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TECHNICAL COMMUNICATION

Production of a Poly-ferric Sulphate Chemical Coagulant by Selective Precipitation of Iron from Acidic Coal Mine Drainage

J. C. S. S. Menezes · R. A. Silva · I. S. Arce · I. A. H. Schneider

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Abstract The aim of this work was to produce a ferric sulphate rich solution from acidic coal mine drainage that could be used as coagulant. Precipitating the iron at pH 3.8, followed by dissolution in sulphuric acid, produced a coagulant consisting of 12.4% iron and 1.3% aluminium. Water treatment tests proved that this coagulant was as efficient as the coagulant chemicals conventionally used in water treatment plants. The process can be easily incorporated into conventional AMD treatment plants, thereby reducing sludge waste issues and producing a valuable chemical reagent.

Keywords Acid mine drainage · Coagulant · Environment · pH control · Recycling

Introduction

Acid mine drainage (AMD) continues to be an important water pollution problem in coal production. The active treatment of AMD involves the addition of alkaline reagents to increase the pH and precipitate the dissolved metals as hydroxides. Although active treatment can provide effective remediation, it has the disadvantages of high operational costs and problems related to the disposal of the bulky sludge that is produced (Johnson and Hallberg 2005; Kontopoulos 1998; Matlock et al. 2002; Skousen et al. 1998).

The AMD treatment plants in Brazil mostly use sodium hydroxide or lime for neutralisation. The metal precipitates are removed in settling ponds, conventional settling tanks, lamellar tanks, and dissolved air flotation units (Rodrigues and Rubio 2007). The sludge typically contains 2–5% solids and high concentrations of iron and aluminium along with minor concentrations of manganese, zinc, and other metals, and represents a huge environmental problem (Marcello et al. 2008).

One potential way to extend the use of natural resources is to recover potentially valuable products, such as some of the precipitated metals, from the AMD sludge (Wei et al. 2005). AMD sludge has been previously considered for the production of coagulants (Rao et al. 1992), ferric oxide nanoparticles (Wei and Viadero 2007), and inorganic pigments (Hedin 2002; Marcello et al. 2008).

In the work conducted by Rao et al. (1992) on an AMD from a Canadian polymetallic mine, ferric sulphate (FS) was produced by the reaction of ferric hydroxide recovered from the AMD with sulphuric acid. To avoid the co-precipitation of undesirable metals, amine was used to reduce the co-precipitation at pH 3.5–3.6. The results suggested that AMD could be a possible source of an effective coagulant.

Coagulants used for treatment of both water and wastewater are predominantly inorganic salts of ferric iron and aluminium. Aluminium salts, including aluminium sulphate (AS) and aluminium chloride (AC), in addition to pre-hydrolysed metal-ion reagents such as poly-aluminium sulphate (PAS) and poly-aluminium chloride (PAC), are the coagulants most widely used for water treatment (ACWA 2000; Bratby 1980). However, the presence of residual amounts of aluminium in drinking water has been controversially implicated to neurological diseases (ACWA 2000; Becaria et al. 2006; Campbell et al. 2001;

J. C. S. S. Menezes (✉) · R. A. Silva · I. S. Arce · I. A. H. Schneider
Centro de Tecnologia, PPGEM—Univ Federal do Rio Grande do Sul, Av Bento Gonçalves, 9500, Porto Alegre, RS 91501-970, Brazil
e-mail: jean.menezes@ufrgs.br

Rondeau et al. 2000). A possible alternative is to use iron-based coagulants, such as ferric chloride (FC), ferric sulphate (FS), or poly-ferric sulphate (PFS) instead of the aluminium salts (Jiang et al. 1996; Jiang and Graham 1998; Tenny and Derka 1992). We assessed the feasibility of producing an inexpensive poly-ferric sulphate coagulant by selective precipitation of acidic coal mine drainage (PFS-SP/AMD) and then compared its effectiveness with other, more conventional coagulants.

Materials and Methods

Metal Recovery and Ferric Sulphate Production

AMD was collected from a drainage channel near a tailings deposit in Santa Catarina State (Brazil) and sealed in high-density polyethylene bottles. At the laboratory, the solids and debris in the water samples were removed by settling and the remaining suspended solids were removed by filtration through a 0.45 μm membrane and stored at 4°C. The AMD was analysed for pH and concentrations of dissolved metals and sulphate.

The reagents used for pH adjustments, titration and precipitation studies were analytical grade NaOH and H_2SO_4, supplied by Nuclear (Fair Lawn, NJ, USA). Distilled water was used for preparation of all solutions. Commercial poly-aluminium sulphate (PAS), produced by the reaction of sulphuric acid with bauxite, was supplied by Companhia Riograndense de Saneamento (CORSAN, RS/Brazil). Commercial ferric sulphate (PFS), produced from scrap iron by sulphuric acid digestion, was obtained from Sulfato Rio Grande (RS/Brazil).

Iron was recovered from the AMD by an oxidation/selective precipitation process. The AMD was aerated for 24 h at pH 2.5–3.0 to convert all of the Fe^{2+} to Fe^{3+}. A titration curve (pH versus 4 N NaOH solution) was determined in the traditional way (Jenke and Diebold 1983) to define the best pH for precipitation of the ferric iron (Fig. 1).

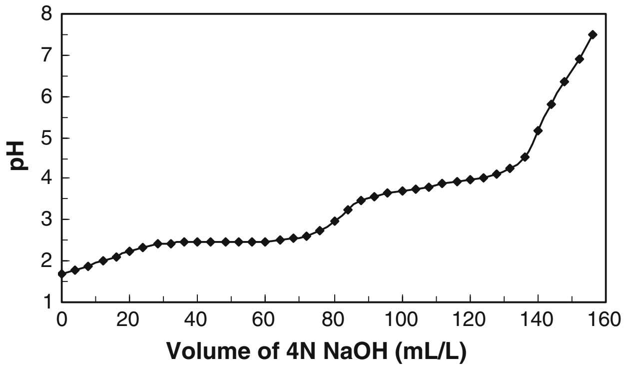

Fig. 1 Titration curve of the aerated AMD with 4 N NaOH

Based on the results, the pH of the solution was then increased to and maintained at 3.8 ± 0.1, with the addition of 4 N NaOH solution, to precipitate the iron as ferric hydroxide/oxyhydroxide, which was further separated from the AMD by centrifugation at 3,000 rpm. The precipitate was washed with distilled water at pH 3.8 ± 0.1, resuspended and centrifuged; this cycle was repeated three times. The final precipitate was dissolved in sulphuric acid to achieve a clear solution, which was used as the chemical coagulant (PFS-SP/AMD). The PFS-SP/AMD, and the commercial PFS and PAS were analysed in terms of the dissolved metals (Fe, Al, Ca, Mg, Mn, Zn, Cu, Cr, Cd, Pb, and As) and sulphate. Metal analyses were carried out by inductively coupled plasma (ICP) spectroscopy using a Perkin Elmer Optime 2100 spectrometer. Sulphate concentrations were determined by the gravimetric method after ignition of the residue (Eaton et al. 2005). The density of the coagulants was determined gravimetrically in 10 mL volumetric flasks.

Water Treatment by Coagulation

Studies involving water treatment were carried out with raw water from Guaiba Lake (Porto Alegre, RS, Brazil) using a conventional Jar Test apparatus. The coagulation procedure was carried out using a 1,000 mL water sample. The samples of PFS-SP/AMD, PFS, and PAS were added at the same molar concentration of 0.4 mM (Fe + Al). The pH was adjusted to 7.0 and the suspension was agitated at 100 rpm for 5 min, followed by a slow stirring at a speed of 20 rpm for 3 min. Subsequently, the agitation was stopped and the samples were left undisturbed without any agitation for a period of 10 min to allow settling of the solids. The sludge generated was filtered using a quantitative filter paper, dried, and weighed. The treated water was analysed for: pH, suspended solids, turbidity, colour, conductivity, metals (Fe, Al, Mn, Zn, Cu, Cr, Cd, Pb, and As), hardness, and sulphate. All analyses followed the procedures described in the Standard Method for the Examination of Water and Wastewater (Eaton et al. 2005).

Results and Discussion

The general characteristics of the AMD are presented in Table 1. The pH of the AMD was 2.3 and the concentration of metals in it was high. The main metal ions in the raw AMD were Fe (70% as Fe^{2+} and 30% as Fe^{3+}) and Al; other metals, such as Mn, Zn, Ca, and Mg, were present at significantly lower concentrations. The pH and the concentrations of Fe, Mn, and Zn in the raw water did not meet the Brazilian standards for wastewater discharge.

Table 1 Chemical analysis of the acid mine drainage (AMD) sample; all parameters in mg/L except for pH

Parameter	Concentration in raw AMD	Brazilian standards for wastewater discharge
pH	2.3	5–9
Fe	5,900	15.0
Al	2,000	–
Mn	129	1.0
Zn	65	5.0
Ca	11.8	–
Mg	8.4	–
Cu	0.07	1.0
Cr	0.24	0.5
Cd	0.06	0.2
As	<0.02	0.5
Pb	<0.03	0.5
SO_4^{-2}	9,120	–

The titration curve of the aerated AMD is shown in Fig. 1. It can be observed that ferric iron hydrolysis and precipitation occurs up to pH 3.5. At a pH of 3.5–3.8, there is an inflection of the curve, possibly showing that all the ferric iron is hydrolysed. Most of the aluminium hydrolysis occurs at pH values higher than 3.9. Therefore, the pH chosen for selective precipitation of iron was pH 3.8.

Table 2 Chemical compositions of the poly-ferric sulphate coagulant produced by selective precipitation of the AMD (PFS-SP/AMD), the poly-ferric sulphate coagulant produced from iron scraps (PFS), and conventional poly-aluminium sulphate (PAS); all parameters in mg/L except for pH

Parameter	PFS-SP/AMD	PFS	PAS
pH	1.7	1.8	2.4
Fe	124,000	115,000	112.5
Al	13,000	4,419	47,662
Ca	4.7	56.8	8.4
Mg	43.7	160.6	0.38
Mn	19.0	1,585	1.3
Zn	65.0	22.4	3.8
Cu	<0.004	11.5	<0.004
Cr	<0.004	305.0	12.0
Cd	<0.005	<0.005	<0.005
Pb	<0.02	15.2	7.5
As	<0.03	<0.03	<0.03
SO_4^{-2}	117,500	130,800	53,000
Density (g/cm^3)	1.50	1.41	1.23

Table 2 summarises the characteristics of the coagulant produced from the metal precipitate obtained at pH 3.8 (PFS-SP/AMD). The coagulant is composed of ferric sulphate (90.5%) and aluminium sulphate (9.5%), and very low concentrations of Mn, Zn, Ca, and Mg. Compared to the raw AMD, the Fe/Al ratio increased from 2.9 to 9.5, the Fe/Mn ratio increased from 45.7 to 6,530, and the Fe/Zn ratio increased from 90.8 to 27,000. The recovery of iron and aluminium in the selective precipitation process was about 90 and 28%, respectively.

Table 3 presents the results obtained in the water treatment tests. All of the coagulants were equally efficient in terms of residual suspended solids, turbidity, and colour. The residual amounts of heavy metals in the treated water were very low with all the coagulants used, even for the FS produced from scrap iron, which showed a slight increase for Zn and Cu. The lake water treated with all of the coagulants met the Brazilian standards for drinking water.

Table 3 Characteristics of raw water and water treated with the coagulants PFS-SP/DAM, PFS, and PAS at a dosage of 0.04 N (Fe + Al) at pH 7.0

Parameter	Raw water	Treated with PFS-SP/AMD	Treated with PFS	Treated with PAS	Brazilian standards for drinking water
pH	6.8	7.0	7.0	7.0	–
Susp. solids[a]	23.0	0.0	0.0	0.0	–
Turbidity[b]	81.3	0.4	0.5	0.3	5.0
Colour[c]	44.0	1.0	2.0	2.0	15.0
EC[d]	0.13	1.01	0.59	0.97	–
Al[a]	<0.08	<0.08	<0.08	<0.08	0.2
As[a]	<0.001	<0.001	<0.001	<0.001	0.01
Cd[a]	<0.002	<0.002	<0.002	<0.002	0.005
Cr[a]	<0.004	<0.004	<0.004	<0.004	0.05
Cu[a]	<0.004	<0.004	0.02	<0.004	2.0
Fe[a]	<0.04	<0.04	<0.04	<0.04	0.3
Mn[a]	<0.02	<0.02	<0.02	<0.02	0.1
Pb[a]	0.06	<0.02	<0.02	<0.02	0.01
Zn[a]	0.04	<0.02	0.06	0.11	5.0
Hardness[e]	22	127	134	86	500
SO_4[a]	7.8	88.7	82.9	60.2	250

[a] mg/L, [b] NTU, [c] Hazen scale, [d] mS/cm @ 25°C, [e] mg/L as $CaCO_3$

Table 4 Raw materials for the production of the PFS-SP/AMD

Material	Amount
AMD (m^3/m^3 coagulant)	23.2
NaOH (kg/m^3 coagulant)	354
Water (precipitate washing) (m^3/m^3 coagulant)	14
H_2SO_4 (L/m^3 coagulant)	70

A previous study by Wei et al. (2005) involving the selective precipitation of coal AMD, reported a recovery of 98.6% for iron and 2.8% for aluminium at pH 3.5 and a recovery of 99.6% for iron and 11.2% for aluminium at pH 4.0. One possible explanation for the superior selectivity achieved by Wei et al. (2005) could be the lower concentrations of metals in their AMD, about 162 mg/L Fe and 80.8 mg/L Al, whereas in this work, the concentrations were 5,900 mg/L Fe and 2,000 mg/L Al. However, the presence of aluminium in our precipitate is not necessarily a drawback. The alumino-iron sulphate coagulant proved to be efficient, achieving even lower residual metal ion concentrations than the PFS, FS, and AS (Jiang and Graham 2003).

The PFS-SP/AMD, with an iron concentration of 12.4%, met the PFS standard of at least 12% iron. The water treatment results were equal to or better than those obtained with FS and AS. Table 4 summarises the amount of AMD, chemicals (NaOH and H_2SO_4), and water necessary to produce the coagulant. Using these raw materials, the cost to produce PFS-SP/AMD in an AMD treatment plant should not exceed \$200 (U.S.)/m^3 (or about 400 Brazilian Reals (R\$)/m^3) while a conventional PFS is commonly sold at a price of \$400–450 (U.S.)/m^3 (or 800–900 R\$). Considering the AMD used in this experiment and a daily flow rate of 1,200 m^3, it would be possible to produce 51.4 m^3 of PFS-SP/AMD, which would treat water for a population of about 850,000 people.

Conclusions

Precipitating the iron at pH 3.8 allowed the recovery of 90% of the iron and 28% of the aluminium in acidic coal mine drainage, which would reduce the overall volume of sludge by 70%. Dissolution in sulphuric acid produced a 12.4% ferric and 1.3% aluminium coagulant. The water treatment tests proved that this inexpensive coagulant is at least as efficient as the coagulants more conventionally used in water treatment plants. The process of producing such a coagulant can be easily adopted at AMD treatment plants, thereby reducing sludge waste issues and producing a valuable chemical reagent.

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