Acid mine drainage as source of iron for the treatment of sewage by coagulation and Fenton's Reaction

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Abstract Acid mine drainage (AMD) from coal mining sites is characterized by low pH and high concentrations of metals. In some situations, the iron concentration is very high (> 12% Fe), at levels that could be used as a reagent for wastewater treatment. The AMD can be used as coagulant when it is rich in iron in the form Fe^{3+} (and secondarily Al^{+3}). The AMD can also be applied in wastewater treatment as Fenton´s Reaction when is rich in iron in the form Fe^{2+}. The objective of this work was to characterize a concentrated AMD obtained from a coal mining site in Santa Catarina State, Brazil, and study the treatment of sewage considering simple coagulation and Fenton´s reaction. The results showed that the AMD can be used in sewage treatment. Both processes, coagulation and Fenton´s Reaction, were effective for the removal of suspended solids, organic matter, phosphorous, and bacteria of the coliform group.

Key Words acid mine drainage, pyrite, wastewater, coagulation, Fenton´s reaction.

Introduction

Coal mining generates large volumes of tailings that may be responsible for serious environmental damage. The oxidation of pyrite (FeS_2), in the presence of air and water, promotes the formation of acid mine drainage (AMD), an aqueous and highly acid solution rich in sulphate and iron (in the form Fe^{3+} and Fe^{2+}), along with other associated metals (Kontopoulos, 1998). The problem of acid generation occurs in Brazil, especially in the carboniferous region of Santa Catarina State (SC). This is an issue that requires studies to find solutions to minimize the damage to the environment.

At the same time, the release of sewage into water bodies is one of the main environmental problems currently faced in urban areas, including inhabited areas near the coalfields in southern Brazil. This domestic wastewater is characterized by the presence of organic matter, microorganisms, nitrogen and phosphorus, and a slight alkalinity (Metcalf and Eddy, 2003).

Recent research has shown that it is possible to produce poly-ferric sulphate and poly-alumino-iron sulphate coagulants by selective precipitation of the metals present in AMD (Rao *et al.*, 1992; Menezes *et al.*, 2009; Menezes *et al.*, 2010). This alternative allowed elimination of sludge generation (or reducing the sludge waste volume/ quantity) and producing a valuable chemical reagent.

Another way to produce the same chemical coagulants, without the addition of chemical reagents, is to directly process tailings to recover and dissolve the pyrite contained within them by a hydrometallurgical process (Colling *et al.*, 2011). It is known that acidophilic bacteria, e.g. *Acidithiobacillus ferrooxidans*, can increase the rate of pyrite oxidation and dissolution by several times (Kontopoulos, 1998; Brett and Jillian, 2003; Johnson and Hallberg, 2003) and that they can be very significant in the bioprocessing of coal tailings for the production of ferric coagulants.

However, in some situations, the iron concentration in the AMD is very high (> 12% Fe), at levels that could be used as a reagent for sanitation operations without any further process. The AMD rich in iron as Fe^{3+} (and secondarily on Al^{3+}) can be used as coagulant. The AMD rich in iron as Fe^{2+} can be applied as a reagent for the Fenton's reaction (1894), an advanced oxidation process (AOP; Metcalf and Eddy, 2003).

The objective of this work was to characterize a concentrated AMD obtained from a coal waste deposit and study the treatment of sewage considering the process of simple coagulation and the Fenton´s Reaction.

Materials and Methods

AMD was collected from an experimental coal waste deposit in Santa Catarina State (Brazil) (Soares *et al.*, 2009). 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. The ADM sample was stored in containers of high-density polyethylene and sealed to avoid iron oxidation by atmospheric oxygen. The characteristics of AMD are shown in Table 1.

Sewage was collected from the Universidade Federal do Rio Grande do Sul wastewater treatment plant (Porto Alegre, RS, Brazil). The current water treatment process occurs exclusively in a single sequential batch biological reactor (SBBR) of 430 m^3. One cycle of SBBR includes the follow-

Parameters	AMD
pH	1.5
Total solids (mg/L)	711
Suspended solids (mg/L)	308
Dissolved solids (mg/L)	403
Total iron (mg/L)	17640
Fe^{2+} (mg/L)	15079
Fe^{3+} (mg/L)	2561
Aluminum (mg/L)	1534
Manganese (mg/L)	90
Copper (mg/L)	34
Zinc (mg/L)	102
COD (mg/L)	67
BOD_5 (mg/L)	22
Total Kjeldahl nitrogen (mg/L)	78
Phosphorus (mg/L)	17
Sulphates (mg/L)	9264

***Table 1** Characteristic of the AMD.*

ing four operational steps: sewage filling, aerobic bioprocessing, solids settling, and effluent drainage.

The sewage treatment tests were carried out in a standard Jar Test apparatus considering two different methodologies (Metcalf and Eddy, 2003):

(a) Simple Coagulation

Addition of 15 mL of AMD in 1 L of sewage, which provided a concentration of 264 mg/L Fe and 38 mg/L Al and a decrease of the pH (range of 3.5 to 4.3, so it is a function of the sewage sample alkalinity). The solution was adjusted to pH 3.5 and mixed for 1 hour, allowing coliform bacteria reduction by acidification (accordingly to McFeters and Stuart, 1972, the best pH for survival is in the range of 5.5 and 7.5, with rapid decline both above and below these values). After that, the pH was adjusted to 9.0 with a 2 M NaOH solution for metals precipitation. Sludge settling was carried out by 1 hour in Imhoff`s cone (APHA, 2005). The sludge was filtered, dried for 24 hours at 60°C, and weighted.

(b) Fenton´s Reaction

Addition of 15 mL of AMD in 1L of sewage, which provided the same Fe and Al concentration. The solution was mixed for 1 hour. After that, the pH was adjusted to 3.5 with a 2M HCl solution and 1.25 mL/L of H_2O_2 35% (w/v) was added. The Fenton´s Reaction was conducted over 3 hours. The mixture was then adjusted to 9.0 with a 2 M NaOH solution for metals precipitation. Sludge settling was carried out over 1 hour in Imhoff`s cone. The sludge was filtered, dried, and weighed as described previously.

In both cases, the treated water was analyzed considering the following parameters: pH, total solids, suspended solids, dissolved solids, settleable solids, thermotolerant coliforms, total coliforms, total Fe, total Al, COD, BOD_5, total Kjeldahl nitrogen, phosphorus, and sulfates (APHA, 2005).

Results and Discussion

Table 2 shows the average results obtained in nine runs of the sequential batch biological reactor (SBBR) at UFRGS. It can be observed that the biological treatment allowed a significant reduction of the organic load, with values of 50% COD removal and 62% BOD_5 removal. The process was efficient in removal of nitrogen and phosphorus, with of 39% and 51% removal, respectively. Regarding the micro-organisms (thermotolerant coliforms and total coliforms) the decay observed was of one order of magnitude.

Table 3 shows the results obtained in the studies conducted by simple coagulation. The treatment showed excellent results in terms of suspended solids removal, with an average efficiency of 74%. The organic load substantially reduced, with values of 62 % for COD and 65% for BOD_5. The efficiency of nitrogen reduction was 28% and phosphorus reduction was 97%. Regarding the micro-organisms, the processes allowed a reduction of three/four orders of magnitude (99% efficiency).

Table 4 shows the results obtained in the studies conducted by the Fenton´s Reaction. This advanced oxidation process combines coagulation and chemical oxidation in one single operation. The reduction of suspended solids was in the same order of magnitude of the simple coagulation, about 78%. This process allowed the best results in terms of organic load, with reduction levels of 80% for COD and BOD_5. The average result for nitrogen reduction was 29% and for phosphorus reduction was 98%. The process performed very well with respect to the microorganisms, with values reaching a reduction of six orders of magnitude (99.99% efficiency).

Table 2 Characteristics of the raw and biologically treated sewage (average: n = 9).

Parameter	Raw sewage	After biological treatment (SBBR)	Efficiency (%)
pH	7.63	6.86	-
Total solids (mg/L)	1083	692	36
Suspended solids (mg/L)	191	93	51
Dissolved solids (mg/L)	892	599	33
Thermotolerant coliforms (NMP/100 mL)	1.04×10^9	2.20×10^8	78
Total coliforms (NMP/100 mL)	1.84×10^9	2.40×10^8	87
Total iron (mg/L)	1.77	1.16	35
Aluminum (mg/L)	2.40	2.23	7
COD (mg/L)	406	204	50
BOD_5 (mg/L)	151	57	62
Total Kjeldahl nitrogen (mg/L)	89.18	54.36	39
Phosphorus (mg/L)	14.78	7.19	51
Sulphates (mg/L)	17.16	32.38	-
Settleable solids (mL/L)	1.31	4.89	-
Sludge mass (g/L)	0.47	0.60	-

Table 3 Characteristics of the raw sewage and treated by simple coagulation with AMD (average: n = 9).

Parameter	Raw sewage	After simple coagulation	Efficiency (%)
pH	7.63	7.77	-
Total solids (mg/L)	1083	1513	-
Suspended solids (mg/L)	191	49	74
Dissolved solids (mg/L)	892	1464	-
Thermotolerant coliforms (NMP/100 mL)	1.04×10^9	3.30×10^5	99
Total coliforms (NMP/100 mL)	1.84×10^9	1.37×10^6	99
Total iron (mg/L)	1.77	9.14	-
Aluminum (mg/L)	2.40	3.77	-
COD (mg/L)	406	151	62
BOD_5 (mg/L)	151	52	65
Total Kjeldahl nitrogen (mg/L)	89.18	63.81	28
Phosphorus (mg/L)	14.78	0.40	97
Sulphates (mg/L)	17.16	1131	-
Settleable solids (mL/L)	1.31	0.3	77
Sludge mass (g/L)	0.47	0.15	68

Table 4 Characteristics of the raw sewage and treated by Fenton´s Reaction with AMD (average: n = 9).

Parameter	Raw sewage	After Fenton's Reaction	Efficiency
pH	7.63	8.21	-
Total solids (mg/L)	1083	1554	-
Suspended solids (mg/L)	191	41	78
Dissolved solids (mg/L)	892	1513	-
Thermotolerant coliforms (NMP/100 mL)	1.04×10^9	8.15×10^3	99.99
Total coliforms (NMP/100 mL)	1.84×10^9	4.21×10^3	99.99
Total iron (mg/L)	1.77	4.08	-
Aluminum (mg/L)	2.40	5.15	-
COD (mg/L)	406	82	80
BOD_5 (mg/L)	151	30	80
Total Kjeldahl nitrogen (mg/L)	89.18	63.55	29
Phosphorus (mg/L)	14.78	0.26	98
Sulphates (mg/L)	17.16	1049	-
Settleable solids (mL/L)	1.31	0.1	92
Sludge mass (g/L)	0.47	0.02	95

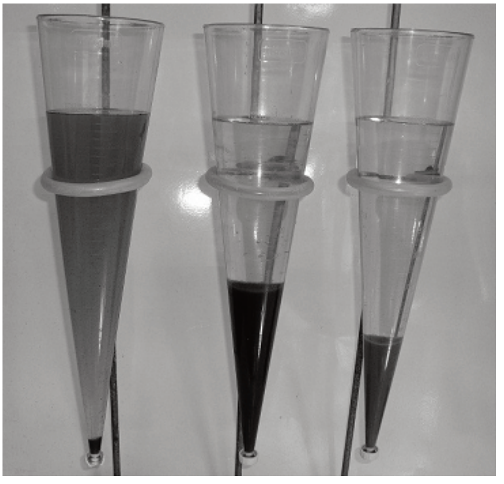

Figure 1 *From left to right: raw sewage, treated by coagulation, treated by the Fenton's reaction.*

Figure 1 shows a picture of the raw sewage, after the treatment by simple coagulation, and after treatment by Fenton´s reaction.

Conclusions

The results showed that the AMD, especially the most concentrated ones (in terms of iron), can be used in wastewater treatment. The treatment by simples coagulation allowed significant reductions in the sewage levels of suspended solids, organic matter, and phosphorous. The treatment by Fenton´s Reaction allowed better results in terms of the final concentration of suspended solids, organic matter, phosphorous and also promoted the disinfection of the treated water. The combined treatment of sewage and AMD can be considered coal mining regions close to inhabited areas.

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References

AWWA-APHA-WEF (2005) Standard Methods for the Examination of Water and Wastewater. Eaton AD, Clesceri LS, Rice EW, Greenberg AE (Eds), 2005 21th Edition. Washington: American Public Health Association

Bratby J (1980) Coagulation and Flocculation: With an Emphasis on Water and Wastewater Treatment. Upland Press, Croydon

Colling AV, Menezes JCSS, Schneider IAH (2011) Bioprocessing of pyrite concentrate from coal tailings for the production of the coagulant ferric sulphate. Minerals Engineering. DOI: 10.1016/j.mineng.2011.04.003

McFeters, GA, Stuart, DG (1972) Survival of coliform bacteria in natural waters: field and laboratory studies with membrane-filter chambers. Applied Microbiology 24(5): 805—811

Fenton HJH (1894) Oxidation of tartaric acid in presence of iron. Journal of the Chemical Society 65:899—910

Johnson DB, Hallberg, KB (2003) The microbiology of acidic mine waters. Research in Microbiology 154:466—473

Kontopoulos A (1998) Acid mine drainage control. In: Effluent treatment in the mining industry. Castro SH, Vergara F, Sánchez MA (Eds). University of Concepciòn, p 7—118

Menezes, JDSS, Silva, RA, Arce, IS, Schneider, IAH (2009) Production of a polyferric sulphate chemical coagulant by selective precipitation of iron from acidic coal mine drainage. Mine Water and the Environment 28: 311–314

Menezes, JDSS, Silva, RA, Arce, IS, Schneider, IAH (2010). Production of a polyalumino-iron sulphate coagulant by chemical precipitation of a coal mining acid drainage. Minerals Engineering 23:249—251

Metcalf and Eddy (2003) Wastewater Engineering: Treatment and Reuse – 4th ed, MGraw-Hill Book Company, New York, 1819 pp

Rao SR, Gehr R, Rindeau M, Lu D, Finch JA (2008) Acid mine drainage as a coagulant. Minerals 5(9):1011—1020

Soares AB, Ubaldo MO, Souza VP, Soares PSM, Barbosa MC, Mendonça MG (2009) Design of a dry cover pilot test for acid mine drainage abatement in Southern Brazil. In: Materials Characterization and Numerical Modeling. Mine Water and Environment 28(3):219—231