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# Evaluation of mature landfill leachates Treatment systems: the case of the landfill Curva de Rodas (Medellín-Colombia)

# Evaluación de sistemas de tratamiento en lixiviados provenientes de un relleno sanitario maduro: caso relleno sanitario Curva de Rodas

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## Abstract

Leachates produced in the closed landfill Curva de Rodas in Medellin, Colombia are catalogued as mature leachates. These are characterized as poorly biodegradable waste containing organic compounds such as fulvic and humic acids, heavy metals, ammonia, nitrogen, and salts. In this paper five possible physicochemical leachate treatments are evaluated: adsorption with five types of granular activated carbon (GAC), adsorption with zeolite type A, Fenton oxidation, chemical precipitation by $Ca(OH)_2$, and coagulation-flocculation with aluminum sulfide type A. The treatments are compared in terms of their capacity to remove Chemical Oxygen Demand (COD) and color. GAC adsorption removals of up to 39% for COD and 50% for color were achieved. In the case of the adsorption with zeolite type A, negligible removals of COD and color were achieved (3% and 7% respectively). Removals using the Fenton oxidation and neutralization with NaOH reached up to 95% for COD and 97% for color. When additionally neutralized with raw leachate the removals were up to 79% for COD and 87% for color. Finally in the chemical precipitation tests, removals of 27% for COD and 63% for color were achieved. Clearly, Fenton oxidation was identified as the most appropriate treatment process.

*Keywords:* Landfill leachate, fenton oxidation, adsorption, coagulation-flocculation, chemical precipitation, mature leachate treatment

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**Resumen**

Los lixiviados producidos en el relleno sanitario clausurado Curva de Rodas de la ciudad de Medellín se catalogan como "lixiviados maduros", estos se caracterizan por ser un residuo poco biodegradable. En este trabajo se evalúa la eficiencia de cinco posibles tratamientos fisicoquímicos: adsorción con 5 tipos de carbón activado granular (CAG), adsorción con Zeolita tipo A, oxidación Fenton, precipitación química con $Ca(OH)_2$ y coagulación-floculación con Sulfato de Aluminio Tipo A. Mediante la adsorción con CAG se alcanzaron remociones de hasta 39% para DQO y 50% para Color. En el caso de adsorción con Zeolita tipo A se lograron remociones de hasta 3% en DQO y 7% en Color. En los ensayos de precipitación química se lograron remociones máximas de 16% en DQO y 50% en color y por el proceso de coagulación-floculación hasta del 27% en DQO y del 63% en color. Los mejores resultados se obtuvieron con el proceso de oxidación Fenton, neutralizando con NaOH se lograron remociones máximas de 95% en DQO y 97% en color. Al neutralizar con lixiviado sin tratar las remociones alcanzadas fueron de hasta 79% en DQO y 87% en color.

*Palabras clave:* Lixiviados, relleno sanitario, oxidación fenton, adsorción, coagulación, floculación, precipitación química, lixiviados maduros

## Introduction

Technified landfills are one of the most used techniques for final solid waste disposal. However, the liquid emissions or leachates produced must be controlled. The leachates are defined as the aqueous effluent generated both by the percolation of rainwater through the wastes and by the biochemical processes occurring in the cells and the water contained in the waste [1, 2].

Leachates are heterogeneous in composition and drag all kinds of pollutants, many of them in high concentrations. Thus the leachates are catalogued as one of the most complex and difficult wastes to treat [3]. Solid wastes contain high loads of Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and Total Organic Carbon (TOC), high concentrations of organic and inorganic pollutants, including humic acids, ammonia nitrogen, heavy metals, inorganic salts, a high amount of total and dissolved solids and high concentrations of chlorides [4-7], as well as soluble compounds which are very resistant to biodegradation [8]. In old and stabilized sanitary landfills the amount of organic matter is reduced and the leachate biodegradability is low, accounting mainly for the accumulation of humic and fulvic substances as well as some heavy metals.

Leachate may be classified as one of the most pollutant liquid wastes because of its high content of organic matter and recalcitrant compounds, and must be treated before being released into the environment. The selection of the adequate type of treatment should consider the biological and physicochemical characteristics of the leachate. Such characteristics tend to vary through time and depend fundamentally on rainfall, the composition of the wastes, age of the landfill, and the grade of stabilization of the wastes [2]. The leachates may be categorized as young, intermediate, or stabilized [9, 10].

The great amount of substances present in the leachates and the wide ranges of variability through time make their treatment difficult [2, 11].

Numerous references have used physicochemical leachate treatments that present disadvantages with regard to reagents costs and generation of great amounts of difficult disposal sludge [7, 12-15]. The need of flexible treatments by stages used in conventional technologies is an aspect that also increases the costs [1, 16]. Several researchers have studied leachate treatments with favorable results [1, 15]. However, due to the wide variability of this waste in terms of its quality and quantity, it may be concluded that favorable results obtained with a specific treatment may not be extrapolated to leachates from a different landfill [15]. It is well known that stabilized leachates are mainly treated using physicochemical procedures such as coagulation-flocculation, flotation, adsorption with activated carbon and/or zeolites and intensive Fenton oxidation among others [6, 9, 14].

In a study made with leachates containing 96% of soluble COD at a landfill in ciudad de Merida (Yucatan, Mexico), removals of 40% and 37% of COD were achieved with processes of coagulation-flocculation and flotation respectively whereas adsorption tests with activated carbon achieved removals around 60% with decay to 30% in 80 and 60 hours (depending on the retention time), and Fenton oxidation tests achieve removals up to 78% of COD and 87% of TOC [15].

There have been some experiences in the treatment of leachates in several waste landfills in Colombia. Some of the most important are described below:

- Doña Juana Sanitary Landfill (Bogotá), in operation since 1988, uses 3.6 hectares for its leachate treatment plant in which the University of Los Andes performed an investigation using wetlands for leachates treatment. This system showed to be unfeasible due to the need of large areas [16].
- Navarro Sanitary Landfill (Cali), in operation since 1968, has presented different failures in its operation and management of leachates. The leachates are produced at an estimated rate of 7.6 l/s and currently a great amount is stored in artificial pounds. Research for the treatment of the leachates was done by coagulation-flocculation-sedimentation with $FeCl_2$, obtaining removals of 97% in color, 47% in COD, 75% in $BOD_5$, 56% in detergents, 86% in Arsenic, and 97% in cyanide. The pH was established as determinant parameter, with an optimal value of 5 [17].

Other experiences reported by Arias, 2010 include:

- Curva de Rodas Sanitary Landfill (Medellín), operated since 1984 and closed definitively in 2003. It is currently treating its leachates at San Fernando Waste Water Treatment Plant.
- El Guayabal Sanitary Landfill (San José de Cúcuta) started operating in 2003. Leachates are removed through perforated pipes and are conduced to and stored in evaporation pounds. A laboratory scale bio-discs system was implemented, which achieved average COD removals of 70%.
- La Esmeralda Sanitary Landfill (Manizales, Caldas), in operation since May 1991, treats its leachates by an UASB, achieving removals around 50% of COD.
- Don Juanito Sanitary Landfill (Villavicencio) started operating in November 1996 and treats its leachates in a wastewater treatment plant and by aspersion. An alternative to evaporation was implemented and research was done about forced evaporation through a greenhouse pilot system.

This paper focuses on the Curva de Rodas Sanitary Landfill, which started operations on November 23$^{rd}$, 1984 and was closed onJune 6th, 2003. This landfill is located at 4 km from the city of Medellín, between the municipalities of Copacabana and Bello, in the Rodas ravine watershed. The total area of the landfill is 73 hectares and the disposal area is 36 hectares. Along its 19 years of operation a total of 8 million tons of wastes of different nature were disposed in this landfill, becoming the first large-scale sanitary landfill that has been totally closed in Colombia [18].

The objective of our study is to assess different physicochemical treatment systems for stabilized leachates from Curva de Rodas Sanitary Landfill (see Table 1), considered here as a mature sanitary landfill, generating knowledge about the alternatives of treatments for these wastes and identifying the ranges of efficiency achieved by the processes studied.

**Table 1** Curva de Rodas sanitary landfill leachate characteristics

| *Parameter* | *Previous Characterizations Average* | *Summer Season 1 Leachate* | *Winter Season 1 Leachate* | *Winter Season 2 Leachate* | *Summer Season 2 Leachate* |
|---|---|---|---|---|---|
| Apparent Color (mg Pt-Co/l) | | 2211 | 397 | 489 | 384 |
| Turbidity (UNT) | | 8.2 | 22.8 | | |
| $BOD_5$ (mg/l) | 80 | | 88 | | |
| Soluble COD (mg/l) | | | | 214 | |
| Total COD (mg/l) | 717 | 1403 | 443 | 322 | 927 |
| Suspended Solids (mg/l) | 1094 | 22 | | | |
| Dissolved Solids (mg/l) | 2848 | 4948 | 2194 | | |
| Total Solids (mg/l) | | | 2212 | | |
| $BOD_5$/COD | 0.11 | | 0.20 | | |
| pH (pH Units) | | | 8.1 | 8.1 | 8.5 |

## Experimental

### *Adsorption tests with granular activated carbon (GAC)*

The waste from the landfill was stored at room temperature in the laboratory. Three tests with different types of GAC and various dosages were performed. A total of five (5) references were used and color and COD were established as response variables. The granular activated carbon references used, characteristics and the doses applied are summarized in table 2. A velocity of mixing of 40 RPM during 15 min was used and the waste was passed through filter paper to separate the residual GAC. In all the tests a volume of 500 ml was employed.

**Table 2** GAC Characteristics and dosages

| *GAC Type* | *GAC Characteristics* | | | *Dosage (g/l)* |
|---|---|---|---|---|
| | *Origin* | *Granulometry (US Mesh)* | *Iodine (mg/g)* | |
| 1 | Coal Based | 4x10 | 961 | 10 dosages between 0.44 and 50 |
| 2 | Coconut Shell Based | 10x40 | 950 | 10 and 40 |
| 3 | Coconut Shell Based | 8x30 | 830 | 10 and 40 |
| 4 | Coconut Shell Based | 4x8 | 1118 | 10 and 40 |
| 5 | Coconut Shell Based | 8x30 | 1131 | 10 and 40 |

## Adsorption tests with type A Zeolite

The initial dose was based on the dosage used by Kargi et al., 2003 in a test in which a volume of leachate pretreated by coagulation flocculation processes and ammonia stripping was subjected to a biological treatment in an aeration tank operated with a repetitive process of feeding by batches in presence of powdered activated carbon (PAC) and zeolite (2 g/l) adsorbents. Removals around 86% of COD were achieved [19].

In another test, the zeolite dosage was varied by applying 5, 10, and 20 g/l of adsorbent, with volumes of 50 ml for each dosage of zeolite. After adding the zeolite, the waste sample was subjected to a stage of 0.5 min. of fast mixing and then a stage of 14.5 min. of slow mixing. A magnetic stirrer was used for mixing. Next, the sample was passed through filter paper to remove the zeolite and finally the pH, temperature, COD, and color were measured, taking the last two as response variables.

### *Fenton oxidation tests*

For these tests, sample volumes of 500 ml of leachate were employed. A magnetic stirrer was used for mixing and the reaction time was 2 hours. The samples were then left in a sedimentation stage for 30 min. Each test was done through the following four stages:

- *Adjustment of pH by addition of 98%$H_2SO_4$*
- *Addition of Fenton Reagents 1.96 g $FeSO_4.7H_2O$ and 1.15 mL $H_2O_2$ (50%) 2 hours of reaction with fast stirring.*
- *Neutralization by addition of a 4%NaOH solution*
- *Sedimentation during 30 min*

Three exploratory phases were followed to optimize the Fenton oxidation process:

1. *pH Optimization*

Five (5) tests were performed, a blank sample with distilled water, a leachate without adjusting the pH (8.2), and three tests adjusting the pH to values of 3.0, 5.0 and 7.0.

*Molar ratio ferrous sulfate/hydrogen peroxide of 2.89*

2122 mg/l $FeSO_4 \rightarrow$ 3920 mg/l $FeSO_4.7H_2O$ (99%)

1375 mg/l $H_2O_2 \rightarrow$ 2.3 ml/l $H_2O_2$ (50%)

2. *Determination of optimal pH and neutralization with leachate test*

After analyzing the results obtained in the exploratory phases, six more tests were performed adjusting the pH to 5.5, 6.0 and 6.5 units. The neutralization for each pH was carried out with NaOH and with raw leachate (alkalinity 1760 mg$CaCO_3$/l). In these tests, the dosage and molar relation of Fenton agents were maintained.

3. *Variation of the molar relation $H_2O_2/FeSO_4$, neutralization tests by mean of wetland effluent, and determination of the volume and humidity of the generated sludge*

Four additional tests were done in order to reduce the intake of reagents using a pH adjusted to 5.5, in which the reagents proportions were varied using molar relations $H_2O_2/FeSO_4$ with values of 1.94 and 2.89 as can be seen in table 3.

**Table 3** Dosage by molar ratios 1.94 and 2.89

| *Molar ratio* | *Dosage* | *Complete dosage* | *Half dosage* |
|---|---|---|---|
| 1.94 | 1 | 2122 mg/l $FeSO_4$ 921 mg/L $H_2O_2$ | 1061 mg/l $FeSO_4$ 460 mg/L $H_2O_2$ |
| 2.89 | 2 | 2122 mg/l $FeSO_4$ 1375 mg/L $H_2O_2$ | 1061 mg/l $FeSO_4$ 687 mg/L $H_2O_2$ |

For assessing both neutralization alternatives, the control volume of leachate for oxidation was 500 ml. The volume was divided into two parts to neutralize 250 ml with raw leachate and 250 ml with leachate treated in an underground wetland (wetland effluent).

The sludge volume produced was determined by sedimentation in Imhoff cones for 15 min and later, two tests were done with two different dosages and molar ratios showed in table 4.

**Table 4** Dosage by molar ratios 5.76 and 11.72

| *Molar ratio* | *Dosage* | |
|---|---|---|
| 5.76 | 3 | 2122 mg/l $FeSO_4$<br>921 mg/L $H_2O_2$ |
| 11.72 | 4 | 2122 mg/l $FeSO_4$<br>1375 mg/L $H_2O_2$ |

### *Chemical precipitation tests*

Three chemical precipitation tests were performed based on the methodology used by Agudelo, 1994 [20]. Lime solution at 20% by mass was added progressively to leachate samples (500 ml) with permanent mixing until obtaining the pH required for each test (10, 11, and 12.40 pH units). The test ended with a sedimentation stage of 15 minutes, after which the COD and the color of the resulting solution were determined.

### *High dosage Coagulation-Flocculation Tests*

Three tests were done by varying the dosage of aluminum sulfate type A (2, 5 and 8 g/l respectively) in a 10% solution. The procedure consists in adding the coagulant with constant mixing simultaneously to several 1 l leachate samples. The samples are left in fast mixing at 180 RPM for 1 min. and then in slow mixing at 40 RPM for 15 min., followed by the stage of sedimentation during 15 min. after which the values of COD and color of the resultant are determined. The test was made in a standard jars facility.

## Results

### *Curva de rodas sanitary landfill leachates characteristics*

Table 1 shows the average characteristics of the Curva de Rodas Sanitary Landfill leachate. The low $DBO_5$/DQO ratio, the presence of dissolved and suspended solids, and the variation of the COD according to climate conditions are included in this table in order to compare characteristics of several samples taken at different dates and under different climate conditions.

## Granular activated carbon adsorption

Table 1 summarizes the results obtained from the waste characterization in the first winter season. In the results obtained from the first test (table 5), color and COD increased, indicating that the dosages of GAC (Type 1) were low and did not produce reductions in the response variables. The increases in color and COD were due to residual GAC present in the filtrate. Considering the results of this early test, the dosages were increased, thereby achieving removals proportional to the GAC dosage up to a maximum of 28.9% of COD and 21.1% of color.

**Table 5** Adsorption with GAC (Type 1) jar Test 1 results

| *CAG Dosage (g/l)* | *g GAC/g COD* | *COD (mg/l)* | *Color (mg Pt-Co/l)* | *% COD Removal* | *% Color Removal* |
|---|---|---|---|---|---|
| 0.00 | 0.00 | 421.6 | 281.5 | 0.0% | 0.0% |
| 0.44 | 1.05 | 430.9 | 312.3 | -2.2% | -10.9% |
| 0.63 | 1.50 | 427.8 | 335.4 | -1.5% | -19.2% |
| 0.88 | 2.10 | 430.9 | 327.7 | -2.2% | -16.4% |
| 1.47 | 3.49 | 424.7 | 327.7 | -0.7% | -16.4% |
| 4.42 | 10.48 | 437.1 | 320.0 | -3.7% | -13.7% |

The variation in the removals of COD and color as a function of the GAC/COD ratio can be observed in figure 1. Based on the removals achieved with the GAC Type 1, tests with the other four references were made. Dosages of 10 and 40 g/l were chosen to observe the behavior of each GAC reference (see table 6). Using a 10 g/l dosage, maximum removals of 21.9% in COD and 24.1% in color were obtained with the GAC Type 3, and minimum removals of 7.4% in COD and 7.1% in color were obtained with the GAC Type 1 (see table 6).

**Figure 1** Adsorption with CAG (Type 1) jars test 2 COD and color percentage removal

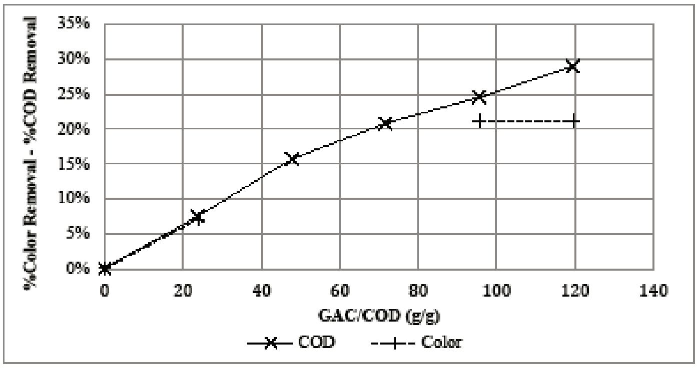


**Table 6** Jar tests with 5 references of GAC results

| *GAC Dosage g/l* | *GAC Type* | *g GAC/g COD* | *COD (mg/l)* | *Color (mg Pt-Co/l)* | *% COD Removal* | *% Color Removal* |
|---|---|---|---|---|---|---|
| 10 | Blank | 0.0 | 452.6 | 350.8 | 0.0% | 0.0% |
| | 1 | 23.9 | 387.4 | 304.6 | 7.4% | 7.1% |
| | 2 | 22.1 | 393.6 | 296.9 | 13.0% | 15.4% |
| | 3 | 22.1 | 353.3 | 266.2 | 21.9% | 24.1% |
| | 4 | 22.1 | 399.8 | 296.9 | 11.7% | 15.4% |
| | 5 | 22.1 | 356.4 | 312.3 | 21.3% | 11.0% |
| 40 | Blank | 0.0 | 452.6 | 350.8 | 0.0% | 0.0% |
| | 1 | 95.6 | 316.0 | 258.5 | 24.5% | 21.1% |
| | 2 | 88.4 | 275.6 | 173.8 | 39.1% | 50.5% |
| | 3 | 88.4 | 424.7 | 296.9 | 6.2% | 15.4% |
| | 4 | 88.4 | 340.8 | 227.7 | 24.7% | 35.1% |
| | 5 | 88.4 | 337.7 | 235.4 | 25.4% | 32.9% |

With a 40 g/l dosage, maximum removals of 39.1% in COD and 50.5% in color were obtained with the GAC Type 2, whereas minimum removals of 6.2% in COD and 15.4% in color were obtained with the GAC Type 3 (see table 6).

### *Zeolite A Adsorption*

The results obtained in the characterization of the waste in the second winter season are summarized in table 1. In the results obtained with Zeolite A adsorption tests, an increase in the pH is observed when more zeolite is added, due to the treatment done to the zeolite with NaOH. The removal percentages with this process were calculated based on the soluble COD, achieving maximum values of 7.0% in COD and 3.5% in color with a decrease in these values for dosages above 10 g/l. These removals are very low for both parameters.

**Fenton Oxidation**

The results obtained in the pH scanning and in the determination of the optimum pH by neutralization with NaOH and raw leachate presented in table 7.

**Table 7** pH Scanning, Optimal pH Determination and Neutralization with NaOH and Raw Leachate Tests Results

| Neutralizing | Sample | Adjusted pH | $H_2SO_4$ Vol. (mL) | pH at the End of the Reaction | Vol. of Neutralizing (mL) | pH after Neutralizing | COD (mg/l) | Color (mg Pt-Co/l) | Total Solids (mg/l) | % COD Removal | % Color Removal | % Total Solids Increase |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solution of NaOH (4%) pH = 13.5 | Blank (Raw Leachate) | 8.2 | | | | | 294.0 | 283.1 | 1782 | | | |
| | Standard (Distilled Water) | 7.0 | | 2.85 | 12.7 | | 9.9 | 2.9 | 1732 | | | |
| | Treated Leachate | 3.0 | 0.56 | | 14.5 | 7.44 | 39.5 | 15.3 | 5164 | 87% | 95% | 190% |
| | | 5.0 | 0.47 | 2.72 | 13.2 | 7.10 | 39.5 | 15.0 | 4882 | 87% | 95% | 174% |
| | | 5.5 | 0.44 | 2.51 | 11.2 | 7.00 | 18.0 | 8.9 | 4548 | 94% | 97% | 155% |
| | | 6.0 | 0.35 | 2.64 | 8.3 | 7.01 | 21.6 | 7.3 | 4254 | 93% | 97% | 139% |
| | | 6.5 | 0.20 | 3.26 | 4.0 | 7.13 | 93.2 | 10.7 | 3686 | 68% | 96% | 107% |
| | | 7.0 | 0.08 | | 10.0 | 9.59 | 121.9 | 30.5 | 3028 | 59% | 89% | 70% |
| | | 8.2 | | 7.07 | 1.9 | 8.15 | 132.7 | 39.2 | 2,456 | 55% | 86% | 38% |
| Leachate | Raw Leachate | 8.2 | | | | | 294.0 | 283.1 | 1782 | | | |
| | Treated Leachate | 5.5 | 0.44 | 2.51 | 400.0 | 6.13 | 75.3 | 50.1 | 3174 | 74% | 82% | 44% |
| | | 6.0 | 0.35 | 2.64 | 250.0 | 6.06 | 61.0 | 36.2 | 2946 | 79% | 87% | 37% |
| | | 6.5 | 0.20 | 3.26 | 100.0 | 6.16 | 154.2 | 15.1 | 3122 | 48% | 95% | 42% |

T.Leachate: Treated Leachate

Figures 2 and 3 present the behavior of the COD and color removals as a function of adjusted pH. Figure 2 shows that the lowest concentrations of COD and color occur in the range between 5.0 and 6.0 adjusted pH units. This is confirmed in figure 3 where maximum removals are observed at a pH value of 6.0, which achieves the highest removal of COD and color. Adjusted pH values between 3.0 and 5.0 units present a constant behavior for COD, color, and their respective removals. In figures 2 and 3 can be seen a sharp increase in COD and color and a decrease in their removals when the adjusted pH exceeds 6.0.

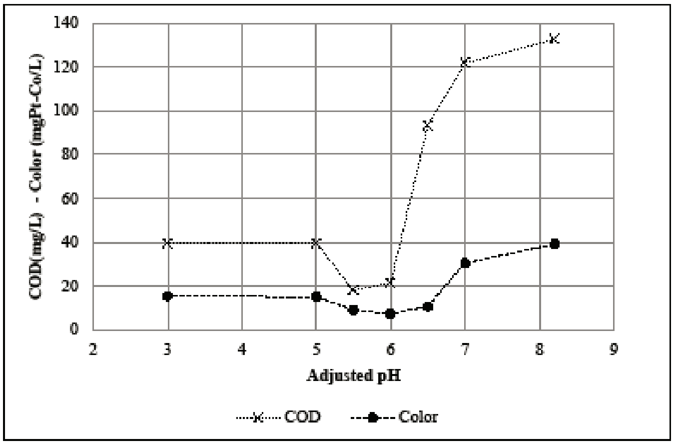


**Figure 2** pH Scanning and optimal pH determination neutralizing with NaOH fenton oxidation tests results

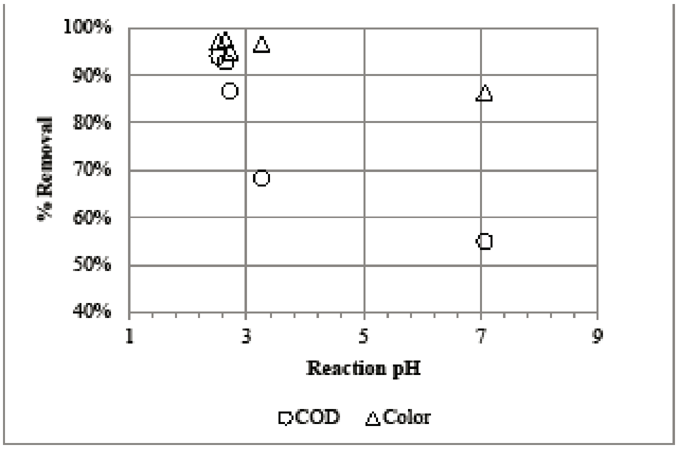


**Figure 3** Fenton oxidation neutralized with NaOH COD and color removals and percentage increase solids as a function of the adjusted pH

The COD and color removals achieved between adjusted pH values of 3.0 and 6.0 that are neutralized with 4% NaOH are over 85%. Figure 2 shows a break point at an adjusted pH of 6.0 and an increase on the slope of the COD at a higher rate. The above results indicate that the optimum adjusted pH is below 6.0. Consequently, figure 3 shows a decrease in the slope at an adjusted pH of 6.0, clearly showing the break point and indicating that the best removals occur above this value.

Table 7 shows that the adjusted pH is different from the reaction pH in most of the cases because the addition of Fenton agents causes a decrease in pH.

The behavior of total solids is illustrated in figure 3. An increase of the total solids is observed when the adjusted pH is reduced, since lower adjusted pH values require more sulfuric acid and a larger amount of NaOH for neutralization.

Figure 4 shows the relationship between the reaction pH value and the removal percentages. From this figure it is observed that the removal percentage decreases while the reaction pH increases and that the optimal reaction pH is between 2.51 and 2.64 units.

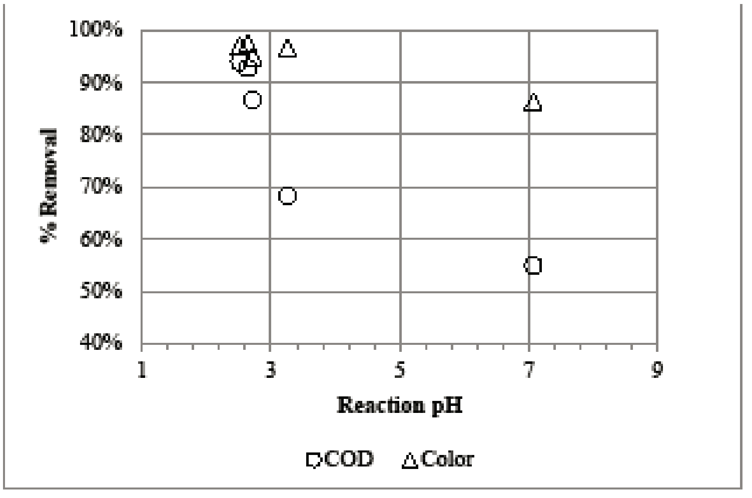


**Figure 4** Percentage removal as a function of the reaction pH

Due to the high alkalinity present in the leachate and in the leachate scale wetland treatment effluent (1760 and 1380 $mgCaCO_3/l$ respectively), the use of both for neutralization purposes was assessed to reduce the amount of agents used and to avoid in this manner the increase of total solids. The results of the Fenton oxidation tests, in which neutralization with raw leachate was used, are summarized in table 7. This table shows that the achieved removals by raw leachate neutralization with an adjusted pH of 5.5 were 74% of COD and 82% of color, and 79% and 87% of COD and color respectively with an adjusted pH of 6.0. Compared with the NaOH neutralization (which reaches 94% COD removal with a 155% increase in dissolved solids), neutralization with raw leachate reaches 74% COD removal with lower increases in dissolved solids (around 45%), making it a technically feasible treatment solution.

Figure 5 shows the behavior of the solids regarding the adjusted pH in the neutralization by raw leachate tests, resulting in an increase of the solids concentration below 44%. In this figure it can be confirmed that there is a break point in the resultant COD when the adjusted pH gets close to 6.0 units, which has corresponding removals above 70% and 80% in COD and color respectively.

The results achieved by the Fenton oxidation tests, where the $H_2O_2/FeSO_4$ molar ratio was varied and neutralized with leachate scale wetland treatment effluent, are presented in tables 8 and 9, indicating the obtained sludge volume. Table 8 shows that the sludge volumes were near 10% of the leachate's initial volume. Figure 6 shows the total solids determined from the Fenton oxidation resultant sludge, where higher concentrations of total solids are linked to higher molar relations, i.e. 2.89.

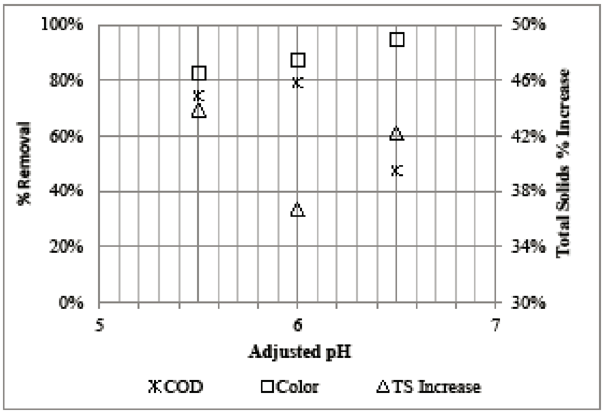


**Figure 5** Fenton oxidation neutralized with raw leachate COD and color removals and increase of total solids

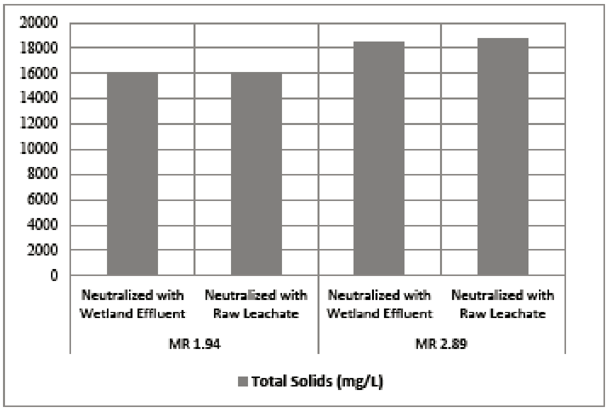


**Figure 6** Resulting sludge total solids

**Table 8** Variation of the molar relation $H_2O_2/FeSO_4$, wetland effluent neutralization and determination of volume and humidity of generated sludge tests results

| ***STAGE*** | ***Molar Relation*** | ***1.94*** | | ***2.89*** | |
|---|---|---|---|---|---|
| | | ***Complete Dosage*** | ***Half Dosage*** | ***Complete Dosage*** | ***Half Dosage*** |
| pH Adjust | WorkVolume (L) | 0.5 | 0.5 | 0.5 | 0.5 |
| | Adjusted pH | 5.5 | 5.5 | 5.5 | 5.5 |
| | $H_2SO_4$ Volume (mL) | 0.44 | 0.44 | 0.44 | 0.44 |
| | $H_2SO_4$ Dosage (ml/l) | 0.88 | 0.88 | 0.88 | 0.88 |
| Addition of Fenton Reagent | $H_2O_2$ Dosage (mg/l) | 921 | 461 | 1,375 | 688 |
| | $H_2O_2$ Volume (50%) (ml) | 0.77 | 0.35 | 1.15 | 0.58 |
| | $FeSO_4$ Dosage (mg/l) | 2122 | 1061 | 2122 | 1061 |
| | $FeSO_4.7H_2O$ Weight (70%) (g) | 1.96 | 0.98 | 1.96 | 0.98 |
| Raw Leachate Neutralization | Work Volume (l) | 0.250 | 0.25 | 0.25 | 0.25 |
| | Leachate Volume (ml) | 220 | 101 | 300 | 115 |
| | Leachate Volume (l/l) | 0.880 | 0.402 | 1.200 | 0.460 |
| Sedimentation | Total Volume (ml) | 470 | 351 | 550 | 365 |
| | Sludge Volume (ml) | 26 | 25 | 18 | 21 |
| Wetland E. Neutralization | Work Volume (l) | 0.250 | 0.250 | 0.250 | 0.250 |
| | Wetland E. Volume (ml) | 270 | 120 | 300 | 150 |
| Sedimentation | Total Volume (ml) | 520 | 370 | 550 | 400 |
| | Sludge Volume (ml) | 21 | 28 | 17 | 22 |

**Table 9** Molar relation variation of fenton tests results

| ***Molar Relation*** | ***Dosage*** | ***Neutralizing*** | ***COD (mg/l)*** | ***Color (mgPt-Co/l)*** | ***Solids (mg/l)*** | ***% COD R.*** | ***% Color R.*** | ***%A. Solids*** |
|---|---|---|---|---|---|---|---|---|
| 1.94 | Dosage 1 | Leachate | 121.9 | 81.4 | 2520 | 58.5% | 71.2% | 41.4% |
| | | Wetland Effluent | 93.2 | 101.4 | 2375 | 68.3% | 64.2% | 33.3% |
| | Half Dosage 1 | Leachate | 182.8 | 70.6 | 2985 | 37.8% | 75.1% | 67.5% |
| | | Wetland Effluent | 96.8 | 413.8 | 2680 | 67.1% | N.A. | 50.4% |
| 2.89 | Dosage 2 | Leachate | 118.3 | 150.5 | 2715 | 59.8% | 46.8% | 52.4% |
| | | Wetland Effluent | 104.0 | 126.8 | 2600 | 64.6% | 55.2% | 45.9% |
| | Half Dosage 2 | Leachate | 89.6 | 176.7 | 2525 | 69.5% | 37.6% | 41.7% |
| | | Wetland Effluent | 78.9 | 195.9 | 2490 | 73.2% | 30.8% | 39.7% |
| 5.76 | Dosage 3 | Leachate | 215.0 | 104.0 | 2095 | 26.9% | 63.3% | 17.6% |
| 11.72 | Dosage 4 | Leachate | 88.2 | 276.0 | 2965 | 70.0% | 2.5% | 66.4% |
| Raw Leachate | | | 294.0 | 283.1 | 1782 | | | |

Figure 7 shows that the best COD removals were achieved with half of the initial dosage, maintaining a molar ratio of 2.89. A low removal of color is observed with regard to a short sedimentation time and a possible destruction of the precipitates while the sample was poured into the Imhoff cones. In some cases, foam is formed during the oxidation reaction. It was also observed that the precipitates started to form at pH values between 4.5 and 5.0 units during the neutralization stage.

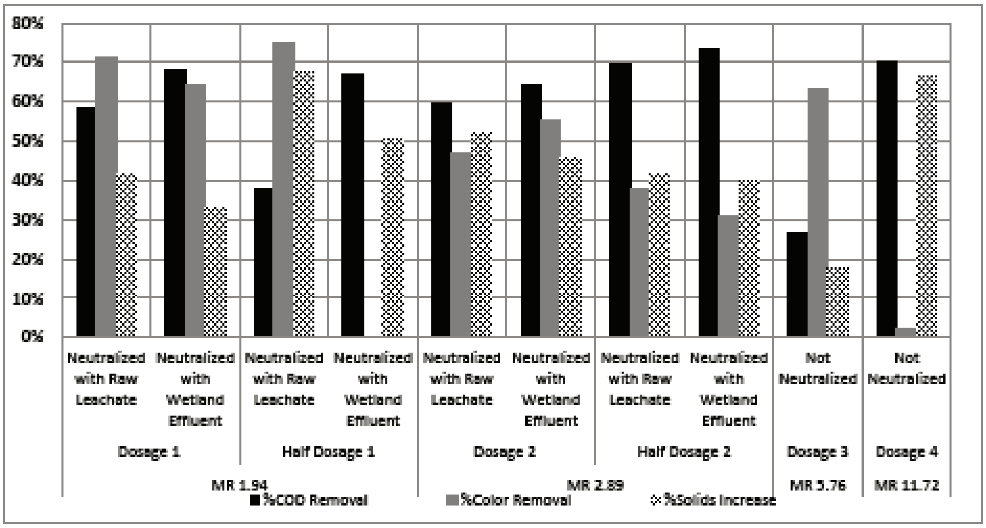


**Figure 7** Fenton oxidation dosage and molar relation variation test results

### *Chemical precipitation*

The characteristics of the leachate generated in the second summer season are presented in table 1. The results obtained using chemical precipitation with lime can be observed in table 10, in which a maximum COD removal of 16% was achieved with a dosage of 8 g $Ca(OH)_2$/l and the color removal remains constant in 50% even with the increase of lime dosage. It can be observed that the COD removal increases as the lime dosage increases, yet the COD removals did not exceed 20% and remain constant at 50% for color.

**Table 10** Chemical precipitation process with lime tests results

| *Test* | *Dosage* | | *pH* | *COD (mg/l)* | *Color (mgPt-Co/l)* | *% COD Removal* | *% Color Removal* |
|---|---|---|---|---|---|---|---|
| | *Unit* | *Value* | | | | | |
| Blank | - | - | 8.5 | 927.0 | 383.8 | 0% | 0% |
| Chemical | g $Ca(OH)_2$/l | 5.20 | 10.0 | 859.7 | 190.9 | 7% | 50% |
| Precipitation | g $Ca(OH)_2$/l | 6.40 | 11.0 | 796.0 | 193.4 | 14% | 50% |
| | g $Ca(OH)_2$/l | 8.00 | 12.4 | 778.3 | 190.9 | 16% | 50% |

## Coagulation-flocculation

In table 11 the results achieved by the coagulation-flocculation process with aluminum sulfate type A are summarized. The highest achieved removals were 27% of COD with a dosage of 8 g $Al_2(SO_4)_3$/l and 63% of color with a dosage of 5 g$Al_2(SO_4)_3$/l.

**Table 11** Coagulation-flocculation with aluminum sulfate type a process tests results

| *Test* | *Dosage* Unit | Value | *pH* | *COD (mg/l)* | *Color (mgPt-Co/l)* | *% COD Removal* | *% Color Removal* |
|---|---|---|---|---|---|---|---|
| Blank | - | - | 8.5 | 927 | 383.8 | 0% | 0% |
| Coagulation Flocculation Sedimentation | g $Al_2(SO_4)_3$/l | 2.0 | 7.8 | 817 | 203.8 | 12% | 47% |
| | g $Al_2(SO_4)_3$/l | 5.0 | 7.1 | 761 | 140.5 | 18% | 63% |
| | g $Al_2(SO_4)_3$/l | 8.0 | 6.7 | 676 | 163.4 | 27% | 57% |

In table 11 the variation of COD and color as a function of coagulant dosage is also observed. In this particular case the COD value tends to decay while the coagulant dosage is increased. Consequently, as the coagulant dosage increases better removals are observed, not exceeding 30% despite of the use of high dosages of coagulant. It is also observed that the color removal does not show an appreciable tendency in the three tests, remaining below 65%.

## Discussion

The adsorption with GAC is one of the techniques used in the treatment of mature sanitary landfill leachates and carbons from different origins have been assessed for this purpose [21]. However, the highest removals achieved by adsorption with GAC Type 2 were 50% in color and 39% in COD (dosages of 40 g/l and retention times of 15 minutes). These are not significant removals compared with a minimum removal of 80% of organic matter present in the leachate, therefore, the dose required to achieve acceptable removal efficiency is high, which implies a high cost taking into account the cost of GAC (around 126 US$/$m^3$) and its regeneration. Through this process color removals between 50% and 70% and COD removals around 60% have been achieved varying the GAC quality [7, 9].

The adsorption with activated carbon may be suggested as a complementary treatment, because through this process dissolved solids may be removed [22]. This process is ideal as a complementary post-treatment after Fenton oxidation process. Renou et al., 2008 report several removals achieved by adsorption with activated carbon at international level, the most of which exceed 70% in terms of COD and dosages near 2 g/l. The low removals achieved in the tests may be attributed to the quality of the product and its grade of commercial quality, in contradiction of what was used in this case, achieving COD removals below 60% [1].

For the case of the adsorption with Zeolite type A, the achieved removals were low, 3% of soluble COD and 7% of color with a dosage of 10 g/l (maximum value). This shows that the zeolite type A is not an ideal adsorbent for the removal of the compounds found in this kind of leachate.

The Fenton oxidation process produces the highest removals and is shown as the ideal treatment for Curva de Rodas landfill leachate among the tested treatments, achieving removals of up to 94% of COD and 97% of color neutralized with NaOH and using concentrations of 2122 mg/l of $FeSO_4$ and 921 mg/l of $H_2O_2$. The disadvantage of this process is the use of $H_2SO_4$ for the pH adjustment and the use of NaOH for the neutralization resulting in an increase of total solids which could exceed 100% in the most favorable cases of the reaction (see figure 4).

Hee-Chan et al., 2001, achieved similar results with the oxidation Fenton process with leachates. They found that the highest COD removal achieved was 72%, with an adjusted pH of 4.0 trough Fenton oxidation with 600 mg/l of $H_2O_2$ and 1000 mg/l of $Fe^{2+}$ [12].

Advanced oxidation processes are an effective alternative, fast and economic, because the chemical oxidation transforms the organic pollutants in harmless compounds, generally carbon oxides and water [23].

The use of raw leachate as a neutralizing agent in the Fenton oxidation was proposed as an alternative given the high alkalinity of the leachate (1760 mg$CaCO_3$/l), thereby the costs of the necessary inputs are reduced. When neutralizing with raw leachate, COD removals of up to 79% and color removals of up to 87% are achieved with an increase in total solids of 37% and with concentrations of 2122 mg/l of $FeSO_4$ and 921 mg/of $H_2O_2$ (see table 7). These percentages make this alternative the most attractive to be implemented. Likewise, the alternative of neutralizing with leachate scale wetland treatment effluent was tested achieving removals of up to 73% of COD and 71% of color (see table 9).

In Curva de Rodas landfill, leachate characterizations shown in this investigation (see table 1) with COD values of 1403 mg/l in summer and 717 mg/l on average (from previous studies until the present). Which indicates, according to Renou et al. 2008, Luna et al., 2007, Durán and Ramírez, 2002, and Deng, 2007, that an average $DBO_5$/DQO relation of 0.075 classifies the leachate as mature leachate. With regard to suspended solids, it was found that their value of 22 mg/l in the summer season is low [1, 3, 9, 24].

Regarding chemical precipitation, COD removals of 16% and color removals of 50% were achieved with a dosage of 8 g $Ca(OH)_2$/l in accomplished tests, which is relatively high dosage for the obtained removals.

The removals achieved during the coagulation-flocculation process with high dosages of coagulant were 27% of COD with a dosage of 8 g $Al_2(SO_4)_3$/l and 63% of color with a dosage of 5 g $Al_2(SO_4)_3$/l. The used dosages were relatively high for the obtained removals, which were below 30% of COD removal (see table 9).

Coagulation-flocculation and flotation processes aim at removing suspended particles present in liquid phase. But as table 1 shows the referred leachates have particularly low concentrations of suspended solids [7]. Consequently, it is possible to use these processes as a pre-treatment to later remove the other pollutants using adsorption and/or advanced oxidation [25].

Since the aim of this work is to achieve a removal of 80% of organic matter, according to the results it is considered that the processes of coagulation-flocculation and chemical precipitation are not recommended as main treatment for mature leachates.

Tables 10 and 11 present the variation of the pH values for each dosage of lime or coagulant (aluminum sulfate). In this sense, the final pH in the chemical precipitation process that corresponds to the highest COD removal (16%) is 12.40, which makes this process unfeasible as pre-treatment. If planned, a Fenton oxidation process with a pH adjustment that obligates its reduction is needed. In the case of the coagulation-flocculation, the highest COD removal achieved (27%) corresponds to a final pH of 6.7, which would be favorable for a subsequent Fenton oxidation treatment. However, the use of this process as a pre-treatment is not warranted due to the generation of a great amount of non-stabilized sludge and the use of high dosages of reagents for achieving relatively low removals.

The Curva de Rodas case is similar to the Sanitary Landfill of Merida, where the best removals of 77.4 % in COD were achieved with Fenton oxidation as well, followed by adsorption with activated carbon (60.0 % COD removal), coagulation-flocculation (42.1 % removal) and flotation (36.8 % removal) due to low suspended solids present in the leachate [15].

Navarro Sanitary Landfill located in Cali, Colombia is another reference because it deals with partially stabilized leachates. In this study, the coagulation-flocculation-sedimentation process was used, achieving removals of 97% of color and 47% of COD. The removal of COD is low and it may be supposed that the removed COD corresponds to the suspended solids. This leachate also classifies as a mature leachate because of its $DBO_5$/DQO relation of 0.12, and its pH of 9.1 units [17].

Regarding the two study cases cited before and the Curva de Rodas Sanitary Landfill, it is determined that the coagulation-flocculation process is not recommended as this kind of mature leachate main treatment given its physicochemical characteristics. However, according to the variability of this waste, it is not possible to completely discard such alternative. Renou et al., 2008 reports some cases with important removals in low biodegradable leachates [1].

## Conclusions

The adsorption process with GAC applied to the treatment of Curva de Rodas Sanitary Landfill leachates achieves removals of 39% COD and 50% color. The dosage costs (around 126 US$/$m^3$) are prohibitive, considering that the tests were type batch. However a preliminary study is required about the possibilities of regeneration of the GAC and adsorption column tests which may result in more reasonable costs for the assessment of the adsorption by GAC as a complementary treatment.

The color and COD removals by mean of adsorption with type A zeolite are low (2.90% of COD and 7.0% of color), thus this alternative is not technically feasible to treatment of leachate on Curva de Rodas Sanitary Landfill.

The optimum adjusted pH determined for Fenton oxidation was 6.0, but it is recommended to operate this system at a pH of 5.5, because at a pH of 6.0 the reaction is near the process efficiency break point.

At pH 6.0, the Fenton oxidation process achieves removals of up to 93% and 97% of COD and color respectively when neutralized with NaOH and of 79% and 87% of COD and color respectively when neutralized with raw leachate; and the resultant sludge production in this last process is around 10% of the initial leachate volume and it has the advantage of being a stabilized sludge. Therefore, although the alternative of using raw leachate for the neutralization has lower COD and color removal, this uses the leachate alkalinity content decreasing treatment costs by replacing the alkalizing and increasing the volume of waste treated per batch. This makes it a good option to evaluate in more detail in future work.

Based on this study, the Fenton oxidation at pH 6.0 with the raw leachate neutralization is the best alternative for cost (around 3.1 US$/$m^3$) and waste (around 10% v/v stabilized sludge). The coagulation-flocculation process is not recommended for treating Curva de Rodas Sanitary Landfill leachates due to its low removals even with high dosages of coagulant and the production of high non-stabilized sludge.

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