billion tons of aggregates every year [18]. After the demolition process, RA produced from concrete debris is mainly composed of a mixture of hydrated cement paste and aggregates. Alkaline materials like RA generated from concrete debris can be used in neutralizing acidic water and immobilizing heavy metals [19, 20]. The utilization of RA reduces the amount of waste in landfills, thus preserving natural resources and contributing to greater environmental sustainability. This study aimed to investigate the effect of different RA/AMD ratios and shaking times on changes in pH value and SO_4^{2-}, Fe, Cu, Zn, Mn, Pb, and Co concentrations in acidic water.

2. Materials and Methods

RA used in this study was obtained from Istanbul Environmental Management Industry and Trade Company (ISTAC), Istanbul, Turkey. The sample was crushed and sieved below 150 microns. A synthetic AMD solution was prepared by dissolving metal sulfates ($FeSO_4$, $CuSO_4$, $ZnSO_4$, $MnSO_4$, $PbSO_4$, and $CoSO_4$) (MERCK, analytical grade) in distilled water. Batch experiments were conducted to evaluate the treatment efficacy by monitoring pH change, and SO_4^{2-} and metal removal rates. Powdered RA samples with masses 20, 40, 60, 80, and 100 g were added to the synthetic AMD solution having a volume of 1000 mL. These rates were adjusted to 2, 4, 6, 8, and 10 g of RA samples in 100 ml of AMD solution and placed in 250 ml Erlenmeyer flasks.

RA and AMD mixtures were agitated in an orbital shaker with continuous agitation at a speed of 180 rpm at room temperature (25°C) for 300 minutes. 10 mL samples were withdrawn using a syringe every 30 minutes, filtered, and stored in sterile tubes at 4°C. The solutions were analyzed to determine the pH value and SO_4^{2-}, Fe, Cu, Zn, Mn, Pb, and Co concentrations.

The chemical composition of RA was determined by X-ray fluorescence (XRF-Philips pW 1400) and reported in wt.%. Solution pH was measured using an Orion model 209 pH meter. The heavy metal concentrations were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES-Perkin Elmer Optima DV 7000). The SO_4^{2-} concentration was measured using a UV/Vis spectrophotometer according to method 375.4 of EPA [21].

3. Results and Discussion

3.1. RA and Synthetic AMD Characterization

The chemical composition of RA is given in Table 1. RA is mainly comprised of CaO (36.28%), SiO_2 (25.88%), Al_2O_3 (5.05%), Fe_2O_3 (2.35%), and MgO (2.18%). A synthetic AMD solution has a composition of 5200±50 mg L^{-1} SO_4^{2-}, 700±20 mg L^{-1} Fe, 50±5 mg L^{-1} Cu, Zn, and Mn; 5±0.5 mg L^{-1} Pb and Co; and pH of 2.31 (Table 2).

Table 1. Chemical composition of the RA (%)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Na_2O	TiO_2	MnO
36.28	25.88	5.05	2.35	2.18	1.00	0.63	0.62	0.26	0.07
P_2O_5	SrO	ZnO	Cl	BaO	ZrO_2	Cr_2O_3	NiO	CuO	LOI
0.06	0.06	0.05	0.05	0.03	0.03	0.02	0.01	0.01	25.38

LOI: Loss of ignition

Table 2. Chemical composition of synthetic AMD (pH = 2.31)

Component	Source	Concentration (mg L^{-1})
Fe	$FeSO_47H_2O$	700±20
Cu	$CuSO_45H_2O$	50±5
Zn	$ZnSO_47H_2O$	50±5
Mn	$MnSO_4H_2O$	50±5
Pb	$PbSO_4H_2O$	5±0.5
Co	$CoSO_47H_2O$	5±0.5
SO_4^{2-}	-	5200±50

3.2. The pH Changes of Synthetic AMD

The time-dependent variations in the pH value, Fe and SO_4^{2-} concentrations measured during batch tests conducted at different RA/AMD ratios are given in Figure 1. The pH increased rapidly at the first 30 minutes and reached an almost steady state for all dose applications. The pH value was measured as 5.57 with a minimum RA dose (20 g L^{-1}) application and increased from 2.31 to 11.18 with a maximum RA (100 g L^{-1}) application after 300 minutes of shaking. The increase in pH value was due to the dissolution of CaO present in RA having high alkalinity. Name and Sheridan [22] state that a high amount of CaO in compounds reacts with water to form calcium hydroxide ($Ca(OH)_2$) and the dissolution of $Ca(OH)_2$ generates the alkalinity.

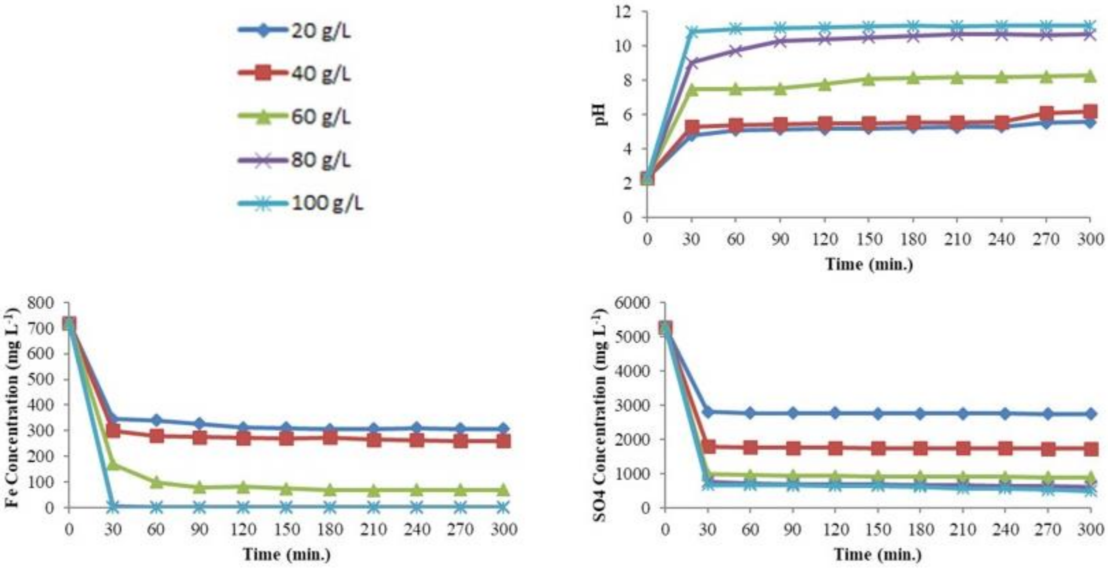

Figure 1. The changes of pH value, Fe, and SO_4^{2-} concentrations at different RA/AMD ratios and shaking times.

3.3. Removal of SO_4^{2-} and Heavy Metals

SO_4^{2-} and Fe concentrations decreased with an increase in RA/AMD ratios. The concentrations dropped very quickly in the first 30 minutes. The removal rate was a function of the RA/AMD ratio with higher ratios showing the highest removal rate. SO_4^{2-} concentration decreased from 5200 mg L^{-1} to 501 mg L^{-1} while Fe concentration decreased from 700 mg L^{-1} to 0.001 mg L^{-1} at RA/AMD ratio of 100 mg L^{-1} after 300 minutes of shaking. The pH value of 11.18 was recorded at this ratio (Figure 1). SO_4^{2-} and Fe concentrations were reduced by 90.51% and 100%, respectively, at RA/AMD ratio of 100 mg L^{-1} at the end of 300 minutes (Table 3). SO_4^{2-} removal is pH-dependent. The drop in the concentration of SO_4^{2-} at high pH is due to the precipitation process [23]. RA, as a calcium-rich neutralizing agent, removed the SO_4^{2-} ions in the acidic mine waters by precipitation. Madzivire et al. [24] explained the SO_4^{2-} ions concentration could be controlled by the precipitation of gypsum ($CaSO_4.2H_2O$) at low pH and ettringite ($Ca_6Al_2(SO_4)_3.32H_2O$) at high pH.

Table 3. Removal efficiencies of SO_4^{2-} and heavy metals at different RA/AMD ratios and shaking times

		Removal efficiency (%)									
	RA/AMD ratio	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**	**270**	**300**
		(minutes)									
SO_4	**20 g L^{-1}**	46.76	47.39	47.46	47.52	47.67	47.71	47.77	47.78	47.82	47.82
	40 g L^{-1}	65.85	66.36	66.59	66.67	66.86	66.88	66.93	66.95	67.03	67.05
	60 g L^{-1}	81.42	81.86	82.05	82.18	82.42	82.48	82.69	82.80	82.94	83.03
	80 g L^{-1}	85.44	86.63	86.88	86.93	87.03	87.16	87.18	87.78	88.05	88.31
	100 g L^{-1}	87.27	87.37	87.42	87.65	87.80	88.16	89.05	89.07	89.83	90.51
Fe	**20 g L^{-1}**	52.08	52.78	54.44	56.67	56.94	57.64	57.36	56.94	57.22	57.36
	40 g L^{-1}	58.33	61.11	61.81	62.22	62.50	61.94	63.19	63.33	63.89	63.89
	60 g L^{-1}	76.39	86.11	88.89	88.61	89.58	90.28	90.56	90.28	90.28	90.28
	80 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	100 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Cu	**20 g L^{-1}**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	40 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	60 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	80 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	100 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Zn	**20 g L^{-1}**	98.54	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	40 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	60 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	80 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	100 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Mn	**20 g L^{-1}**	83.78	89.49	91.37	93.91	95.72	96.84	97.71	98.22	98.60	100.00
	40 g L^{-1}	98.83	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	60 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	80 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	100 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Pb	**20 g L^{-1}**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	40 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	60 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	80 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	100 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Co	**20 g L^{-1}**	91.44	95.20	96.40	97.56	98.34	98.70	98.56	98.76	99.04	100.00
	40 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	60 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	80 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	100 g L^{-1}	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Initial concentrations: SO_4^{2-} = 5200 mg/L; Fe = 700 mg/L; Cu = 50 mg/L; Zn = 50 mg/L; Mn = 50 mg/L; Pb = 5 mg/L; Co = 5 mg/L.

All the soluble Fe was removed using RA, which was attributed to the formation of various precipitates. Name and Sheridan [22] explained that the potential-pH diagram for Fe–S–H_2O system indicated that $Fe(OH)_3$ and $Fe(OH)_2$ were formed as precipitates. Rose [25] also explained that more Fe precipitates such as (FeOOH), (Fe_2O_3), and ($Fe_5O_8H.4H_2O$) could be formed at different pH values. Soluble Fe was removed from the AMD as a form of different insoluble compounds. The results indicated that RA is well suited for pH increase as well as SO_4^{2-} and Fe reductions. Cu, Zn, Mn, Pb, and Co were also totally removed from acidic water at RA/AMD ratio of 100 mg L^{-1} after 300 minutes of shaking (Table 3). Rodríguez-Jordá et al. [26] stated that heavy metals could be removed from AMD by precipitation using alkaline materials.

4. Conclusion

RA was used in this study as a neutralizing agent for the treatment of AMD. The results clearly indicated that RA reduced the acidity, SO_4^{2-}, Fe, and other heavy metals (Cu, Zn, Mn, Pb, and Co) concentrations. The removal rate of SO_4^{2-} and heavy metals increased parallel to the RA/AMD ratios. SO_4^{2-} and heavy metal removal was very rapid in the first 30 minutes. The results show that RA could be effectively used as an alternative alkaline material to neutralize acidity and remove heavy metals from AMD.

Conflict of Interest: The author declares no conflict of interest.

Compliance with Research and Publication Ethics: This work was carried out by obeying research and ethics rules.

The Declaration of Ethics Committee Approval: The author declares that this document does not require ethics committee approval or any special permission. Our study does not cause any harm to the environment.

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