Treatment of Acid Drainage from Coal Mines Produced in the Boyacá Region, Colombia, using an Anaerobic Wetland with an Upward Flow*

Tratamiento de drenajes ácidos de minas de carbón producidas en la región de Boyacá, Colombia, mediante el uso de un Humedal Anaerobio con flujo ascendente

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Abstract

Coal mining represents one of the primary economic incomes in the department of Boyacá, Colombia. However, the acid mine drainage (AMD) generated has a tremendous environmental impact in the area due to the presence of sulfate ions (SO4-2), heavy metals, and low pH This article studies the behavior in the content of Fe and sulfates in AMD samples when treated within an artificial anaerobic vertical flow wetland, analyzing the concentration of these elementsand the content of dissolved oxygen (DO) and pH at different time intervals. The treatment of a MAD from the department of Boyacá was carried out using a bioreactor prototype with an organic substrate to provide the necessary conditions for the development of sulfate-reducing bacteria. Measurements were made with hydraulic retention times between 24 to 120 hours, monitoring the changes in the content of total Fe, SO4-2, pH, and DO. The data obtained show a reduction for total Fe of 88.3%, established at 5.61g·m-2·day-1, and for SO4-2 of 34.3% with 9.35g·m-2·day-1; reaching a maximum removal degree of 52.32% at 120h for sulfates and 92% for Fe, where the maximum removal peak is achieved, reducing the Fe removal rate for longer times. The reduction in the concentration of Fe is related to the reduction of DO and regulation of the pH, in addition to favoring the reduction of sulfate ions through the formation of the mineralogical phases pyrite and siderite. These data show that the anoxic conditions of the organic environment are maintained, for which a subsequent aeration stage is suggested.

Keywords: Acid Mine Drainage (AMD), Hydraulic Retention Time, Organic Substrate, Anaerobic Wetland, Sulfate-reducing bacteria (SRB).

Resumen

La minería del carbón representa uno de los principales ingresos económicos en el departamento de Boyacá, Colombia. No obstante, los drenajes ácidos de minas (DAM) generados tienen un gran impacto ambiental en la zona debido a la presencia de iones sulfato (SO4-2), metales pesados y bajo pH Este articulo estudia el comportamiento en el contenido de Fe y sulfatos en muestras de AMD cuando son tratadas dentro de un humedal de flujo vertical anaeróbico artificial, analizando la concentración de estos elementos, además del contenido de oxígeno disuelto (OD) y pH en diferentes intervalos de tiempo. Se realizó el tratamiento de una DAM provenientes del departamento de Boyacá utilizando un prototipo de biorreactor con adición de un sustrato orgánico con el fin de proporcionar las condiciones necesarias para el desarrollo de bacterias reductoras de sulfato. Se realizaron mediciones con tiempos de retención hidráulica entre 24 a 120 horas, monitoreando los cambios en el contenido de Fe total, SO4-2, pH y OD. Los datos obtenidos muestran una reducción para Fe total de 88,3%, establecida en 5,61 g·m-2·día-1, y para SO4-2 de 34,3% con 9,35g·m-2·día-1; alcanzando un grado de remoción máximo de 52,32% a los 120h para sulfatos y 92% para Fe, donde se consigue el pico máximo de remoción, lo que redujo la tasa de remoción de Fe para tiempos mayores. La reducción en la concentración de Fe se relaciona con la reducción de OD y una regulación del pH, además de favorecer la reducción de iones sulfato mediante la formación de las fases mineralógicas pirita y siderita. Estos datos muestran que las condiciones anóxicas del medio orgánico se mantienen, para lo cual se sugiere una etapa de aireación posterior

Palabras clave: Drenaje acido de mina (DAM), tiempo de retención hidráulico, substrato orgánico, humedal anaeróbico, bacteria sulfato-reductora (BSR)

Introduction

Mining activities present various types and levels of contamination that alter the ecosystems surrounding the mining area. In Colombia, one of the leading mining activities carried out is the exploitation of coal [1]. For 2015, the Boyacá department concentrated 9% of the mining titles in Colombia, having a 38% of the participation regarding coal production. This is the highest value in terms of the country's distribution of coal mining titles. 3.087 million tons of coal are estimated in this department for use in the thermal and metallurgical areas [2]. However, the department only assumes 3.21% of the national production, so this operation is not done efficiently, generating a greater quantity of pollutants and heavy metal liberation in nearby tributaries [3], [4].

The generation of acid mine drainage (AMD) is one of the primary water pollutants generated by this type of activity, characterized by a low pH and a high presence of sulfates and dissolved metals in the water [5], [6]. Stormwater runoff can transport large amounts of these AMD along with dissolved particles and materials, reducing the oxygen and nutrient content from the soil, negatively affecting the biota that depends on these aquatic ecosystems where this water is deposited. In addition, this causes degradation of aquatic systems, including erosion, sedimentation, and thermal stress [7], [8].

The application of constructed aerobic wetlands gives a potential treatment alternative for treating storms and polluted water [9]. Constructed wetlands are ecological systems that use biological processes commonly found in nature to treat AMD. The physicochemical processes associated with these systems favor the exchange and adsorption of metals, reduction of sulfates, precipitation of iron, sulfates, and hydroxides, so on [10]. The slow flow of water in the wetland allows the retention time necessary for the slow water purification processes [11]. Additionally, these systems present organic residues, which favor the reduction in costs of the process. However, these processes are affected by applying mining waste such as AMD. The generation of large quantities of sludge increases the costs of its control [12], [13]. Thus, a viable alternative is the application of reactors that allow the simulation of conventional anaerobic wetlands, such as pH regulation and the oxidation of metals present in water [11].

These systems allow having a suitable control and supervision of waste. Furthermore, for the treatment of AMD, the adequacy of vegetative and microbiological mechanisms is essential in eliminating contaminants [10].

The vegetation and the use of plants in wetlands create channels for atmospheric oxygen transfer within the organic substrate into the rhizosphere region [14], [15]. The presence of plants plays a fundamental role as a direct pollutant adsorption mechanism. Removal processes are influenced by the type of plant, whether emergent, floating, or submerged, and its interaction with the organic substrate [16]. The selection of the plant species is essential as metal uptake and accumulation capacities are specific, and it has to be according to AMD characteristics to ensure the system's effectiveness [17]. The pH influences these in terms of the assimilation capacity of pollutants [18].

The direct absorption by plants is usually calculated by measuring plant growth and metal content stored in plant tissues [19]. Nevertheless, in larger-scale systems, plant uptake tends to be negligible and difficult to measure, at least in short-time operations. Some low heavy metal concentrations as 0,1% related to Pb, Zn, Cu, and Cd; were measured as accumulations in plants tissues used in wetlands treating AMD [20]. Generally, plants bioaccumulate metals in the roots and emergent parts, favoring metal oxides and hydroxides precipitation through oxidation and hydrolysis reactions [21]. The plants should be selected according to the concentrations and variety of metals present in the AMD [22]. Near the water surface, the environment is oxidative. The oxidized forms of Fe and Mn are present, facilitating their precipitation as hydroxides as long as there is sufficient OH^- alkalinity available [23].

Sulfate removal efficiency by plants in wetlands is still unclear. Some authors report low or negligible removal [24], while other studies reported high rates of sulfate removal [25], [26]. The main limitation of wetlands that treat AMD is the metals' toxic effect on plants and microorganisms [16], [27]. Another important issue regarding plants in wetlands treating mine wastewater is the presence of phytotoxic concentrations of metals, which can affect the plant growth or create problems associated with reduced nutrient uptake due to the presence of high concentrations of metal and H^+ ions [28].

The application of organic material inside these reactors favor the production of bacteria, reducing treatment costs [29]. Various organic substrates have been used, which vary depending on their availability in the area, implementing, for example, horse feces, mushroom compost, sawdust, peat, or straw [30], [31]. The slow degradation of the organic substrate allows the consumption of dissolved oxygen from AMD while acting as a long-term carbon source for iron and sulfate-reducing bacteria, important during AMD remediation processes [32], [33]. However, the application of this process has not been sufficiently studied [34].

In vertical flow anaerobic wetlands (VFW), a descending hydraulic head of the AMD forces it down through an organic substrate passing through a limestone bed [35]. Anaerobic wetland systems can also contemplate successive alkalinity production systems (SAPS) [36], where water passes through the organic subsurface layer and becomes anaerobic due to the high biochemical oxygen demand (BOD). The lack of oxygen promotes the bacterial reduction of sulfates to produce sulfides for later forming insoluble metallic precipitates generating alkalinity, which favors the precipitation of metals such as oxyhydroxides [37].

The recommended construction for SAPS includes a minimum compost thickness of 50cm, periodic compost replacement or addition of fresh material, as well as the installation of pipes in the lower part of the limestone bed [38]. In Canada, passive treatment systems have been used to treat of AMD. Between 1990 and 1993, two experimental anaerobic experimental wetlands were constructed to treat acidic waters from the Bell Copper mine (British Columbia). In both systems, the pH was increased from 3 to 6-8, achieving reductions of 40% and 80% of Cu in a retention time of 12 and 23 days, respectively. Performance improved with increasing retention time and decreased with decreasing temperature reflecting lower biological activity [39].

In contrast, more than 14 wetlands exist in the UK operating like alkalinity production systems, aerobic and anaerobic processes, or a combination of these. These are dedicated to the treatment of acidic water from coal mines, where more than 50% of Fe has been eliminated. The anaerobic wetland of Quaking Houses in Durham (England) was the first anaerobic wetland in Europe in 1995, reducing the acidity of the water by 70% (9.6 g/m2·day) and its Fe content by 62%. Similarly, in April 1998, the first SAPS was built in Pelenna (Wales), where it was possible to eliminate between 72-99% Fe with a water retention time in the system of 14 hours [40], [41].

Additionally, implementing these systems on a larger scale becomes a viable option for the treatment of AMD, allowing control of the variables present in the process and the by-products generated. Due to this, the application of a pilot-scale reactor was studied in this work, which simulated a conventional anaerobic subsurface flow wetland system to treat AMD generated within coal mining processes. The focus of this work aims to analyze the behavior in the content of Fe and sulfates within the AMD samples when treated within an artificial anaerobic vertical flow wetland, analyzing the concentration of these elements and the content of dissolved oxygen and pH at different time intervals. The direction of the water flow was arranged in an ascending way for this research, contrary to the traditional way these systems operate. There is no existing literature on the evaluation of the effect of a first state of alkalization on the conditions from AMD.

Materials and Methods

Raw Material

The samples of acidic water generated by coal mining processes were supplied by the Cooperativa Agro-minera de Paipa Ltda (Cooagromin) collection center, located at Km 5 via Paipa - Tunja in the department of Boyacá, Colombia. Water samples were collected in 5-gallon capacity screw cap containers at room temperature (17 °C). Table 1 shows the initial data gathered from the collected samples.

Table 1. Initial characteristics of the sample.

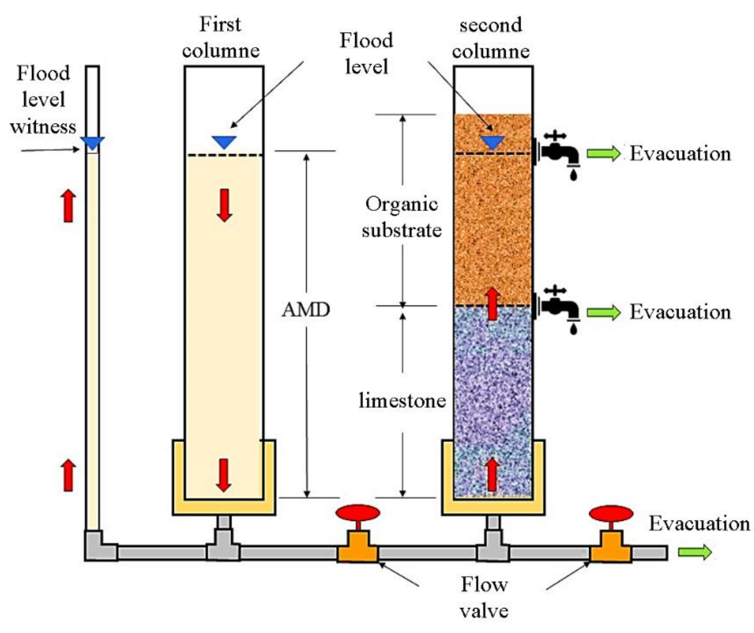
Parameter	Concentration
OD	6,80 $mg \cdot L^{-1}$
pH	3,09 $mg \cdot L^{-1}$
Fe	112 $mg \cdot L^{-1}$
SO_4^{-2}	590 $mg \cdot L^{-1}$

Source: Own elaboration

Reactor Construction Design and Calibration

The reactor prototype worked in this study was made from a two-column anaerobic wetland using a vertical flow [42], shown in Figure 1. The columns were built using 4" PVC pipes, whose internal area is $8.1 \cdot 10^{-3} m^2$. The AMD sample was deposited within the first column. The second column was filled with $3.24 \cdot 10^{-3} m^3$ of limestone and a particle size of ½" to 1", and a mixture of $4.05 \cdot 10^{-3} m^3$ of organic substrate whose ratio was: 14.2% clay, 28.6% of sawdust, 28.6% of straw and 28.6% of dry horse feces. These materials were mixed and homogenized before being deposited in the second column as proposed. [10].

Figure 1. Scheme of the vertical-flow artificial anaerobic wetland developed in this study.



Source: Own elaboration

The clay used in this study was obtained near the collection center in Paipa, Boyacá, Colombia, and analyzed by x-ray diffraction (XRD) using the powder technique in a PANanalytical diffractometer with a lamp. Co and 1.75 Å wavelength, with a Pixel-Bragg-Brentano variable angle detector.

The adaptation of the organic substrate was carried out using distilled water, which was deposited within the entire system, remaining retained for five days. Subsequently, its anoxic state was examined, showing the consumption of DO due to microbiological activity due to the decomposition of organic matter. This operation generates the optimal conditions for the proliferation and distribution of microorganisms within the substrate. Then, the water is evacuated, allowing the entry of the AMD samples. In this study, emergent plants of any kind were not used to evaluate pollutant load removal by reduction and adsorption processes in the organic substrate, leaving aside processes such as oxidation and hydrolysis that can occur on the surface of the organic substrate by the aeration process induced by plant roots [21]. Additionally, plants have a low contribution to heavy metal removal in wetlands at short periods of experiments [19], [43], and sulfate removal efficiencies by plants in wetlands are still unclear, and some authors report low or negligible removal [24].

Prototype Operation

The prototype was operated for five days as a sequential reactor in hydraulic retention periods of 24h, 48h, 72h, 96h, and 120h, favoring the entry of the AMD upwards in the second column and evacuating the treated water by gravity. The procedure was controlled using shut-off valves. Acidic water was continuously added in the first column to maintain a stable flood level throughout the study. Subsequently, water samples were selected for physical-chemical analysis, extracted from the organic substrate by evacuation in the lower part. The level of flooding of the organic substrate was always 10cm below its surface to guarantee anaerobic conditions in the unsaturated zone. Microphyte plants were not implemented due to the short period of experimentation.

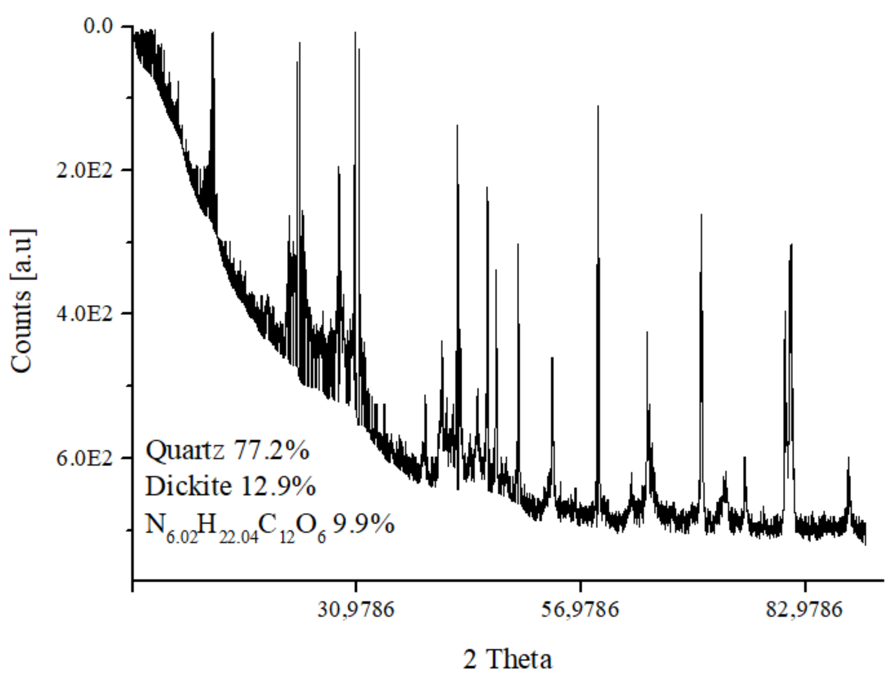
Sample Collection and Analysis

Once the retention and saturation time of the organic substrate has elapsed, all the water it contains is removed, with a volume of 2L. After this process, the first column is filled again with AMD to re-saturate the substrate, reaching the established flood level. For each one of the samples obtained, in each of the time intervals, the parameters of pH, total iron (Fe), sulfates content ($SO4^{-2}$), and dissolved oxygen (DO) were analyzed in this work. The pH measurements were developed using a SCHOTT Handylab pH-11 pH meter, dissolved oxygen using a Hach-flexi HQ30d US Pat. 6912050. The measurement of Fe was carried out through the Colorimetric method SM3500 Fe-B and that of sulfates $SO4^{-2}$, through the Turbidimetric method SM 4500 - $SO4^{-2}$ E, using the Spectroquant® Multy Colorimeter for both. All AMD samples were previously filtered to avoid interferences due to the presence of total suspended solids. On the other hand, some AMD samples were diluted with distilled water to work within the detection ranges of the equipment, as well as the use of the reagents. Three replicates for this study were made. The data obtained in this work were analyzed using the free R software, using linear regression methods. These data will allow us to observe the behavior of AMD samples processed using a bioreactor prototype. The direction of the water flow was arranged in an ascending way, contrary to the traditional way in which these systems operate, for which there is no existing literature on the evaluation of the effect of a first state of alkalization on the conditions. from AMD.

Results

The data obtained in this study are the result of measuring each of the established parameters and carrying out three replicates per measurement to obtain a more precise value of each of the data obtained. Initially, a compositional analysis of the clays used inside the bioreactor was carried out. The spectrum analysis was performed using the HighScore-Plus software, and the data obtained are presented in Figure 2. It was found that the clay presents a composition mainly of quartz (77.2%) and dickite, as a type of phyllosilicate (12.9%), similar to kaolinite, presenting a chemical composition $Al_2Si_2(OH)_4$. Likewise, a low percentage of organic material (9.9%) is observed, which is common in these types of samples.

Figure 2. XRD pattern of the clays used inside the bioreactor



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The data obtained for each parameter analyzed are presented in Table 2, facilitating the generation of graphs that allow to better observe the behavior in the variation of the parameters as a function of time.

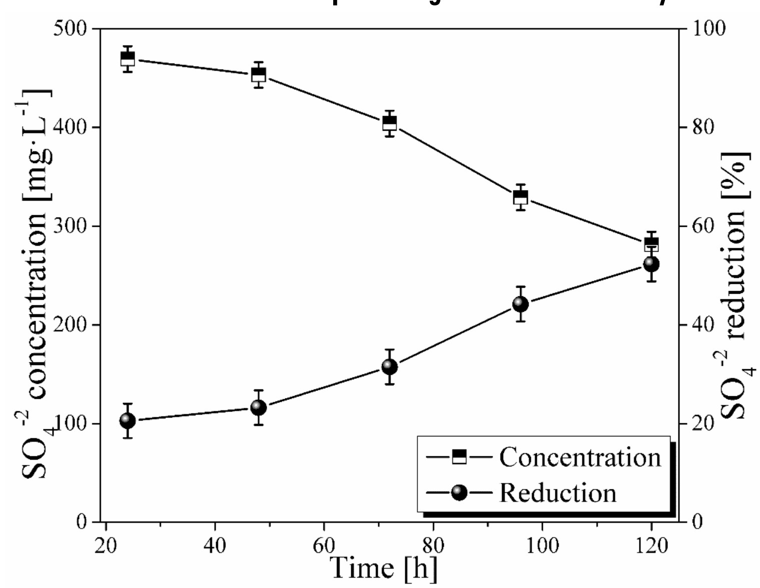
Table 2. Data obtained in this study

Parameter	Hydraulic retention time [h]					
	0	24	48	72	96	120
SO_4^{-2} content [$mg \cdot L^{-1}$]	590.00	468.70	453.00	404.30	329.30	281.30
SO_4^{-2} Reduction [%]	-	20.56	23.22	31.47	44.19	52.32
SO_4^{-2} remotion [$g \cdot m^{-2} \cdot día^{-1}$]	-	14.98	8.46	7.64	8.05	7.62
Fe total [$mg \cdot L^{-1}$]	112.00	10.35	14.03	16.95	14.78	9.37
Fe reduction [%]	-	90.76	87.47	84.87	86.80	91.63
Fe remotion [$g \cdot m^{-2} \cdot día^{-1}$]	-	12.55	6.05	3.91	3.00	2.53
pH [a.u.]	3.09	5.68	6.73	6.58	6.68	6.64
DO [$mg \cdot L^{-1}$]	6.80	0.15	0.18	0.72	0.63	0.73

Source: own elaboration

Figure 3 shows the behavior suffered by the sulfate ion ($SO4^{-2}$) based on the hydraulic retention time. A linear trend is observed regarding reducing sulfates, reaching a maximum value of 52.32% at 120h and an average experimentation value of 34.35%. The trend of the reduction percentage indicates that the hydraulic retention time should be 231h to obtain a removal greater than 90%.

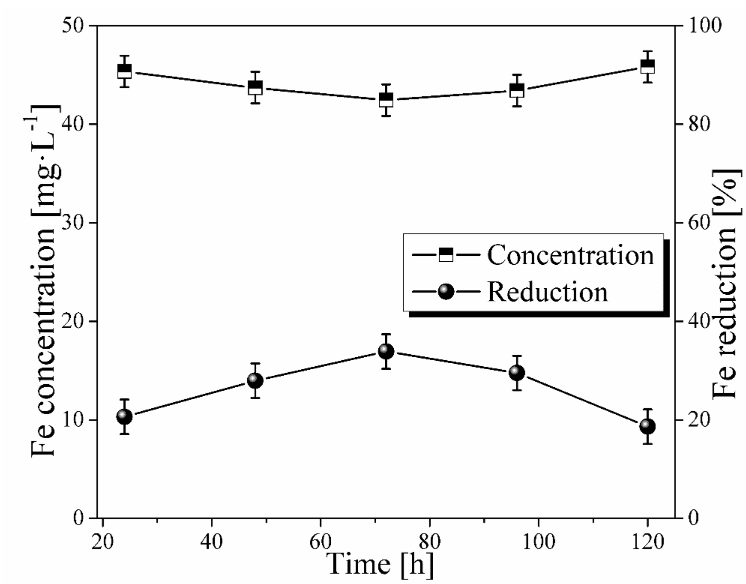
Figure 3. SO_4^{-2} concentration and reduction percentage as a function of hydraulic retention time



Source: own elaboration

Figure 4 shows the behavior of total Fe as a function of the hydraulic retention time. Note that the percentage of iron reduction does not present any specific trend and maintains me as an average value that oscillates in a range of 84.87% and 91.63%, establishing a general average of 88.31%. This situation shows that the reduction of Fe has a behavior that does not depend exclusively on the hydraulic retention time. On the other hand, the final concentrations of total Fe ranged from 9.37 to 16.95 $mg \cdot L^{-1}$.

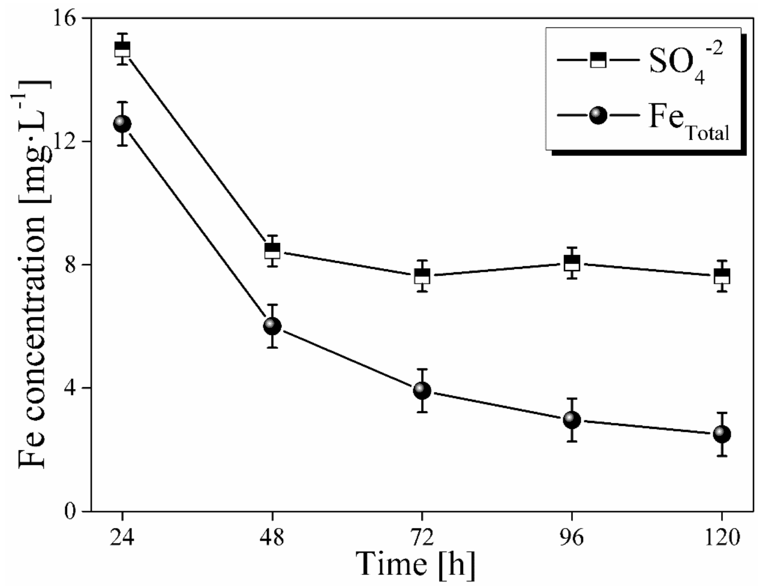
Figure 4. Concentration and percentage of Total Fe reduction as a function of hydraulic retention time



Source: own elaboration

In Figure 5, the removal rate is presented in $g \cdot m^{-2} \cdot day^{-1}$ for both Total Fe as well as for sulfates. As can be seen, the removal rate for SO_4^{-2} shows a decreasing trend in the first24h, but it stabilizes at an average value of 8 $g \cdot m^{-2} \cdot day^{-1}$ in the range of 48 to 120h. In addition, the removal rate for Total Fe shows a downward trend from 24 to 120h.

Figure 5. Removal rate for Fe and SO_4^{-2}



Source: own elaboration

Discussion

A sample of AMD obtained from a coal collection center was treated during a week (5 days), where variation in the physicochemical characteristics in relation to the hydraulic retention time in a range from 24 to 120h can be evidenced. It was used as a subsurface flow anaerobic wetland reactor, changing the AMD flow upward. Using this method increases the pH to improve the water alkalinity first when contact occurs directly with the limestone layer. The optimal value for SRBs bacteria is near 7.0 [44], and some species are inhibited at values of 5.5. The SRBs activity is related to the pH of the medium being maximal to 6.0 - 9.0 pH, and they can disappear when the pH is inferior to 5.0 [45][46].

The pH data in the sample treated inside the reactor reveal an increase until obtaining an approximate value of 6.8 ± 1.6 in the first 24 h of the process and stabilizing until 6.6 ± 1.2 (120 h of the process). This evidences the neutralizing capacity of the limestone (calcium carbonate), when in contact with acid drainage, as a cause of the equation (1 - 2) generated within the system. This situation favors an optimal environment for the development of SRBs in the organic substrate confined within the reactor [6], [47], [48]. Calcite in the presence of hydrogen (H^+) dissolves, releasing calcium and bicarbonate, which reacts again with hydrogen to neutralize the proton acidity within the wetland, releasing carbon dioxide and water [11].

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (1)$$

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (2)$$

As shown in equation (3), the reduction of sulfates within the reactor was 34.35% on average during the entire experimentation time. However, this value is higher than expected in relation to what was reported by other authors, who have stated a greater degree of reduction at the same time [49]. This low efficiency can be linked to an Arrhenius model effect in which the degree of reduction of Fe, sulfates, and an increase in the pH of the samples, will be gradually regulated until they are stable values [50]. The reduction in the sulfate content of the sample reveals the presence, interaction, and proliferation of sulfate-reducing bacteria (SBR) within the organic substrate, which consumes the present carbon and sulfates, which play a terminal receptor function of electrons for your metabolism [51]. These bacteria convert sulfates to sulfides under anaerobic conditions [11].

$$2CH_2O + SO_4^{-2} + 2H^+ \rightarrow H_2S + CO_2 + H_2O \quad (3)$$

The reduction percentages of Total Fe do not present any predictable trend as a function of TRH, establishing an average value of 88.31% throughout the experimentation. The chemical reactions in equations (4 - 6) show the behavior of ferrous iron in the fluid. Ferrous iron (Fe^{2+}) present in AMD can be initially precipitated as ferrous sulfide (FeS) and as iron carbonate ($FeCO_3$), which can be retained within the structure of the organic substrate by adsorption phenomena. Finally, ferrous sulfide reacts with the remaining sulfur to form pyrite [51]. Under these circumstances, it is presumed that there is a partial reduction of the iron contained in AMD [11].

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad (4)$$

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+ \quad (5)$$

$$FeS + S^0 \rightarrow FeS_2 \quad (6)$$

As observed, complete removal of Total Fe was not obtained, even with a retention time of 120h, obtaining a final concentration of 9.37 $mg\cdot L^{-1}$, this being the lowest value obtained. The iron present in an anoxic wetland can be conditioned by the same compost (organic substrate) since physical, chemical, and biological changes can occur that induce mineralization within it. The chemical properties of the substrates (concentrations of humic substances, organic carbon, ash, and pH) can influence the transformation and distribution of metal species. These data can be compared to other authors' research, where they show that the application of bioreactors in AMD allows the efficient reduction of the content of sulfate ions and heavy metals while regulating the pH of the AMD with conditions similar to those used in this study [49], [52].

The initial DO of the AMD was established at 6.8 $mg\cdot L^{-1}$. However, after 24 h, this drops to an average value of 0.57 $mg\cdot L^{-1}$, evidencing its consumption by the microorganisms present in the organic substrate which favors the degradation of organic matter. Under this circumstance, only anaerobic microorganisms will proliferate inside the reactor. The low levels of DO obtained in the first stages of the process provide the anoxic conditions required for removing iron and sulfates in the samples by the bacteria generated by organic matter [53]–[56]. According to Pat-Espadas et al. [16], the Fe remotion in an aerobic or anaerobic wetland can achieve 92%. However, it is important to mention that wetlands without plants are less efficient than those without them [57]. This situation possibly reveals that the use of plants on a real scale can moderately enhance this study's results since other missing processes such as oxidation and hydrolysis can further reduce the contaminant load associated with metals."

Conclusion

The management of an artificial anaerobic wetland, destined for the passive treatment of acid mine drainage (AMD) from the coal mining industry in Boyacá, Colombia, was studied on a pilot scale. The system and organic material from the zone effectively raised the pH and removed sulfates and total Fe within the AMD samples for a relatively short time, even when the AMD flow was changed upward achieving optimal alkalinity generation and pH for the SRBs process.

The results obtained show that applying these types of systems for the treatment of AMD reduces 91.63% of total Fe in a short treatment time, while a 52.32% reduction of sulfates is obtained within 120h of treatment afterward.

The results in the decrease of the total content of Fe are closely related to the variation of pH and DO. The removal of total Fe generates a slight increase in pH in the samples from 3.09 to an average value of 6.5. Likewise, the dissolved oxygen DO content goes from 6.8 $mg\cdot L^{-1}$ to 0.57 $mg\cdot L^{-1}$ after 24h of treatment. These changes may be related due to the formation of iron compounds in the form of pyrite and siderite. The application of microbial systems also reduces the content of DO present in AMD samples; therefore, this technique will require subsequent stages of aeration to regulate the DO content to an optimal value.

The change in the flow direction of the AMD does notseem to influence the removal of the pollutant load directly, showing promising results in removing iron and sulfates. A higher hydraulic retention period can contribute to better long-term sulfate removal. AMD's passive treatment systems represent an efficient and economical alternative for companies that want to improve their treatment techniques, presenting an optimal process for the removal of sulfates and iron, in addition to the leveling of pH of AMD generated by coal mining processes. The application of a subsurface flow anaerobic wetland system has an optimal efficiency on the sulfate removal and is low in cost regarding maintenance and operation when compared to active treatments. The authors demonstrated their interest in applying this type of system to other waste generated by different industries in the region in subsequent studies, as well as the application of new raw materials within the area that allows for optimizing this type of process.

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