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# Treatment of combined acid mine drainage (AMD)—Flotation circuit effluents from copper mine via Fenton's process

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## ABSTRACT

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*Keywords:* Acid mine drainage Copper mine Fenton process Oxidation The treatability of a copper mine wastewater, including heavy metals, AMD, as well as flotation chemicals, with Fenton process was investigated. Fenton process seems advantageous for this treatment, because of  $Fe^{2+}$  content and low pH of AMD. First, optimum  $Fe^{2+}$  condition under constant  $H_2O_2$  was determined, and initial  $Fe^{2+}$  content of AMD was found sufficient (120 mg/L for removal of chemical oxygen demand (COD) of 6125 mg/L). In the second step, without any additional  $Fe^{2+}$ , optimum  $H_2O_2$  dosage was determined as 40 mg/L.  $Fe^{2+}/H_2O_2$  molar ratio of 1.8 was enough to achieve the best treatment performance. In all trials, initial pH of AMD was 4.8 and pH adjustment was not performed. Utilization of existing pH and  $Fe^{2+}$ , low  $H_2O_2$  requirements, and up to 98% treatment performances in COD, turbidity, color,  $Cu^{2+}$ ,  $Zn^{2+}$  made the proposed treatment system promising. Since the reaction occurs stepwise, a two-step kinetic model was applied and calculated theoretical maximum removal rate was consistent to experimental one, which validates the applied model. For the optimum molar ratio (1.8), 140 mL/L sludge of high density (1.094 g/mL), high settling velocity (0.16 cm/s) with low specific resistance (3.15 × 10<sup>8</sup> m/kg) was obtained. High reaction rates and easily dewaterable sludge characteristics also made the proposed method advantageous.

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## 1. Introduction

Mine pits and underground workings; waste rock piles; tailings; spent leach piles are of particular concern in the copper industry, because these are the areas in which toxic contaminants are most commonly found having the potential to present harm to the environment. Contaminants associated with these areas may include heavy metals and acid drainage, as well as flotation chemicals. These contaminants may degrade groundwater, surface water, soil, and air quality during mine operation and after mine closure.

In most of the cases, flotation circuits employ near open pits or underground mines, and flotation effluents containing several organic collectors and other chemicals are mixed with acidic drainages from the mine in a pond and discharged together. Acid mine drainages (AMD) are highly contaminated liquid wastes in which natural water with dissolved sulphur compounds of local geological formation. Sulphur compounds are oxidized by bacteria in the presence of oxygen giving sulphuric acid and dissolved metals depending upon the pH and environmental potential [1,2]. These compounds are generally chalcopyrite (CuFeS<sub>2</sub>), galen (PbS) and sphalerite (ZnS), etc. When pyrite is exposed to air and water, it can oxidize by using oxygen and the reaction generates Fe<sup>2+</sup> and sulphuric acid [3,4]. Acid drainage has several characteristics (low pH, contaminants, and latency) that contribute to the severity of its effects. The acids, sulphates and dissolved metals contained in AMD may be detrimental to aquatic life, and therefore, it requires treatment prior to discharge [2]. Active and passive chemical methods have been applied for the treatment of AMD. Some of them are chemical precipitation [5], electrochemical treatment [6], neutralization [7,8], precipitation and ion exchange [9] and physico-chemical adsorption [10].

The separation of minerals from ores is a very important industrial process. The commonly applied separation method is flotation, which ensures the required balanced relation between the hydrophobic and hydrophilic properties on the surface of the mineral particles. This is achieved by adding organic reagents known as collectors to the crushed ores, dispersed in water. Xanthates (R'OCS<sup>2–</sup>, where R' is an aliphatic chain) are commonly used as collectors for the selective hydrophobization of minerals in flotation process [11,12]. Ethyl ( $C_2H_5OCS_2^{-}$ ) to amyl ( $C_5H_{11}OCS_2^{-}$ ) xanthate, which are the most commonly used separation reagents show the formation of hydrophobic products on the minerals at open circuit potentials [13]. For chalcopyrite the cuprous xanthate is the major adsorption product formed in the region of higher potentials.

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Studies with AMD have focused on removal of acidity, metal and sulphate content of the drainage itself. However, in case of combined effluents, existence of organic matter in varying quantities from flotation circuit helps this waste to be oxidized via various oxidation processes, which can oxidize heavy metals and other constituents simultaneously. This has not been considered anywhere before.

Fenton's oxidation process is one of the advanced oxidation processes. It has been applied to various types of wastewaters [14–18], but not to AMD combined with mineral processing effluents.

Fenton's reagent is one of the best known metal-catalyzed oxidation reactions. It consists of ferrous salt or any other ferrous complex and  $H_2O_2$ . This mixture, at sufficiently low pH results in ferrous catalytic decomposition of  $H_2O_2$  and proceeds via a free radical chain process producing hydroxyl radicals (OH•) [19,20]. Peroxide dose and iron concentration are important factors for a better degradation efficiency and reaction kinetics, respectively [19]. Following chemical mechanisms (1)–(7) manage the Fenton oxidation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$$
 (1)

Hydroxyl radicals may be scavenged by reaction with another Fe<sup>2+</sup>:

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$$
<sup>(2)</sup>

 $Fe^{3+}$  catalytically decomposes  $H_2O_2$  following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, including (1) and (2):

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^+$$
(3)

$$Fe-OOH^{2+} \rightarrow HO^{\bullet}_{2} + Fe^{2+}$$
(4)

$$\mathrm{Fe}^{2+} + \mathrm{HO}^{\bullet}_{2} \to \mathrm{Fe}^{3+} + \mathrm{HO}_{2}^{-} \tag{5}$$

$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + H^+ + O_2$$
 (6)

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet}_2 \tag{7}$$

Generally, Fenton's oxidation process was composed of four stages: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. The organic substances are degraded at the oxidation and coagulation stages. The presence of H<sup>+</sup> is required in the oxidation stage for the decomposition of  $H_2O_2$  indicating the need for an acidic environment to produce maximum OH<sup>•</sup>. AMD are originally acidic and contain heavy metals including Fe<sup>2+</sup> [1], and this makes them suitable for Fenton's oxidation.

The purpose of this study is to investigate the applicability of Fenton's oxidation process to AMD combined with flotation effluents. The objective of the study is to achieve maximum treatment of the effluent (in terms of COD, color, turbidity and heavy metals) with minimal chemical consumption by using acidic character and Fe<sup>2+</sup> content of the AMD.

#### 2. Materials and methods

#### 2.1. Wastewater source and characterization

Wastewater sample was taken from a copper (Cu) mine in Turkey, enriching Cu from chalcopyrite (CuFeS<sub>2</sub>) in the presence of pyrite (FeS<sub>2</sub>). Massive rich copper ore contain 0.2–7.43% Cu, 0.044% Pb, 0.33% Zn, 0.08% Co, 0.002% Ni, 1 g/t Au, 14 g/t Ag [21]. Plant is composed of two main parts: mine and mineral processing. Mine is an open pit with an acidic drainage. In the mineral processing plant, the ore is mixed to contain average 1.7% Cu and fed to flotation circuit where 15–17% Cu concentrate and 46% S concentrate are produced with 80% efficiency. The ore is enriched via a series of flotation system in which collector and frother reagents (potassium amyl xanthate and potassium ethyl xanthate) are used besides some other organic chemicals for frothing and pH adjustment, and

#### Table 1

Characteristics of the wastewater sample.

Parameter	Value	
рН	4.8	
COD, mg/L	6125	
Turbidity, NTU	1160	
Color, Pt–Co	3600	
SO <sub>4</sub> <sup>2–</sup> , mg/L	6700	
Fe <sup>2+</sup> , mg/L	120	
Cu <sup>2+</sup> , mg/L	10.34	
$Zn^{2+}$ , mg/L	31.16	
UV <sub>254</sub> , 1/m	1.6	

the effluents of this flotation circuit were combined with AMD of higher flowrate in the pond. The characteristics of wastewater sample taken from the pond are presented in Table 1. As can be seen in Table 1, the sample contains high organic matter (as COD) due to flotation reagents which is crucial for Fenton's oxidation. Aromatic fraction of this COD is also high which is represented by  $UV_{254}$ .

#### 2.2. Experimental

A 250 mL beaker equipped with stainless-steel stirrer was used as a reactor. The reactor was first filled with 200 mL wastewater. The second step was the addition of analytical grade ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) solution, which was supplied from Merck. In the third step, hydrogen peroxide (medical extra pure grade 35% from Merck) was added to the medium and the reaction was started without any pH adjustment. After the addition of chemicals, the liquid was mixed 1.5 min at 450 rad/min (rapid mixing) and 60 min at 50 rad/min (slow mixing). Following the completion of the slow mixing period, pH of the mixed liquor was adjusted to 7-8 with 1N NaOH. The residual H<sub>2</sub>O<sub>2</sub> was measured by using the iodometric method suggested by Boltz and Howell [22], and was immediately quenched by using a slight excess of sulfite [20] to stop the oxidation reaction, and the mixed liquor was allowed to precipitate for 2 h. Then, the supernatant was separated from the precipitate for analysis of the monitoring parameters. All experiments were carried out at  $20 \pm 2$  °C, which corresponds to average room temperature.

After optimization and kinetic studies, characteristics of Fenton sludge were also examined. On sludge samples, settled sludge volume (SSV), density, specific cake resistance (r) were measured, and sludge volume index (SVI) and sludge settling velocity ( $v_s$ ) were calculated in the settled sludges.

#### 2.3. Analytical methods

All parameters monitored throughout the experiments were analyzed according to Standard Methods by APHA/AWWA/WEF [23]. Cu<sup>2+</sup> and Zn<sup>2+</sup> were analyzed with Atomic Absorption Spectrometer (AAS) GBC Model with Air/Acetylene Flame atomizer; color and turbidity were measured as Pt–Co unit and NTU, respectively, with HACH DR 4000 spectrophotometer; pH of the samples was measured with a SELECTA pH meter.

Sulphate (SO<sub>4</sub><sup>2-</sup>) content of the sample was also high, which has considerable interference on COD analysis, therefore, the given COD value was the one measured with method modification against the interference as suggested in the Standard Methods [23]. Similarly, H<sub>2</sub>O<sub>2</sub> in the samples have influence on COD. To overcome this, first H<sub>2</sub>O<sub>2</sub>-COD calibration was performed with known concentrations of H<sub>2</sub>O<sub>2</sub> in the system, and corrections were performed in the subsequent COD analyses.

The sludge volume index (SVI) may be used as a standard parameter for expressing sludge settleability and hence dewatering potential by simple settlement. The SVI is defined as the volume in millilitres occupied by one gram of dry solids after settling the



Fig. 1. Effect of  $Fe^{2+}$  dosage (initial values: pH 4.8,  $H_2O_2 = 100$  mg/L, COD = 6125 mg/L, color = 3600 Pt-Co, turbidity = 1160 NTU).

mixed liquor for 30 min. In sludge studies, first volumes of settled sludges (SSV) were measured by placing them in a graduated cylinder and simply recording the final sludge volume at the end of settling time. Also, suspended solids contents of the sludges were determined gravimetrically, and SVI was calculated by dividing SSV

to sludge suspended solids. Sludge densities were determined by weighing the settled sludge and dividing the weight to volume of the sludge. During the settling period, height of settled sludge was recorded against time and slope of the initial portion of the settling height versus time plot gave the sludge settling velocity.



Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> dosage (initial values: pH 4.8, Fe<sup>2+</sup> = 120 mg/L, COD = 6125 mg/L, color = 3600 Pt-Co, turbidity = 1160 NTU, UV<sub>254</sub> = 1.623 1/m).



Fig. 3. Effect of Fe<sup>2+</sup> dosage on the removal of Cu<sup>2+</sup> and Zn<sup>2+</sup> (initial values: pH 4.8,  $H_2O_2 = 100 \text{ mg/L}$ ,  $Cu^{2+} = 10.34 \text{ mg/L}$ ,  $Zn^{2+} = 31.16 \text{ mg/L}$ ).



Fig. 4. Effect of  $H_2O_2$  dosage on the removal of  $Cu^{2+}$  and  $Zn^{2+}$  (initial values: pH 4.8, Fe<sup>2+</sup> = 120 mg/L,  $Cu^{2+}$  = 10.34 mg/L,  $Zn^{2+}$  = 31.16 mg/L).

The specific resistance to filtration may be defined as the resistance of sludge (r), having a unit weight of dry solids per unit area at a given pressure, to a unit rate of flow of liquid having unit viscosity. The filtration of sludge was analyzed based on the flow of a liquid through a porous medium. Using a laboratory filtration apparatus settled volume was recorded against time and r was calculated from the slope of t/V against V plot. In reporting a value of specific resistance to filtration, it is necessary to quote the pressure difference at which the measurement was carried out. A vacuum of 49 kN/m<sup>2</sup> is standard [24]. The results of the specific resistance to filtration test are reported as m/kg.

#### 3. Results and discussion

### 3.1. Effect of $Fe^{2+}$ and $H_2O_2$ dosage on Fenton's oxidation

Experiments were performed by varying the Fe<sup>2+</sup> dosage keeping the other conditions constant at original pH (4.8) and 100 mg/L  $H_2O_2$  dosage to determine the effect of  $Fe^{2+}$  on the degradation efficiency. 120 mg/L of Fe<sup>2+</sup> concentration in the original matrix of the wastewater was used as initial dose of Fe<sup>2+</sup> in order to initiate the Fenton reaction. Variation of Fe<sup>2+</sup> dosage was maintained by adding prepared FeSO<sub>4</sub>.7H<sub>2</sub>O solution in varying quantities up to 1120 mg/L. It was observed that most of the reduction achieved within the first 2 min; and rest of the reaction took about 1-2 h for practically complete degradation and settling. Change of residual quantities of monitored parameters with  $Fe^{2+}/H_2O_2$  molar ratio, and removal efficiencies of COD, color, turbidity with varying Fe<sup>2+</sup> dosage are indicated in Fig. 1. It appears that the extent of degradation of COD, color and turbidity increases and reaches a maximum when the  $Fe^{2+}/H_2O_2$  molar ratio reaches around 2.5. For COD, turbidity and color, removal efficiencies reached up to 98-99% between Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> molar ratio of 1-2.5. These ratios correspond to 165-415 mg/L of Fe<sup>2+</sup> dosages. Here COD and color was removed during the oxidation, and coagulation step was the main turbidity removal phase. Hydrous ferric oxides (HFO), which are sparingly soluble solids, form during initial reaction [25], act as coagulant aids, and cause sweep floc mechanism as well as adsorption of colloids and settling them via interparticle bridging

Lower molar ratios with higher efficiencies indicated that existing Fe<sup>2+</sup> in the original matrix of wastewater would be sufficient to initiate the Fenton reaction and to remove the impurities, if suitable  $H_2O_2$  dosage could be applied. Therefore, in the second optimization step of chemical dosage, molar ratio interval of 1–2.5 was studied by varying the  $H_2O_2$  dosage keeping the other conditions constant (Fig. 2). Fig. 2 also indicates the removal efficiencies of COD, color, turbidity and  $UV_{254}$  against  $H_2O_2$  dosage.

Determining the optimum H<sub>2</sub>O<sub>2</sub> dosage is very important from the economical point of view, due to the cost of the H<sub>2</sub>O<sub>2</sub> solution. As indicated in Fig. 2, the fractional removal remains almost the same up to  $Fe^{2+}/H_2O_2$  molar ratio of 1.8, a decrease in fractional conversion was observed beyond this, and after 2.5 there is no considerable positive effect of H<sub>2</sub>O<sub>2</sub> addition. At Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> molar ratio of 1.8 (which corresponds to 40 mg/L of  $H_2O_2$  dosage) and less, up to 98% COD removal was achieved as well as turbidity (97%), color (98%) and UV<sub>254</sub> (99.9%). For Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> molar ratios less than 1.8, still same performances were achieved, but, since low ratio means higher H<sub>2</sub>O<sub>2</sub> dose, this is not suggested due to economical considerations for the chemical. At low H<sub>2</sub>O<sub>2</sub> dosages, according to the literature, the OH• preferentially attack the organics present in wastewater, however, at high H<sub>2</sub>O<sub>2</sub> dosages, there is a competition between organics and  $H_2O_2$ , in other words,  $H_2O_2$  in high dosages acts as a scavenger of the OH• to produce perhydroxyl radical, which is rather innocent towards redox action [16].

It was thought important to verify whether the COD and color of the wastewater actually degraded by Fenton reactions or the disappearance was due to some other effects. To investigate this, UV absorbance values at 254 nm (UV<sub>254</sub>) were measured. The UV<sub>254</sub> could represent the degree of aromaticity and unsaturated compounds present in water, which also cause color. Measurements indicated that up to 99% UV<sub>254</sub> reduction occurred, which proves that color causing molecules were destroyed through oxidative degradation (Fig. 2).

In the degradation of organics via Fenton process, the reactions may be divided into three major groups [15]. In the first group are the principal inorganic reactions that represent the interactions among various inorganic species including OH<sup>•</sup>, HO<sub>2</sub>, O<sub>2</sub><sup>-</sup>,  $H_2O_2$ ,  $Fe^{2+}$ , and  $Fe^{3+}$ . The second group includes the interactions among organic species (parent compounds and their break-down intermediates and/or products) and the reactive inorganic species except the Fe species. In the third group are the reactions among Fe and the organic species that influence the Fe-redox cycle. The first group is now considered relatively well established. In the second group, identification of the unstable intermediates is critical but often incomplete. Among the interactions in the third group, of particular concern is the roles of the organic intermediates or final products in the Fe-redox cycle. They might accelerate Fe<sup>3+</sup> reduction to  $\mathrm{Fe}^{2+}$  and/or potentially deactivate iron by forming stable complexes. Given certain experimental conditions, initial oxidation rates by Fenton's reagent appear primarily to depend on the rate between OH<sup>•</sup> and the parent compounds. However, as a



**Fig. 5.** Relationship between  $t/(1 - C/C_0)$  and oxidation time *t*.  $[Fe^{2+}]_0 = 120 \text{ mg/L}$ ,  $[H_2O_2]_0 = 40 \text{ mg/L}$ .

significant portion of initial Fe<sup>2+</sup> is rapidly consumed, the subsequent decomposition rate is likely to be affected by the third group types of interactions among the intermediates and the Fe species [15].

Cu<sup>2+</sup> and Zn<sup>2+</sup> originally present in AMD were also followed and indicated in Figs. 3 and 4. For  $Fe^{2+}/H_2O_2$  molar ratio between 1–2.5, which was found as the chemical condition of highest performance, up to 95% Cu<sup>2+</sup> and 80% Zn<sup>2+</sup> removals were achieved. Literature indicates that, presence of Cu<sup>2+</sup> ions in the system affects oxidation process in a positive way, such that Cu shows reasonably well Fenton activity over pH range 3-8 [26]. In case, presence of sufficient Fe<sup>2+</sup> ions in the system, excess OH• produced via Cu-H<sub>2</sub>O<sub>2</sub> reaction cause excess HFO, sparingly soluble solids adsorbing metals (here Zn<sup>2+</sup>) under pH conditions less than 6. Limited studies have shown that sorption of heavy metals onto HFO is a two-step process: rapid adsorption of metal ion to the external surface is followed by slow intraparticle diffusion along the oxide micropore walls [27]. This intraparticle diffusion is determined as the ratelimiting mechanism in the sorption process of Zn<sup>2+</sup> to microporous oxides [25].

It is reported in the literature that the decomposition of  $H_2O_2$  catalyzed by iron leading to the formation of OH• occurs best when the molar ratio of  $Fe^{2+}/H_2O_2$  is at a value of 1/15 at pH of 3 [16]. This ratio is significantly different from the values obtained in that study, and more advantageous in terms of required  $H_2O_2$  dosage. Main reason might be the pH of the solution, which was higher here, and effectiveness of other constituents of the AMD under this pH, e.g.  $Cu^{2+}$ , which was effective in presence of sufficient  $Fe^{2+}$  ions in the system, by producing excess OH• via  $Cu-H_2O_2$  reaction resulting in excess HFO formation as explained above. This  $Cu^{2+}$  reaction might also increased the  $Cu^{2+}$  and  $Zn^{2+}$  removal performance up to 97% and 85%, respectively.

#### 3.2. Kinetic assessment

The overall degradation of the dissolved organic matter contained in the wastewater by Fenton reaction is a complex process with many reactions, which cannot be individually distinguished. Therefore an approximate kinetic study of the oxidation of AMD by Fenton reaction could be performed by using any of the global parameters directly related to the organic load present in the effluent and measured by COD, color, UV<sub>254</sub> and turbidity. As found from the dimensionless concentration versus time plots, decrease in the concentration is dramatically in the first 2 min, which corresponds to rapid mixing stage. However, this is followed by slow mixing Table 2

Correlation coefficients and characteristics of kinetic model.

	т	b	$r^2$
COD	0.3155	1.0534	0.9996
Color	1.2246	1.1811	0.9987
Turbidity	0.7552	1.2431	0.9996
UV <sub>254</sub>	0.9160	1.3583	0.9994

stage in which flocculation occurs. Therefore, straight forward first order kinetics could not be applied to the whole reaction. A new mathematical model (Eq. (8)) derived by Behnajady et al. [28] was used determining the reaction kinetics:

$$\frac{C}{C_0} = \frac{1-t}{(m+bt)} \tag{8}$$

where *C* is the parameter concentration and/or value at any time, and  $C_0$  is the initial concentration/value of the parameter. *m* and *b* are the two characteristics of model and represent initial removal rate and theoretical maximum removal fraction of any parameter studied respectively. To determine the characteristics of *m* and *b*, Eq. (8) can be linearized as follows (Eq. (9));

$$\frac{t}{1 - C/C_0} = m + bt \tag{9}$$

120 mg/L of Fe<sup>2+</sup> and 40 mg/L of H<sub>2</sub>O<sub>2</sub> doses, previously determined as optimum values of Fenton oxidation, were used in kinetic studies. A straight line was obtained by plotting  $t/(1 - C/C_0)$  for each parameter versus oxidation time t, and m and b the coefficients of Eq. (8) were obtained from the intercept and the slope of the line (Fig. 5). Model characteristics m and b are also given in Table 2. As can be seen from Table 2 that a successful correlation coefficients were obtained.

Fig. 6 shows the dimensionless experimental data and model results of studied parameters COD, color, turbidity and  $UV_{254}$ . Model values of parameters were reproduced by substituting the values of model characteristics *m* and *b* in Eq. (8) for each one. It can be seen from Fig. 6 that the values for each parameter obtained from the model were in good agreement with the experimental data.

#### 3.3. Sludge characteristics

Characteristics of the resultant sludge of Fenton's oxidation were examined for five different  $Fe^{2+}/H_2O_2$  molar ratios including 1.8, which was suggested as the best in above discussions. Findings were presented in Table 3. For easier handling, treatment sludge



Fig. 6. Dimensionless experimental and model data.

#### Table 3

Sludge characteristics of five different  $Fe^{2+}/H_2O_2$  molar ratios.

$Fe^{2+}/H_2O_2$ (mol/mol)	SSV (mL/L)	SVI (mL/g)	Density (g/mL)	<i>r</i> (m/kg)	$v_{\rm s}$ (cm/s)
0.73	195	18	1.071	$2.49\times 10^8$	0.0921
1.21	150	12	1.010	$11 \times 10^{8}$	0.1218
1.34	200	12	1.059	$8.94\times10^8$	0.1008
1.82	140	11	1.094	$3.15  imes 10^8$	0.1617
5.28	200	12	1.084	$0.3\times10^8$	0.0907

should be of good quality. Its volume should be as low as possible which is indicated with SSV and SVI. It should be dense and easily settleable, and easily dewaterable. As indicated in Table 3, all studied Fenton sludges are of low SSV and SVI values; suggested optimum  $Fe^{2+}/H_2O_2$  molar ratio of 1.8 has the lowest. This sludge has also highest density and highest settling velocity ( $v_s$ ). Specific cake resistance (r) represents the dewaterability of the sludge. The higher value of r indicates a sludge which is more difficult to dewater. At lower values, no further conditioning of sludge is required [24], and here, Table 3 indicates all these Fenton sludges were easily dewaterable.

#### 4. Conclusions

Up to 97–98% treatment of COD, color and turbidity: and up to 85–97% Zn<sup>2+</sup> and Cu<sup>2+</sup> removal can be achieved via Fenton's oxidation treatment of combined AMD and flotation effluent from a copper mine. The best performance was achieved at  $Fe^{2+}/H_2O_2$ molar ratio of 1.8. It is suggested that, additional Fe<sup>2+</sup> dosing is not necessary, the Fe<sup>2+</sup> content of the AMD can be used in the reactions, only H<sub>2</sub>O<sub>2</sub> addition could be sufficient to initiate and complete Fenton's oxidation. Only chemical dosage adjustment may be required, depending upon influent Fe<sup>2+</sup> content of the AMD. Since original pH of AMD is already acidic, no additional pH adjustment at the beginning of the reaction is required. The utilization of existing Fe<sup>2+</sup> and pH of the AMD will have considerable savings in the chemical costs for the oxidation. Under these conditions, the H<sub>2</sub>O<sub>2</sub> requirement of the system is also considerably low as compared to other studies. Sludge quality of the process is sufficiently high in terms of dewaterability and handling characteristics of the sludge, which is also an advantageous property of a treatment process. Heavy metals in the AMD can also be reduced to very low levels via Fenton reactions by taking part in oxidation steps. In conclusion, considering the low pH and high Fe<sup>2+</sup> content of AMD, this wastewater can be treated efficiently via Fenton's process with very low chemical requirements and very high efficiency.

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