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TECHNICAL ARTICLE

Using Acid Mine Drainage to Recover a Coagulant from Water Treatment Residuals

Everton Skoronski[1] · Anderson Claiton Ohrt[1] · Rossano de Oliveira Cordella[1] · Viviane Trevisan[1] · Mylena Fernandes[1] · Thayná Fortunato Miguel[2] · Diana Aurerio Menegaro[2] · Lucas Dominguini[2] · Priscilla Reis Martins[3]

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Abstract We evaluated the recovery of aluminum from water treatment residuals by acidification using acidic coal mine drainage as an extraction solution. The water treatment residuals had Al and total Fe concentrations of 1.2 and 1.3%, respectively, based on mass. The influence of contact time of the mine water with the water treatment residuals and the percent of excess sulfate were assessed. The results showed that 28 min of contact and 100% of excess sulfate allowed recovery of >90% of the Al. Color was reduced from 25.9 to 0.8 total color units (TCU) and turbidity was reduced from 6 to 0 nephelometric turbidity units (NTU). The recovered coagulant performed appropriately in water treatment tests, based on physical–chemical parameters. The only parameter that requires more attention is antimony, which was close to the maximum concentration limits for drinking water.

Keywords Co-treatment · Aluminum · Waste management · Sulfate

Introduction

Coagulation/flocculation followed by sedimentation or flotation are commonly used to treat drinking water. The most commonly used coagulants in water treatment plants (WTP) are aluminum salts such as poly-aluminum chloride (PAC) and aluminum sulfate [$Al_2(SO_4)_3·14H_2O$]. These compounds are responsible for the removal of suspended solids by flocculation, forming a sludge known as water treatment residuals (WTR) (Howe et al. 2012).

The management of WTR in the environment remains a challenge, due to its impact on local water resources. In this context, the toxicity to the benthos is primarily associated with decreased water transparency or a high level of total suspended solids (TSS), which affects the phytoplankton. Toxic effects have also been observed in micro-crustaceans, affecting the food chain (ASCE and AWWA 1996). In addition, the Al^{3+} ions bind strongly to phosphorus, altering the biogeochemical cycle of this macronutrient (Kaggwa et al. 2001).

Despite knowledge of the environmental problems from poor WTR management, direct discharge of WTR to water resources remains as a common management practice in Brazilian WTPs. Thus, there exists a need for new management methods that are technically and economically feasible. According to the most recent National Survey of Basic Sanitation carried out in Brazil in 2008 (Instituto Brasileiro de Geografia e Estatística 2008), 1415 of the 2100 WTPs surveyed discharge their WTR into rivers and seven discharge them to the sea.

Alternative methods for more appropriate disposal of WTR to the environment include disposal in industrial landfills, controlled land disposal, using it as a raw material in the cement and ceramics industry, using it to improve coagulation of water with low turbidity, incorporation into

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✉ Everton Skoronski
skoronski@cav.udesc.br

[1] Department of Environmental Engineering, University of the State of Santa Catarina, Lages, Santa Catarina 88520-000, Brazil

[2] Federal Institute of Technological Education of Santa Catarina, Criciúma, Santa Catarina 88813-600, Brazil

[3] Criciúma Coal Mine S.A., Forquilhinha, Santa Catarina 88850-000, Brazil

the sewage system, and recovery of the coagulant. Recovery and recycling of the coagulant can reduce the environmental impact and in addition, reduces the volume of disposed sludge and decreases the demand for new coagulant by up to 70% (Keeley et al. 2014), though the recovered coagulant must be purified to treat drinking water (Keeley et al. 2012).

The most cost effective and commonly used method to recover the coagulant is acidification with sulfuric acid (Bishop et al. 1987; Oliveira et al. 2004). The recovery of aluminum sulfate with sulfuric acid is less expensive than acquiring the coagulant from an external source and reduces the release of Al ions into the environment (de Freitas et al. 2005; Keeley et al. 2014; Masschelein et al. 1985). Previous studies on the use of sulfuric acid in WTP demonstrated Al recovery efficiencies of 90% (Okuda et al. 2014) and 70% (Jiménez et al. 2007). This coagulant recovery process is established. However, the use of waste materials, such as acid mine drainage (AMD), to replace the sulfuric acid has not been studied.

AMD is generated in large quantities in the Criciúma region of southern Brazil. Conventional AMD treatment involves the removal of suspended solids and some metals, such as iron and manganese ions. Sulfate ions are highly soluble and persist in the effluent after AMD treatment. This effluent is disposed directly into water resources, often at levels that can be problematic for the environment (Blodau 2006; Bocanegra-García and Carrillo-Chávez 2003; Campaner and Luiz-Silva 2009; Hakkou et al. 2008; Lenter et al. 2002).

In this context, there exists an incentive to search for alternative processes. For example, studies have related the extent to which alkalinity could be biotically and abiotically generated by passively co-treating AMD and raw municipal wastewater (MWW); (Strosnider et al. 2011). The effect of AMD loading have been analyzed in laboratory-scale activated sludge reactors with respect to the removal of some physical–chemical properties, as well as the sludge characteristics (Hughes and Gray 2013). Another co-treatment study evaluated the impact of blending typical Marcellus shale post-frac flowback water with AMD (Kondash et al. 2014). The objective of the present study was to assess the use of AMD to recover Al from WTR to obtain a coagulant that could be used to treat drinking water.

Materials and Methods

Characterization of the Acid Mine Drainage and Water Treatment Residuals

The AMD used in this study was collected in a 5 L polypropylene flask at a coal mine in the municipality of Forquilhinha, Santa Catarina (Brazil). The bottle was filled completely to minimize incorporation of air and consequent oxidation of the Fe in the sample. The parameters analyzed to characterize the AMD were pH (WTW pH meter, model 3210), total Fe, Al, and sulfate.

Total Fe was determined using a Spectroquant Merck reagent kit and method 14761. This method uses triazine, which reduces the Fe ions to Fe(II). Spectrophotometry was then used to measure the intensity of the generated red complex (Merck photometer, model Pharo 300). The Al concentration was determined using Merck method 14825, which uses chromazurol S to form a blue-violet compound, the intensity again being measured spectrophotometrically. The sulfate ions were determined using Merck method 14791. The reaction uses iodate barium ions to create iodine, which oxidizes tannin to yield brown compounds, which were measured colorimetrically.

The WTR used in this study was from a WTP drying bed in the municipality of Orleans, where PAC is used as a coagulant. The moisture and total Fe and Al concentrations were evaluated to characterize the WTR. To determine the moisture, the gravimetric method was used in a drying oven (at 105 °C). The total Fe and Al were extracted from the WTR using a sulfuric acid solution 10% (v/v) at a pH of 2.0. This concentration was sufficient to solubilize the metal present in the sludge (Keeley et al. 2014). One gram of WTR (previously dried) was mixed with 100 mL of acid solution. The solution was kept under orbital stirring at 200 rpm for 30 min. Then, the sample was centrifuged at 5000 rpm for 5 min. Sodium hydroxide was added to neutralize the solution. The Fe and Al were determined following the protocols previously described. The concentrations of these ions in the WTR were expressed as percent, i.e. weight of ion (Fe or Al) per 100 g of dried WTR.

Coagulant Recovery

To extract the Al present in the WTR, the samples were initially dried in an oven at 105 °C. Then, the dried WTR was reduced in size by manual maceration. The objective was to reduce the particles until they appeared homogeneous. This material was then mixed with 100 mL of AMD. The weight of the dried WTR added to the AMD was varied to generate different values of excess sulfate relative to the stoichiometric demand (Eq. 1).

$$2\mathrm{Al}^{3+} + 3\mathrm{SO}_4^{2-} \xrightarrow{\mathrm{H_2O}} \mathrm{Al}_2\left(\mathrm{SO}_4\right)_3 \tag{1}$$

Contact time was also investigated. The mixture was stirred in a shaker at 25 °C, at 200 rpm. Table 1 shows the experimental design. A central composite rotatable design (CCRD) was used with the addition of a rotational point and a triplicate of the central point. The CCRD consisted

Table 1 Results for the experiments of aluminum extraction from WTR

Trial	Dried WTR (g)	Volume of AMD (mL)	Sulfate excess (%)	Contact time (min)	Yield of aluminum recovery (%)
1	14.70	100.00	36 (−1)	28.00 (−1)	30.61
2	14.70	100.00	36 (−1)	88.00 (+1)	29.88
3	10.00	100.00	100 (+1)	28.00 (−1)	94.31
4	10.00	100.00	100 (+1)	88.00 (+1)	92.34
5	16.40	100.00	22 (−1.41)	60.00 (0)	28.34
6	9.40	100.00	113 (+1.41)	60.00 (0)	93.26
7	11.90	100.00	68 (0)	15.00 (−1.41)	43.42
8	11.90	100.00	68 (0)	105.00 (+1.41)	50.42
9	11.90	100.00	68 (0)	60.00 (0)	51.02
10	11.90	100.00	68 (0)	60.00 (0)	49.33
11	11.90	100.00	68 (0)	60.00 (0)	47.32

The table shows the original values and the coded values (in parentheses) of each level used in the experiment

of 2^2+4 (axial points) and three repetitions of the central point, for a total of 11 trials. The Al concentration in the supernatant was measured as the response of the tests. The obtained data were fit to a second order mathematical model with a linear combination of variables (Eq. 2). This empirical model is frequently applied to represent the response surface in CCRD to verify the effects of the parameters and the interaction between then (Rodrigues and Lemma 2014).

$$Y = A_0 + A_1X_1 + A_2X_1^2 + A_3X_2 + A_4X_2^2 + A_5X_1X_2 \quad (2)$$

where Y = percentage of extracted Al; A_i = coefficients of the mathematical model; X_1 = excess sulfate; and X_2 = contact time.

Jar Tests Using Recovered Coagulants

Water samples were collected in the Caveiras River in the municipality of Lages and the dosage of recovered coagulant (0–60 mg/L) were investigated in jar tests using a mixing time of 1 min and a coagulation velocity gradient of 200 s^{-1}. Flocculation took 30 min with a velocity gradient of 50 s^{-1}. The efficacy of the treatment process was assessed by the color, turbidity, and suspended solids in the supernatant. The settling velocity of the sludge was measured by collecting samples 7 cm below the water surface and monitoring color, turbidity, and suspended solids over time using a Spectroquant NOVA60 photometer (Merck). The Al, total Fe, and sulfate concentrations of the treated water were compared with the maximum contaminant levels (MCLs) in ordinance 2914/2011 of the Brazilian Ministry of Health (Brasil 2011). This ordinance regulates the guidelines for drinking water in Brazil, and follows the 'World Health Organization' drinking water quality criteria (2011). The tests were repeated three times and the results were expressed as averages.

Several parameters were also analyzed for both the untreated and treated water. These analyses were carried out to verify if any chemical substance would remain in the treated water after recovering the coagulant. The chemical analyses were carried out in an external laboratory that was ISO 17025 certified. All parameters were determined according to standard methods for the examination of water and wastewater (Rice et al. 2012).

Results and Discussion

Characterization of AMD and WTR

The AMD contained 12,800 mg/L of sulfate, 3400 mg/L of total Fe, and a pH of 2.3. The Al concentration was relatively negligible. This sludge had a moisture content of 75%, an Al concentration of 1.2% (m/m), and an Fe concentration of 1.3% (m/m), based on dry weight. The AMD is conventionally treated using PAC as a coagulant.

Extraction of Aluminum from WTR

The results obtained from extraction of the Al from the WTR using AMD are shown in Table 1. A second order model was fit to the data that relates Al recovery as a function of excess sulfate and the contact time of the WTR with the AMD. The analysis of variance (ANOVA) is shown in Table 2. The F_{calc} for the regression (432.94) was significant while the percentage of variation (R^2) was 95.54%, suggesting that although the model fit the experimental data well, it was not justified due to the significant lack of fit (p = 0.0039). According to this observation, the

Table 2 Analysis of variance for the aluminum recovery ($R^2 = 95.54\%$)

	Sum of squares (SS)	Degrees of freedom (DF)	Mean of squares (MS)	F value	p value
Model	5143.33	5	1028.66	432.94	0.0020
X_1	4757.25	1	4757.25	2002.06	<0.0001
X_1^2	366.01	1	366.01	154.03	0.0011
X_2	9.57	1	9.57	4.03	0.1384
X_2^2	4.25	1	4.25	1.79	0.2736
X_1X_2	6.25	1	6.25	2.63	0.2034
Lack of fit	279.26	2	139.63	58.76	0.0039
Pure error	7.13	3	2.38		
Total SS	6599.56	10			

purposed model only suggests a tendency of the most significant variable. The ANOVA (Table 2) demonstrated that the excess sulfate was the most significant variable in the extraction process. Both the linear effect of the excess sulfate (X_1) and the quadratic effect of the excess sulfate (X_1^2) were significant at $p < 0.0001$ and $p = 0.0011$, respectively. The linear and quadratic effects of contact time and interaction between the factors (X_2, X_2^2, X_1X_2) were not significant ($p > 0.05$).

Previous studies have used sulfuric acid to recover aluminum from WTR and observed the effect of excess sulfate in this process. Bishop et al. (1987) reported that excess sulfate is essential for extraction. Stendahl et al. (2006) demonstrated that the stoichiometric ratio is sufficient to recover 100% of metal. It is important to emphasize that the authors of the present study have worked with a WTR that also contained Fe ions and, therefore, the excess sulfate required to recover the Al is feasible for the simultaneous extraction of both the Fe and Al.

The response surface is shown in Fig. 1. A sulfate excess of 100% was observed to remove over 90% of the Al from the WTR in 28 min of contact time. This is in accordance with the pioneer study by (Cornwell and Zoltek Jr 1977), which acidified the solution to reach a pH of 2.0 and recovered the Al at yields between 80 and 93% using a contact time of 15 min.

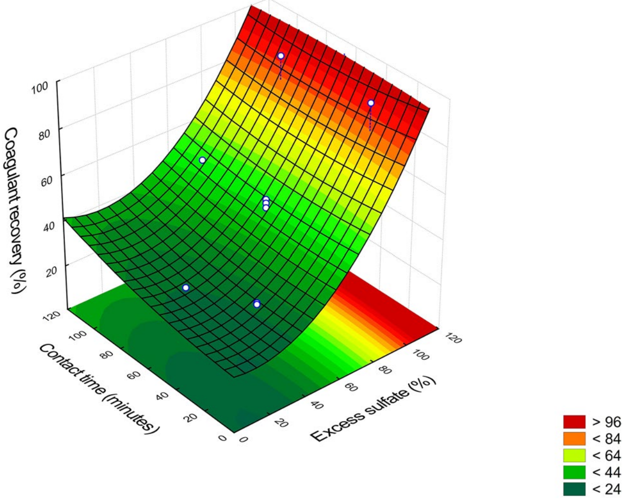

Fig. 1 Surface response for the aluminum recovery

Jar Test Performance

For the treatability tests, recovered coagulants were added to obtain a sulfate concentration between 0 and 60 mg/L (Fig. 2). The maximum contaminant levels (MCLs) for color and turbidity are 15 TCU (true color units) and 0.5 NTU (nephelometric turbidity units; Brasil 2011). Raw water values in the present study were 25.9 TCU and 6 NTU for color and turbidity, respectively. The concentration of total Fe in the raw water was 0.44 mg/L, which is above the recommended MCL (0.3 mg/L). The Al concentration in the raw water was 0.16 mg/L, below the MCL (0.2 mg/L). At a sulfate concentration of 20 mg/L, the color and turbidity were reduced below the MCL and, the Al concentration was reduced to 0.1 mg/L. The Fe concentration, however, increased to 1.11 mg/L, likely due to the Fe in the AMD. Considering that the pH of the AMD was between 2 and 3, the Fe was dissolved and was incorporated into the coagulant and consequently in the treated water. In this context, tests were carried out aiming to convert the ferrous ions to ferric ions to precipitate the iron and permit its removal during the jar tests. The previous tests were repeated with the addition of sodium hypochlorite solution (2.5% m/v) as a pre-oxidation treatment. The free residual chlorine to Fe ion ratio was 0.62:1. The results are shown in Fig. 3.

The chlorine addition allowed removal of the Fe, which decreased from 0.44 to 0.04 mg/L when dosed with a sulfate concentration of 15 mg/L. The color decreased from 25.9 to 0.8 TCU and the turbidity was 0 NTU in the treated water. The TCU of the treated water in the tests with pre-oxidation was less due to the removal of organic matter and/

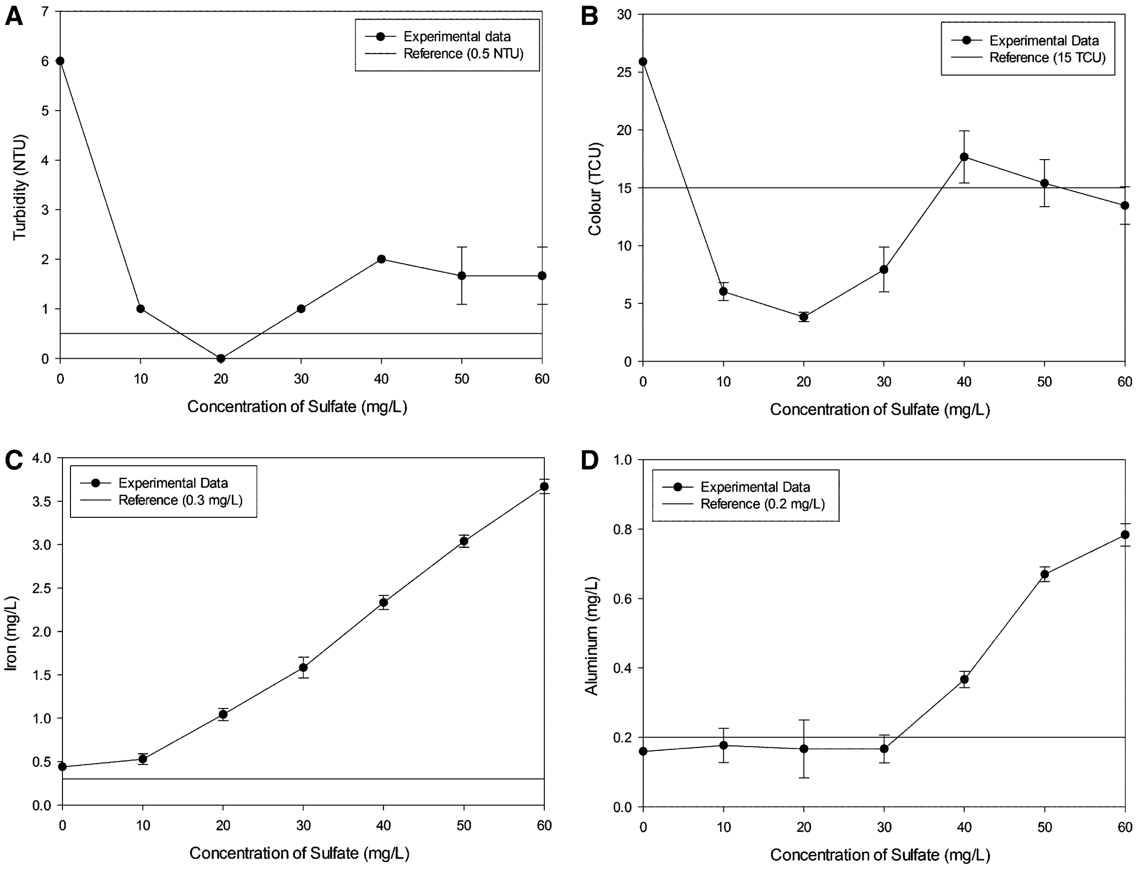

Fig. 2 Results obtained after jar test applying the recovered coagulant. **a** *Color*, **b** turbidity, **c** concentration of iron and, **d** concentration of aluminum. The *dots* represents the average of triplicates and the error bars are related to standard deviation.

or the removal of Fe from the water. The pH was adjusted to 6–7 using 0.1 mol/L NaOH.

Several parameters that influence drinking water quality were compared with ordinance 2914/2011 (Brasil 2011). The results (Supplemental Table 1) demonstrated that the only potentially toxic substances that increased in the water due to the treatment were antimony and arsenic. The Sb concentration increased from 0.0024 to 0.0055 mg/L, slightly above the MCL of 0.0050 mg/L; (Brasil 2011). The As concentration also increased, to 0.002 mg/L; however, this was still below the MCL for drinking water (0.01 mg/L). Nonetheless, both should be considered when using a coagulant to treat drinking water.

Concentrations of organic compounds and pesticides were not changed by the treatment processes. Furthermore, the compounds analyzed in Supplemental Tables 2 and 3 were absent or detected in low concentrations in both the WTR and AMD. For the disinfection by-products (DBPs; Supplemental Table 4), the concentration of trihalomethanes was 0.15 mg/L, which is above the 0.10 mg/L limit recommended by ordinance 2914. This presumably was due to the use of chlorine to precipitate the Fe; chlorine can react with natural organic matter (NOM) to form DBPs. The release of DBPs can also be controlled during the pre-oxidation step. Further studies should also evaluate the quality of the treated water relative to free residual chlorine and heterotrophic bacteria, as these characteristics were not the focus of the present study.

For the substances responsible for organoleptic characteristics (Supplemental Table 5), increased concentrations of chloride (1.06–7.75 mg/L), total hardness (7.49–11.7 mg/L), Mn (<limit of quantification (LQ) to 0.05 mg/L), Na (1.37–9.98 mg/L), total dissolved solids (55.0–194 mg/L), sulfate (<LQ for 16 mg/L), and Zn (<LQ to 0.03 mg/L) were observed. These were less than the drinking water standards; however, the recovered coagulant did not affect the organoleptic characteristics of the treated water. There were no changes observed for other indicators of treated water quality, with the exception of the color, turbidity, and total Fe, which were all reduced to less than their detectable limits.

AMD and WTR are wastes generated by mining and sanitation, respectively, and both must be available for companies interested in exploiting the two wastes to

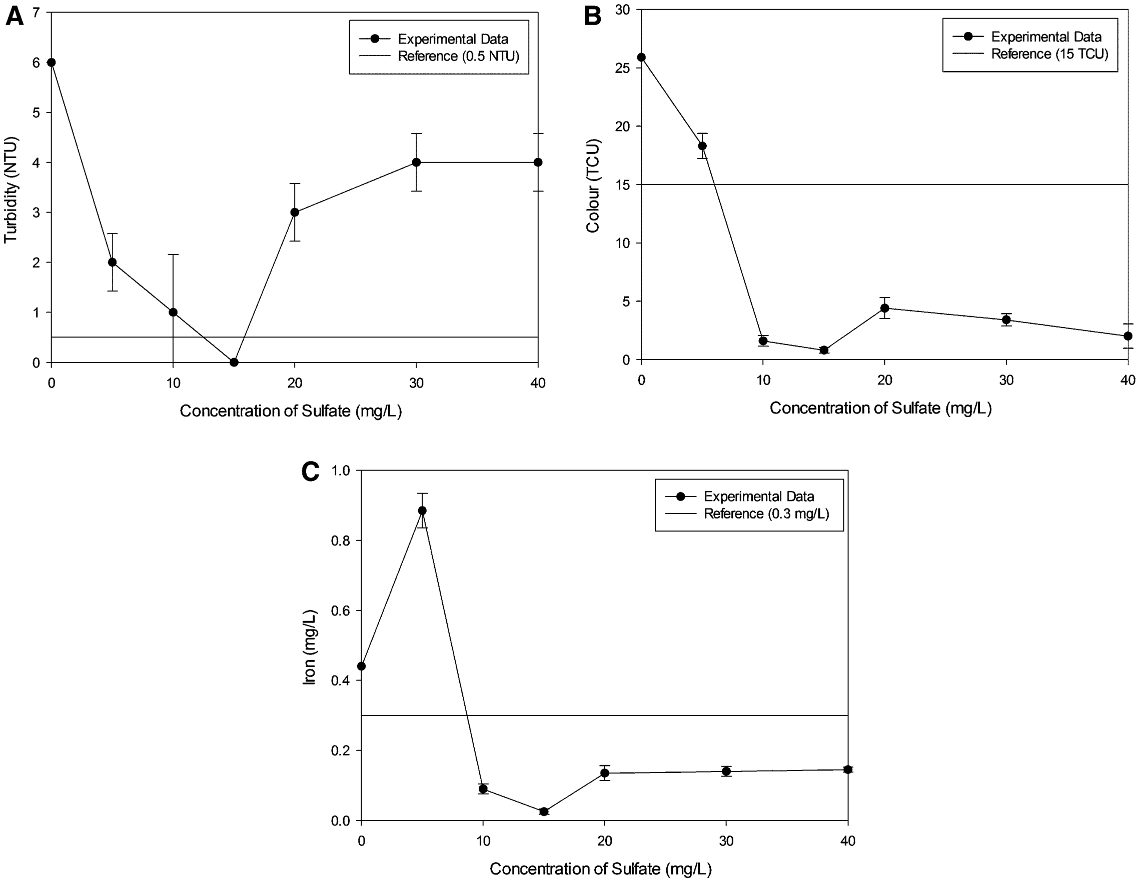

Fig. 3 Results obtained after jar test applying the recovered coagulant with the pre-oxidizing step. **a** *Color*, **b** turbidity and, **c** concentration of iron. The *dots* represent the average of triplicates and the error bars are related to standard deviation

produce coagulants. Due to logistics, the best potential strategy would be to transfer the more concentrated WTR to the mine site to recover the coagulant and then send it to the application point. Transporting the AMD, which would be classified as a hazardous material due to its acidity, would be difficult, so transporting the WTR, which is not a hazardous waste, would be more attractive.

Conclusion

The present study demonstrated that Al can be recovered from WTR using AMD as a source of sulfate ions. The use of AMD produced a coagulant that reduced color, turbidity, and Fe in the raw water without the addition of substances that might undermine the conventional treatment of water, with the exception of Sb. Further tests should be carried out to evaluate the composition of AMD and WTR in terms of compounds that present critical concentrations. Further research should establish standards that would enable the use of this coagulant in drinking water without affecting drinking water standards.

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