The use of Microfiltration and Electrodialysis for Treatment of Acid Mine Drainage

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Abstract Acid mine drainage (AMD), from coal mine, is the result of the natural oxidation of sulphide minerals, mainly pyrite, when exposed to the combined action of water and oxygen. This effluent is characterized by a low pH and high concentrations of dissolved metals. Currently the mining industries have opted for the conventional effluent treatment (neutralization/precipitation). The electrodialysis emerges as a new technology for the wastewater treatment and has proven effective for the recovery of water and electrolyte concentration. In this study the possibility of using the pretreatment with microfiltration and electrodialysis technique to the AMD treatment, was evaluated aiming water reuse.

Key Words acid mine drainage, electrodialysis, microfiltration

Introduction

Coal mining brings economic and social benefits to the community in which it is located, but also an environmental impact. Therefore, it is necessary to take preventive measures to control this pollution.

Environmental problems caused by coal mining are aggravated due to the impurity level of Brazilian coal, which has an average of 25 to 30% of usable coal and the rest of pyritic waste, which is the unusable part, composed of matter mixed with coal mining pyrite, clays, sandstones and shales (Gaivizzo *et al.* 2000).

To Wei *et al.* (2008) one of the major impacts caused by coal mining activity is water pollution caused by acid mine drainage (AMD), which is characterized by a low pH and high concentrations of dissolved metals (Fe, Al, Mn and traces of Pb, Cu and Zn).

AMD is formed through the oxidation of sulfide minerals, mainly pyrite (FeS_2), and combines low pH, about 2.0, and high concentrations of metals that can have serious toxicological effects on aquatic ecosystems, such as mortality, growth disorders, lower rates of reproduction, deformities and injuries (Kontopoulos 1998; Lewis and Clark 1996).

The reactions involved in the formation of AMD occur by chemical and biological processes, through the following equations (Evangelou 1995).

$$FeS_2 + 7/2O_2 + H_2O \text{ à } Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + 1/4O_2 + H^+ \text{ à } Fe^{3+} + 1/2H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \text{ à } Fe(OH)_3 + 3H^+ \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \text{ à } 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

According to Evangelou (1995), equation (1) shows the oxidation of pyrite (FeS_2), thus releasing Fe^{2+} and two H^+. In equation (2), Fe^{2+} is oxidized to Fe^{3+} which hydrolyzes to form ferric hydroxide (an insoluble compound at pH greater than 3.5) and in the process, as shown in equation (3), three more H^+ are released. Therefore, for every mole of FeS_2 five H^+ are released. However, since one H^+ is consumed for the oxidation of Fe^{2+} to Fe^{3+}, only four H^+ are actually produced.

After initiating the pyrite oxidation, the Fe^{3+} itself can be reduced by pyrite, as shown in equation (4). Therefore, pyrite is still rusting while Fe^{3+} is produced. In this case, the conversion of Fe^{+2} to Fe^{+3} is the limiting step in pyrite oxidation reaction (Evangelou 1995).

However, as the oxidation of Fe^{2+} to Fe^{3+} at pH 3 is very slow (approximately 100 days), the pyrite oxidation in this pH range also becomes slow, unless the iron oxidation is catalyzed by microorganisms that work in this pH range. It turns out that this pH range between 2.5 and 3.5, the bacterium Thiobacillus ferroxidans quickly oxidize Fe^{2+} to Fe^{3+} (Evangelou 1995).

According to Campaner and Silva (2009), in Brazil, currently, the mining industries have opted for the conventional effluent treatment followed by neutralization of the precipitation in the form of metal hydroxides. Thus, the sludge is generated which represents a new problem, because it is necessary to be disposed according to their classification, provided in ABNT NBR 10004/2004, as a solid residue.

New approaches for the wastewater treatment contaminated with metals are being studied to replace conventional methods, and electrodialysis (ED) emerges as a new technology and has proven effective for the recovery of water and electrolyte concentration. It is considered a clean technology, and attractive to several segments since it presents several advantages over traditional processes, such as: does not require level changes; runs continuously, does not need reagents addition and generates no waste polluting in the environment (Noble and Stern 1995).

As defined by Arsand (2005) the ED is based on a membrane separation process in which a concentrated solution of ions is transformed into two new solutions, a more focused and a more diluted than the original. This is an interesting proposal for wastewater treatment, because the more diluted solution, can be reused as water and the more concentrated solution can be directed to another process for the recovery of ions, which will be facilitated by the higher concentration of the elements and lower volume.

The aim of this study is to verify the possibility of using microfiltration (MF), as pretreatment, followed by ED technique to AMD treatment, aiming water reuse.

Methods

Sample Collection

The AMD sample used in this experiment was collected in a carboniferous in operation in Criciúma/SC, the pluvial drainage from the coal, called AMD PL1, therefore, a more diluted drainage when compared to the drainage from the percolation of deposits of waste water in the same carboniferous.

AMD PL1 was chemically characterized according to the following parameters: pH, conductivity, total dissolved solids (TDS), Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, F^-, Cl^-, NO_3^- and SO_4^{2-}. These tests were performed according to the methodologies presented in Tab 1.

Pretreatment – Microfiltration

One pretreatment with MF was necessary to prevent fouling and scaling of the ED, so the entire sample of AMD PL1 used in this experiment was filtered through a membrane of 0.45 µm before the experiments. After MF, AMD PL1 was again chemically characterized. Fig 1 shows the apparatus used for MF.

Determination of Polarization Curves

To define the current to be applied during the ED it was, initially determined the current density limit. This test was conducted in an ED cell with 5 compartments in order to obtain the polarization curve, from which it was defined the current density to be applied in trials of ED for AMD PL1.

Figure 1 *Apparatus used to microfiltration.*

The assembly of this cell was carried out with the "placement in a filter press assembly" of Chinese origin membranes, cationic – HDX100 (pink) and anionic – HDX200 (green), with a surface area of 16cm^2.

The cell was prepared as follows: in the central compartment, called Diluted, a solution of AMD PL1 after MF was placed and other compartments, called Cathode, Anode, Concentrate Cathode and Concentrate Anode, solutions of sodium sulphate (Na_2SO_4) were placed, to maintain conductivity in the system. Each container was connected to a pump that caused the recirculation of the solutions. Both ends of the cell, the cathode and anode were both Ti/Ru, in which successive currents were applied.

The currents applied varied gradually from 1 to 1mA, every 2 minutes with an interval of 3 minutes without current application. Every variation of current values were collected from the potential difference between electrodes and also anionic and cationic membranes, using Pt wires as electrodes, placed at the ends of each membrane. This test was performed in triplicate.

Electrodialysis

ED tests were also conducted in a laboratory cell with 5 compartments, and for these tests the assembly was performed the same form it was used to determination of polarization curves. AMD PL1

Table 1 *Methodologies used for chemical characterization of AMD PL1.*

Parameters	Methodology
pH	Potenciometric
Conductivity	Potenciometric
TDS	Gravimetric
Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}	Ionic Chromatography

Table 2 *Chemical Characterization of AMD PL1 – Cations.*

	Parameters (mg · L^{-1})								
	Na^+	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**Fe^{3+}**	**Cu^{2+}**	**Zn^{2+}**	**Mn^{2+}**	**Fe^{2+-}**
Original	296.760	21.957	72.125	250.334	110.500	0.010	1.510	7.58	N.D.
After MF	296.059	20.029	70.942	230.379	80.053	N.D.	1.448	8.886	N.D.

Table 3 *Chemical Characterization of AMD PL1 – Anions.*

	Parameters (mg · L^{-1})			
	F^-	**Cl^-**	**NO_3^-**	**SO_4^{2-}**
Original	11.017	278.125	27.061	1,849.865
After MF	9.059	193.787	24.278	1,569.699

just in the Diluted compartment, and Na_2SO_4 in the other compartments. And the current applied during the ED was predetermined in polarization curves.

The test was conducted for 55 hours and samples were taken for chemical analysis to verify the percent extraction, and also the pH and conductivity of all compartments were monitored.

Results and Discussion

From chemical characterization of original AMD PL1, the following results were obtained: pH equal to 2.80, conductivity equal to 4.26 mS. $^{-2}$ and total dissolved solids equal to 4.2 g/L.

According to Audinos (1986), the greater efficiency of the ED is with suspended solid concentrations below 1 mg/L, thus, from the result of the TDS of AMD PL1 was chosen by a MF, in membrane of 0.45 µm, prior to ED experiments.

It was observed that after the MF, in addition to solids removal, there was also a decrease in pH from 2.80 to 2.41 and an increase in conductivity from 4.26 to 4.41 mS. cm^{-2}.

The other results of the chemical characterization of original AMD PL1 and after MF, are presented in Tab 2 and Tab 3.

Analyzing Tab 2 and Tab 3, it is observed that the MF hardly changed the initial concentrations of ions in original AMD PL1.

After that, the MF, tests were performed to obtain the polarization curves in triplicate. Considering that there was reproducibility of results in Fig 2 and Fig 3, it is presented graphic of current versus potential obtained for the cationic and anionic membranes, respectively.

It is observed that both curves obtained for the membrane to the anionic and cationic have three well defined regions, (I) linear, (II) plateau – the current limit, (III) linear – after the current limit, as shown by Strathmann, Wessling, and Krol (1999).

It can be seen in Fig 2 that the current limit to the anionic membrane is approximately equal to 3.3 mA. $^{-2}$ and Fig 3 has to cationic membrane current of 5.9 mA. cm^{-2}. These values have been calculated according to the membrane surface area of 16 cm^2.

For Meng, Deng, Chen and Zhang (2005), the maximum current to be applied should be 70—80% of the determined current density limit. In this case, the current applied to ED of the AMD PL1 was defined based on the curve obtained for the anionic membrane, which showed a lower current density limit is set at 2.6 mA. cm^{-2} or 42 mA for this system.

With the definition of current density to be applied to the system, began the ED. Considering the total experiment time of 55 hours, the withdrawal of samples for chemical characterization and monitoring of pH and conductivity of the compartments was random. Tab 4 shows the initial and final results monitoring of the compartments.

The results in Tab 4 suggest that over the 55 hour test, there was a decrease in the conductivity of the diluted compartment and an increase in the conductivity of the other compartments, as it was expected. Because the aim of this work is the dilution of AMD PL1 in the central compartment and the concentration of that sample in the Concentrated Anode and Concentrated Cathode compartments.

Table 4 *Experiment monitoring of ED.*

Time	Parameters	Anode	Conc. Anode	Diluted	Conc. Cathode	Cathode
Initial	pH	3.75	3.75	2.41	3.75	3.75
	Conductivity (mS · cm^{-2})	4.17	4.17	4.49	4.17	4.17
55h	pH	1.57	1.72	2.92	2.50	12.87
	Conductivity (mS · cm^{-2})	9.60	12.50	0.30	8.60	11.70

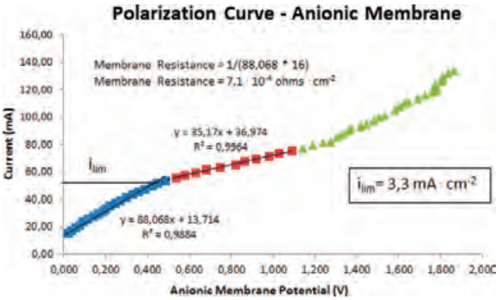

Figure 2 *Polarization curve of anionic membrane.*

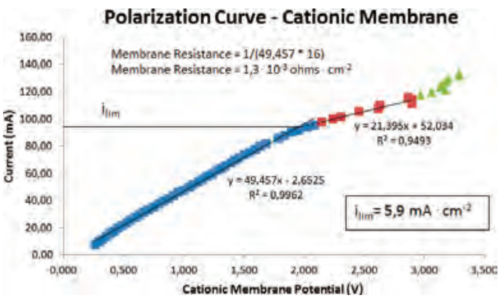

Figure 3 *Polarization curve of cationic membrane.*

The reactions that occur at the electrodes justify changes in pH and conductivity found in these compartments, anode and cathode, during the experiment. For the anode compartment there was an increase in acidity, represented by the decrease in pH in the cathode compartment and it was observed a decrease in acidity, or increase in the pH value, and both the increase in conductivity justified by the presence of H^+ and OH^-, the anode and cathode, respectively. The reactions at the electrodes were:

Cathode: $2H^+ + 2e$ à $H_{2(g)}$

Anode: $2H_2O$ à $4H^+ + O_{2(g)} + 4e$

The chemical characterization of the AMD PL1 in diluted compartment along the ED test is shown in Fig 4 and Fig 5 for the analysis of extraction of cations and anions, respectively.

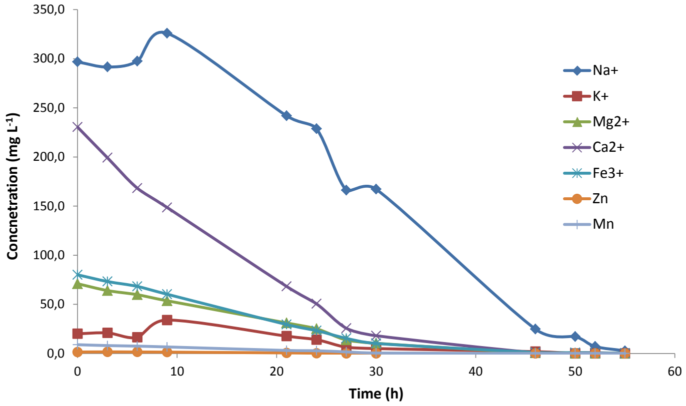

Figure 4 *Variation of the concentration of the cations in the diluted compartment as a function of time.*

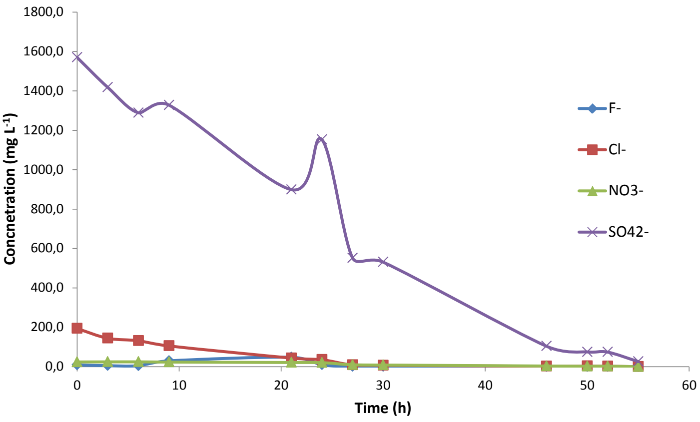

Figure 5 *Variation of the concentration of the anions in the diluted compartment as a function of time.*

From results presented in Fig 4 and Fig 5, it appears that the ED process was efficient for the extraction of cations and anions, removing over 97.5% of them after 55 hours of testing. These results indicated that water could be recovered by ED from AMD PL1.

Conclusion

The pretreatment of AMD PL1 with MF combined with ED proved to be an effective method for water recovery from AMD PL1 in 55 hours, when applying the current density of 2.6 mA. cm^{-2}.

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