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Efficiency of Combined Processes Coagulation/Solar Photo Fenton in the Treatment of Landfill Leachate

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Abstract: The combined coagulation-solar photo Fenton treatment of leachate from the sanitary landfill located in Atlantico-Colombia was investigated. Firstly, the efficiency of two alternative combined treatments for the reduction of chemical oxygen demand in leachate was assessed, coagulation with poly-aluminum chloride followed by solar photo-Fenton process (Treatment 1) and coagulation with $FeCl_3{\cdot}6H_2O$ followed by ferrioxalate-induced solar photo-Fenton process (Treatment 2). Afterwards, treatments 1 and 2 were compared with the treatment currently used in the sanitary landfill (only coagulation with poly-aluminum chloride), in terms of efficiency and costs. An optimization study of alternative treatments was performed combining central-composite experimental design and response surface methodology. The optimum conditions resulted in a chemical oxygen demand reduction of 73 % and 80 % for Treatment 1 and 2, respectively. Both alternative treatments for the leachate are more efficient than the treatment currently used in the sanitary landfill (chemical oxygen demand reduction of 20 %). In terms of costs, treatment 1 would be the most competitive to implement in the sanitary landfill, since this would have an increase of 13.3 % in the total unitary cost compared to an increase of 39.5 % of treatment 2.

Keywords: leachates; coagulation; solar photo-fenton; ferrioxalate-induced

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1. Introduction

Modern anthropic activity generates large amounts of solid waste. Sanitary landfills are a strategic option for waste treatment. In Latin America, this is strategy is used by 50% of countries and 80% in developed countries [1]. One of the main problems of sanitary landfills is the production of leachate, which is considered the residual liquid generated by the biological decomposition of the organic part or biodegradable of solid waste under aerobic and anaerobic conditions and/or as a result of water percolation through waste in the degradation process. The leachate has high variability in its composition and quantity and also contains recalcitrant substances, such as humic and fluvic acids, xenobiotics, pesticides, heavy metals and inorganic salts [2]. Many of these pollutants are present in high concentrations, thus the leachate is classified as one of the most complex and difficult substances to treat as it requires rigorous management and control. In addition, it depends on the age of the landfill, climatic conditions, soil properties, type and composition of waste [3]. The discharge of leachate into the environment without a suitable treatment can generate serious environmental problems, since it can percolate through soils, causing contamination of surface and groundwater resources [4]. Therefore, it is very important to pretreatment of leachate before discharge to the environment. Leachate can be subjected to biological treatments (anaerobic and/or aerobic degradation), physicochemical treatment (coagulation/flocculation, reverse osmosis, adsorption with activated carbon, advanced oxidation processes (POA)) and different combinations of these processes [5–12].

The sanitary landfill located in the Atlantico department, Colombia, is classified as an intermediate sanitary landfill. The leachate presents high levels of recalcitrant organic matter and a relation between biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) less than 0.1, indicating low biodegradability. This limits the application of biological processes and implies that the leachate must be treated with physicochemical processes or a combination of technologies [5]. Currently, the treatment of this leachate involves a process of coagulation using poly-aluminum chloride (PAC) coagulant with a low efficiency of removal of organic matter ($\leq$20%). Therefore, the combination of coagulation and solar photo-Fenton processes for treatment of leachate is necessary, first to reduce the suspended solids and turbidity of the leachate and second to take advantage of solar radiation, using it as a renewable resource to reduce the operative costs and to degrade recalcitrant organic pollutants by the action of hydroxyl radicals (HO•) and other reactive oxygen species [13–15]. The compound parabolic collector (CPC) can efficiently use diffuse and incident solar radiation [16].

In the literature, studies related to the treatment of landfill leachate by integrating coagulation/ flocculation processes with solar photo Fenton were found [13,15,16]. The results were promising for the removal of organic matter in landfill leachate. Taking into account the fact that each leachate is unique due to its characteristics and conditions, it is necessary to evaluate these treatments and find the best alternative for each case. In the case of the sanitary landfill located in the Atlantico department-Colombia, an inefficient coagulation process is currently used to reduce COD. Therefore, choosing the best treatment strategy considering two possibilities and finding the optimal operational conditions to improve the biodegradability of the leachate is necessary. Since some important parameters affect the efficiency in coagulation processes and solar photo Fenton, it is necessary to optimize these operating conditions to reduce the consumption of reagents and consequently operating costs. Statistical analysis allows to experimental design to evaluate the effects of various factors and their interaction, with the aim to establish optimal operating conditions with a limited number of experiments. The objectives of this study were: (1) Optimize treatment 1: coagulation/sedimentation using PAC followed by solar photo-Fenton process for landfill leachate using central-composite experimental design, (2) Optimize treatment 2: coagulation/sedimentation using $FeCl_3{\cdot}6H_2O$ followed by ferrioxalate-induced solar photo-Fenton process for landfill leachate using central-composite experimental, (3) Compare treatments 1 and 2 with the treatment carried out in the sanitary landfill located in the Atlantico department-Colombia, in terms of efficiency and costs.

2. Materials and Methods

2.1. Landfill Leachate

The leachate was obtained from the municipal sanitary landfill located in Tubará city (Atlantico, Colombia), the location of which can be seen in Figure 1. According to the physicochemical properties of leachate, it can be classified as stabilized (Table 1).

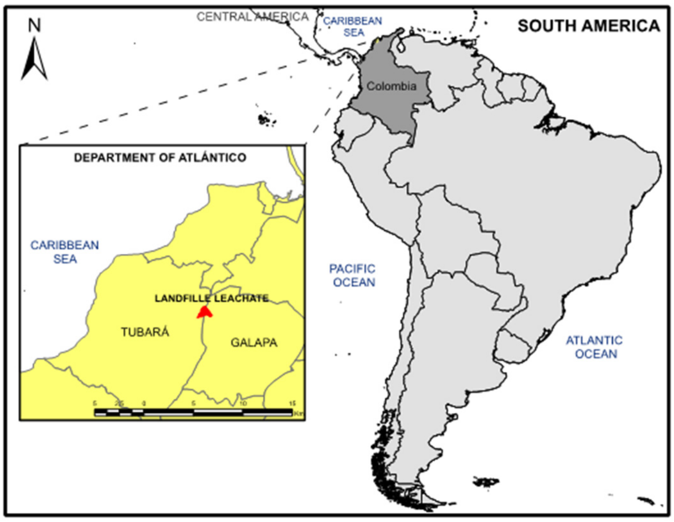

Figure 1. Ubication of the municipal sanitary landfill.

Table 1. Physicochemical properties of landfill leachate.

Parameter	Value
Temperature (°C)	30
pH	8.3
Conductivity (mS cm^{-1})	23.8
Dissolved oxygen (mg L^{-1})	1.7
Turbidity (NTU)	354
Salinity (ppt)	13.5
Total dissolved solids (g L^{-1})	15.5
BOD_5 (mg O_2 L^{-1})	426
COD (mg O_2 L^{-1})	6200
BOD_5/COD	0.07
Al (mg L^{-1})	1595
Cr (mg L^{-1})	0.52
Fe (mg L^{-1})	11.4
Cu (mg L^{-1})	<0.02
Pb (mg L^{-1})	<0.10
Cd (mg L^{-1})	<0.02
Na (mg L^{-1})	3243
Ca (mg L^{-1})	95.9
Mg (mg L^{-1})	201.8

2.2. *Reagents and Materials*

Analytical grade reagents were used as received without further purification. Ferric chloride ($FeCl_3 \cdot 6H_2O$, Merck KGaA, Darmstadt, Germany, 99.0–102.0%) and poly-aluminum chloride (PAC, $Al_n(OH)_mCl_{3n\text{-}m}$, Productos Químicos Panamericana, Medellín, Colombia, 70%) were used as coagulants. Sulfuric acid (H_2SO_4, Merck KGaA, Darmstadt, Germany, 95–97%) was used to the pH adjustment. Iron sulfate ($FeSO_4 \cdot 7H_2O$, Merck KGaA, Darmstadt, Germany, 99.5–102.0%) and hydrogen peroxide (H_2O_2, Merck KGaA, Darmstadt, Germany, 30%) were used as Fenton reagents. Oxalic acid di-hydrate ($C_2H_2O_4 \cdot 2H_2O$, Merck KGaA, Darmstadt, Germany, 99.5–102.0%) was used to form ferrioxalate complexes.

2.3. *Analytic Measurements*

Measurements of temperature, pH, conductivity, dissolved oxygen, salinity and total dissolved solids were performed using a multiparameter analyzer (556 MPS, YSI, Yellow springs, USA, Accuracy

± 2%). Turbidity was measured using a portable turbidity meter (2100 Q, Hach Company, Loveland, USA, Accuracy ± 2%). Biology Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were determined according to APHA Standard Methods (5210 D. Respirometric Method and 5220 D. Closed Reflux, Colorimetric Method) [17]. A thermo-reactor (ECO 25, VELP Scientifica, Usmate Velate, Italy, Accuracy ± 1 °C) and a UV-VIS spectrophometer (Genesys 10 S, Thermo Fisher Scientific, Waltham, USA, Accuracy < 2%) at a wavelength of 600 nm were used to determine COD. Metal ions concentrations (Al, Cr, Fe, Cu, Pb, Cd, Na, Ca and Mg) were obtained after a previous digestion of the landfill leachate, according to EPA Methods [18], by inductively coupled plasma atomic emission spectroscopy (ICAP 7200 DUO, Thermo Fisher Scientific, Waltham, USA, Accuracy < 2%).

2.4. Combination of Treatments

Two different combinations of processes were performed: (i) Treatment 1: coagulation/sedimentation using PAC followed by solar photo-Fenton process and (ii) Treatment 2: coagulation/sedimentation using $FeCl_3{\cdot}6H_2O$ followed by ferrioxalate-induced solar photo-Fenton process, to evaluate the efficiency of removal organic matter, carried out in a lab-scale photoreactor.

2.5. Experiment Design

A two-levels factorial design (2^3) was used for the coagulation/sedimentation process, which consisted of three factors, each at two levels [19]. Sixteen experiments were performed, including duplicates. The factors were coagulant dose, pH and slow mixing time. The levels maximum (+1) and minimum (−1). The response factor was percentage reduction of COD.

A central-composite experimental design (CCED) was used for the solar photo-Fenton process, performing 32 experiments including duplicates. Three series of experiments were developed: (i) A two-levels factorial design (2^k), with three factors (k), each at two levels (+1 and −1), resulting in 8 experiments; (ii) axial points (coded values $\alpha = 2^{k/4} = \pm 1.6817$, where k corresponds to three factors), resulting in 6 experiments (2k); and (iii) replicates of the central point (2 experiments). The factors were concentrations of H_2O_2, concentrations of Fe^{2+} and accumulated UV energy. The response factor was percentage reduction of COD.

A CCED was used for the ferrioxalate-induced solar photo-Fenton process, performing 40 experiments including duplicates. Three series of experiments were developed: (i) A two-levels factorial design (2^k), with three factors (k), each at two levels (+1 and −1), resulting in 8 experiments; (ii) axial points (coded values $\alpha = 2^{k/4} = \pm 1.6817$, where k corresponds to three factors), resulting in 6 experiments (2k); and (iii) replicates of the central point (6 experiments). The variables were concentrations of H_2O_2, $[Fe^{2+}]/[C_2H_2O_4]$ and pH. The response factor was the percentage reduction of COD.

The experimental designs, analysis of variance (ANOVA), mathematical modeling and optimization were carried out with Statgraphics Centurion XVI software (StatPoint Technologies, Inc., The Plains, USA) [20]. Second-order polynomial models were created to optimize the factors studied, resulting in a maximum value of response factor in the different processes evaluated, according to the Equation (1) [19].

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{1}$$

In which Y is the response factor, X_i and X_j are the coded levels of the studied factors, k is the number of studied factors, β_0 is a constant coefficient while β_i, β_{ij}, β_{ii} are coefficients of linear, interaction and quadratic term, respectively and ε the experimental error.

2.6. Coagulation/Sedimentation Experiments

The coagulation/sedimentation experiments were performed with PAC and $FeCl_3{\cdot}6H_2O$ coagulants. Ferric chloride was selected as an alternative coagulant due to its capacity to reduced substantially

COD from leachate [21]. Preliminary experiments were conducted based on the same reagent (PAC) and doses used in the landfill to choose the PAC dose range and based on the literature reported to choose the $FeCl_3{\cdot}6H_2O$ dose range [3,5,13,14,21]. The pH range was selected based on the best performance of the coagulants and close to the pH of raw landfill leachate, in order to reduce operating costs by pH adjustment. A jar test equipment (JLT-6, VELP Scientifica, Usmate Velate, Italy) was used with capacity for 6 beakers of 2 L each. To 1 L of leachate was added predetermined coagulant dose (PAC, 0.615–0.984 g L^{-1} and $FeCl_3{\cdot}6H_2O$, 1.5–2.5 g L^{-1}) and pH was adjusted (6–8). The rapid mixing conditions for experiment was 2 min at 300 rpm, followed by a slow mixing conditions (40 rpm) during predetermined time (20–30 min). The sedimentation time was 30 min. The supernatant was withdrawn from the beaker and COD was measured.

2.7. Lab-Scale Photoreactor

A compound parabolic collector (CPC) was used as a photoreactor to perform the experiments. The CPC consists of three polymethyl methacrylate tubes (length 40 cm, internal diameter 25 mm and thickness 3 mm) connected in series and exposed to an anodized aluminum reflecting surface, with an inclination of 10.9° corresponding to the local latitude and exposed surface area 0.36 m^2. The photoreactor has a recirculation tank of 2 L and a recirculation pumps with a flow rate of 18 L min^{-1}. The total radiation accumulated in the photo-reactor was measured using a digital radiometer (UV513 AB, General Tools & Instruments, New York, EE. UU., Accuracy ± 4%) mounted in the same inclination. The amount of accumulated UV energy ($Q_{UV,n}$ kJ L^{-1}) in the time interval Δt was calculated according to Equation (2) [22].

$$Q_{UV,n} = Q_{UV,n-1} + \left[\Delta t\overline{UV}_{G,n}\frac{A_r}{V_t}\right];\ \Delta t = t_n - t_{n-1} \tag{2}$$

where, $Q_{UV,n}$ is accumulated radiation per unit volume in the range of n (kJ L^{-1}); $Q_{UV,n-1}$ is accumulated radiation per unit volume in the range of $n-1$ (kJ L^{-1}); Δt_n is elapsed time in interval n (s); $\overline{UV}_{G,n}$ is incident radiation (kW m^{-2}); A_r is exposed surface of reactor (m^2); V_t is total volume treated (L).

2.8. Solar Photo-Fenton Experiments

The solar photo-Fenton experiments were performed in a photoreactor installed at the roof of the Corporación Universidad de la Costa CUC (Barranquilla, Colombia). For the solar photo-Fenton experiments, the effluents pre-treated with PAC coagulant was added to the recirculation tank of the CPC unit, which was homogenized in the darkness and pH was adjusted to 3.0 (the photo-Fenton processes are performed efficiently at acidic conditions, prevented iron and other metallic ions from precipitating as insoluble species) [23]. The pre-determined concentrations of $FeSO_4{\cdot}7H_2O$ and H_2O_2 were added and the amount of accumulated radiation UV energy was established according to the time intervals of solar exposure (Equation (2)). Finally, the sample was taken for analyses of COD. For the ferrioxalate-induced solar photo-Fenton experiments, the effluents pre-treated with $FeCl_3{\cdot}6H_2O$ coagulant was added to the recirculation tank of the CPC unit, the mixture was homogenized by recirculation in the darkness and the pH was adjusted to the predetermined values. The ferrioxalate complex was prepared as literature reported [24,25]. The amount of H_2O_2 was added to the photoreactor after the addition of the Fe^{2+} and $C_2H_2O_4{\cdot}2H_2O$ until reach the concentration established for each substance. The final solution was exposed to the accumulated UV energy of 167 kJ L^{-1}, then the sample was taken and the COD was analyzed.

3. Results and Discussion

3.1. Coagulation/Sedimentation Experiments

Landfill leachate has a COD higher than 5000 mg L^{-1} and a BOD_5/COD ratio less than 0.10 (Table 1). This indicates the presence of persistent organic compounds and non-biodegradable substances. Therefore, effective treatment is required, such as combined physicochemical treatments, excluding biological [26]. A coagulation/sedimentation process as a first step in the leachate treatment was applied. The effect of some factors such as coagulant dose, pH and slow mixing time on the efficiency of the removal of organic matter for coagulation/sedimentation process were evaluated. Table 2 presents complete experimental design of coagulation/sedimentation experiments using PAC and $FeCl_3{\cdot}6H_2O$ coagulant and COD reduction results obtained in this study.

Table 2. Effect of coagulant dose, pH, slow mixing time when it is applied to raw landfill leachate. Factorial design 2^3 matrix of coagulation/sedimentation experiments. Results in % COD reduction.

pH	Slow Mixing Time (min)	PAC (g L^{-1})		$FeCl_3{\cdot}6H_2O$ (g L^{-1})	
		0.615	**0.984**	**1.5**	**2.5**
8	20	**36.1**	21.9	29.6	25.9
8	30	34.6	35.8	32.6	21.4
6	20	28.9	29.0	40.8	62.4
6	30	34.8	29.4	41.7	**65.0**

Average values in experiments.

The significant main and interaction effects of factors that influences the COD reduction was determined with ANOVA. Table 3 presents a summary of ANOVA results for coagulation/sedimentation experiments with PAC coagulant. The most significant factors for COD reduction in order of importance were slow mixing time (C) and coagulant dose (A), according to the high calculated values of F and low values-p (<0.05). The pH resulted to be non-significant in evaluated experimental range. The self-double-effect of each factor (A^2, B^2 and C^2 terms) were not taken into account because they were non-significant.

Table 3. ANOVA results for coagulation/sedimentation experiments with PAC coagulant.

Factors	Sum of Squares	df [a]	Mean Square	F	Value-p [b]
A: PAC dose	83.08	1	83.08	5.78	0.0397
B: pH	10.76	1	10.76	0.75	0.4095
C: slow mixing time	90.25	1	90.25	6.28	0.0336
AB	13.51	1	13.51	0.94	0.3578
AC	27.30	1	27.30	1.90	0.2015
BC	10.82	1	10.82	0.75	0.4081
Pure error	129.42	9	14.38		
Total	365.14	15			

[a] Degree of freedom, [b] Considered significant when $p < 0.05$.

The Pareto diagram represents graphically the standardized effects of each factor and its interactions. The positive (+) or negative (−) effect on the response factor is given by the increase in the level of factor [27]. Figure 2 presents a Pareto diagram for coagulation/sedimentation experiments with PAC coagulant. The coagulant dose and slow mixing time were the factors with the highest effect over the COD reduction. The coagulant dose presented negative sign, it indicates that the highest COD reduction was obtained at the lowest levels of this factor. The coagulant PAC at low doses can neutralize the surface charge of the particles and allow aggregation but at high doses the effectiveness of the process is reduced [12]. The increase of coagulant beyond a certain concentration could re-stabilize colloidal particles, forming smaller and weaker floccules through adsorption and bridging due to additional PAC [14]. The slow mixing time presented positive sign, it indicates that the highest COD reduction was obtained at the highest levels of this factor, this depends on the characteristics of the leachate, being this complex in its components [28]. The best conditions for COD reduction were obtained. COD reduction of 36.1% were obtained with pH 8, 0.615 g L^{-1} of PAC and 20 min of slow mixing, similar to the reported results reported with removal rates of between 25% and 38% [28].

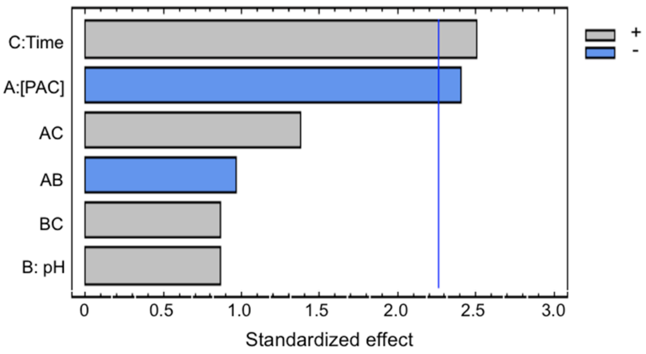

Figure 2. Pareto diagram of coagulation/sedimentation experiments with PAC coagulant.

Table 4 presents a summary of ANOVA results for coagulation/sedimentation experiments with $FeCl_3{\cdot}6H_2O$ coagulant. The most significant factors for COD reduction in order of importance were pH (A) and the interaction pH-$FeCl_3$ dose (AB), according to the high calculated values of F and low values-*p* (<0.05). The slow mixing time resulted to be non-significant in evaluated experimental range. The self-double-effect of each factor (A^2, B^2 and C^2 terms) were not taken into account because they were non-significant.

Table 4. ANOVA results for coagulation/sedimentation experiment with $FeCl_3{\cdot}6H_2O$ coagulant.

Factors	Sum of Squares	df [a]	Mean Square	F	Value-*p* [b]
A: pH	2514.52	1	2514.52	37.07	0.0003
B: $FeCl_3$ dose	224.25	1	224.25	3.31	0.1065
C: slow mixing time	169.26	1	169.26	2.50	0.1528
AB	896.40	1	896.40	13.22	0.0066
AC	204.76	1	204.76	0.30	0.5977
BC	286.46	1	286.46	4.22	0.0739
Pure error	542.64	8	678.31		
Total	4655.04	15			

[a] Degree of freedom, [b] Considered significant when $p < 0.05$.

Figure 3 presents a Pareto diagram for coagulation/sedimentation experiments with $FeCl_3{\cdot}6H_2O$ coagulant. The pH and the interaction pH-$FeCl_3$ dose were the factors with the highest effect over the COD reduction. Both factors presented negative sign, it indicates that the highest COD reduction was obtained at the lowest levels of these factors. The negative effect of pH influenced COD reduction, due to the nature of the leachate, which does not allow for the solubility of iron ions. At pH value > 8 the species $Fe(OH)^{4-}$ appear, the efficiency to precipitate of which is null according to the coagulation diagrams for $FeCl_3$, however at pH < 6, appear species such as Fe^{3+}, $Fe_2(OH)^{2+}$, $FeOH^{2+}$, which promote the restabilization of colloidal particles [6].

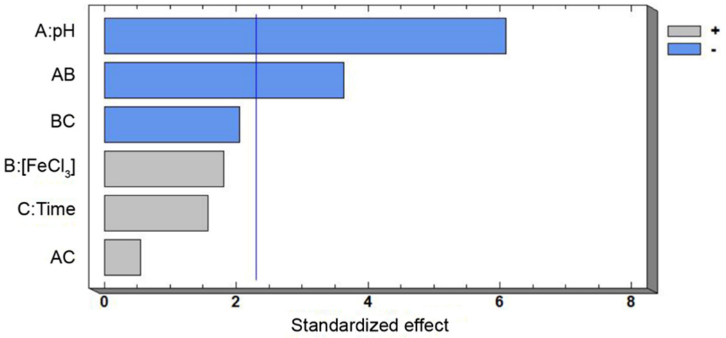

Figure 3. Pareto diagram of coagulation/sedimentation experiments with $FeCl_3{\cdot}6H_2O$ coagulant.

The conditions of greater COD reduction using $FeCl_3{\cdot}6H_2O$ coagulant were pH 6, 2.5 g L^{-1} of $FeCl_3{\cdot}6H_2O$ and 30 min of slow mixing, COD reduction of 65.0 % were obtained. These results were consistent with other studies in which $FeCl_3{\cdot}6H_2O$ showed a higher removal efficiency of organic matter compared with the PAC [2]. Moradi and Ghanbari [5] reported similar data for the treatment of leachate with $FeCl_3{\cdot}6H_2O$, finding COD removal of 65.0 %. Liu and co-workers [13] reported optimal results at pH close to 6 and dose of 10 g L^{-1} of $FeCl_3{\cdot}6H_2O$ with COD reduction of 68.7 %, finding that the initial pH and the coagulant dose play an important role. They also point out that it is viable to use coagulation processes for the pre-treatment of leachates. The predominant coagulation mechanisms are charge neutralization, in which the charged hydrolysis species of coagulant can adsorb into the surface of the colloidal particle and destabilize it; and sweep-floc coagulation, the presence of precipitate of ferric hydroxide can physically sweep the colloidal particles from the suspension [29]. When increasing the dose of $FeCl_3{\cdot}6H_2O$, the elimination of COD increases maintaining the pH in 6, as reported by Long and co-workers [30]. This indicates that $FeCl_3{\cdot}6H_2O$ presents greater COD removal with pH values close to neutrality. On the contrary, with pH values that oscillate between 8 or more, the COD removal is less, because the Fe^{3+} cations allow the colloidal particles to be positively charged, stabilizing the colloids [31].

With the optimal conditions determined in this study, 36.1 % and 65.0 % COD reduction were obtained using PAC and $FeCl_3{\cdot}6H_2O$ coagulants, respectively. Comparing these results, the $FeCl_3{\cdot}6H_2O$ presents higher COD reduction with respect to the PAC, this is a great advantage to use $FeCl_3{\cdot}6H_2O$, however it is extremely corrosive and presents higher costs. On the other hand, comparing the results with the conditions obtained with PAC coagulant in this study (pH 8, 0.615 g L^{-1} of PAC and 20 min of slow mixing, final COD of 3968 mg O_2 L^{-1}) and the conditions used in the sanitary landfill (pH 8.0, 1.5 g L^{-1} of PAC and 30 min of slow mixing, final COD of 4960 mg O_2 L^{-1}), an increase of 80% was obtained in the removal of organic matter and the consumption of coagulant was reduced to 59%, maintaining the initial pH of the leachate, therefore, operating costs decrease in this process.

3.2. Solar Photo-Fenton Experiments with PAC Coagulant Pre-Treated

The leachate treated with PAC coagulant increased the removal of organic matter (final COD of 3968 mg O_2 L^{-1}) compared to the process used in the landfill sanitary (final COD of 4960 mg O_2 L^{-1}). However, the pre-treated leachate exceeds the legal limit of discharge into natural water streams, according to Colombian legislation the concentration of COD for the final leachate effluent is set at < 180 mg O_2 L^{-1} [32]. Therefore, the combination with photo-oxidation processes is required. The solar photo Fenton process is considered a suitable way for the treatment of leachate. The most important variables related to the rate of removal of COD are the intensity of irradiation, concentration of H_2O_2 and Fe^{2+} in the system, pH values and the initial COD, therefore the first three variables were evaluated in this study with the aim to determine the optimal conditions and its effects on COD removal in the pre-treated leachate [23]. Central composite design (CCD) was used to optimize the three main factors in solar photo Fenton: H_2O_2 dose, Fe^{2+} dose and accumulate UV energy. According to conditions reported literature a $[H_2O_2]/[Fe^{2+}]$ ratio between 5 and 20 was used, considering that the excess of hydrogen peroxide with respect to the amount of iron added is essential to maintain the catalytic character in the chemical reaction [33]. The pH after the coagulation/sedimentation process was adjusted to a value 3 with addition of $H_2\ SO_4$ to avoid iron precipitation in the form of hydroxide, $Fe(OH)_3$ [14].

Table 5 shows the results of complete experimental design and the COD reduction of solar photo-Fenton experiments in pre-treated leachate with PAC coagulant. The highest COD reduction (56.4%) was achieved for the experiment 12, with 13.3 g L^{-1} of H_2O_2, 2.56 g L^{-1} of Fe^{2+} and 122 kJ L^{-1} of accumulated radiation. These results are very similar to characterization and detoxification of a mature landfill leachate using combined treatments of coagulation/flocculation and photo-Fenton with Fe^{2+} dose of 5.5 mg L^{-1} and H_2O_2 dose of 630 mg L^{-1}, which achieved COD reduction of 56% [14]. Similarly, combinations of treatments have been tested at landfills, obtaining in the coagulation process a COD reduction of 26% and when combined with the solar photo-Fenton process, a COD reduction of 60% was achieved with accumulated radiation of 165 kJ L^{-1} over five days [7].

Table 5. The 3-factor central composite experimental design of solar photo-Fenton experiments for leachate pre-treated with PAC coagulant. Results of % COD reduction.

Exp.	$[H_2O_2]$ (g L^{-1})	$[Fe^{2+}]$ (g L^{-1})	Q_{uv} (kJ L^{-1})	% COD Reduction [a]
1	11.7	0.78	78	47.7
2	14.9	0.78	78	42.1
3	11.7	2.34	78	47.7
4	14.9	2.34	78	54.9
5	11.7	0.78	167	34.4
6	14.9	0.78	167	36.9
7	11.7	2.34	167	43.0
8	14.9	2.34	167	47.1
9	11.2	1.56	122	27.8
10	15.4	1.56	122	34.9
11	13.3	0.56	122	44.7
12	13.3	2.56	122	56.4
13	13.3	1.56	48	46.2
14	13.3	1.56	197	42.0
15	13.3	1.56	122	30.0
16	13.3	1.56	122	32.7

[a] Average values in experiments.

The results of the ANOVA are presented in the Table 6. The factors in order of significance and contribution were: quadratic B, concentration of Fe^{2+} (B), quadratic C, accumulated UV energy (C) and quadratic A. All the terms have a p value lower than 0.05 and a high F value.

Table 6. ANOVA results for solar photo-Fenton experiments experiment with leachate pre-treated with PAC coagulant.

Factors	Sum of Squares	Df [a]	Mean Square	F	Value-*p* [b]
A: $[H_2O_2]$	52.94	1	52.94	4.06	0.0569
B: $[Fe^{2+}]$	386.88	1	386.88	29.67	0.0000
C: Q_{uv}	233.59	1	233.59	17.92	0.0004
AA	83.11	1	83.11	6.37	0.0197
AB	52.09	1	52.09	4.00	0.0587
AC	5.84	1	5.84	0.45	0.5105
BB	860.47	1	860.47	66.00	0.0000
BC	9.20	1	9.20	0.71	0.4105
CC	272.04	1	272.04	20.86	0.0002
Pure error	273.80	21	13.04		
Total	2230.46	31			

[a] Degree of freedom, [b] Considered significant when $p < 0.05$.

The quality of the fitted model was evaluated based on the determination coefficients, R^2 and R^2_{adj}. The high values of R^2 (93.87%) and R^2_{adj} (84.67%) indicate that Equation (3) present a satisfactory correlation between the model and observed results. Similarity the Figure 4 demonstrated the concordance between the observed values and the values obtained with the adjusted model.

$$\begin{gathered} Y = 24.82 + 14.41\ X_1 - 67.70\ X_2 - 0.68\ X_3 - 0.63\ X_1^2 + 1.44\ X_1\ X_2 + 0.0088\ X_1\ X_3 \\ + 16.39\ X_2^2 + 0.022\ X_2\ X_3 + 0.0019\ X_3^2 \end{gathered} \tag{3}$$

where, Y is COD reduction, X_1 is H_2O_2 dose, X_2 is Fe^{2+} dose and X_3 is accumulate UV energy.

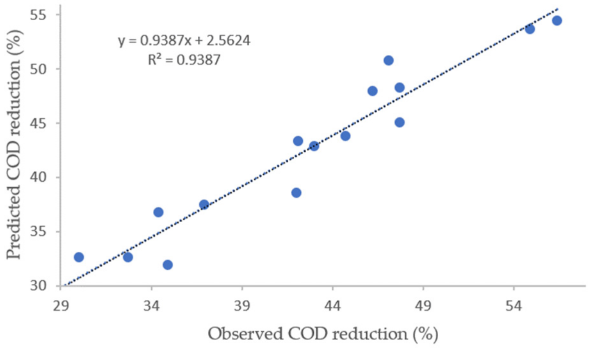

Figure 4. Observed vs Predicted value plot for COD reduction for solar photo-Fenton experiments in pre-treated leachate with PAC coagulant.

Figure 5 shows the optimization of the operation conditions of solar photo-Fenton experiments in pre-treated leachate with PAC coagulant. The COD reduction predicted obtained in the optimization was 65% with 14.68 g L^{-1} of H_2O_2, 2.56 g L^{-1} of Fe^{2+} and 48 kJ L^{-1} of accumulated UV energy. The results show that a higher addition of iron doses and accumulated solar radiation promotes the formation of oxidant species to reduce COD [34–36].

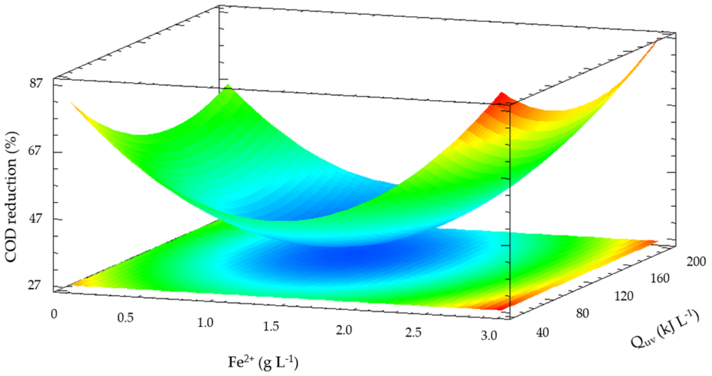

Figure 5. Response surface plot for interactive effect of Fe^{2+} dose and accumulate UV energy on COD reduction for solar photo-Fenton experiments in pre-treated leachate with PAC coagulant. H_2O_2 dose = 14.68 g L^{-1}.

3.3. Ferrioxalate-Induced Solar Photo-Fenton Process with $FeCl_3$ Coagulant Pre-Treated

In this case, the efficiency of COD reduction of ferrioxalate-induced solar photo-Fenton process in pre-treated leachate with $FeCl_3$ coagulant was evaluated. The H_2O_2 dose is determined from the COD of the pre-treated leachate, which was calculated based on the stoichiometric ratio COD:H_2O_2 proposed by Kim and co-workers [37], where 1 g of COD = 2.125 g of H_2O_2. The dose of Fe^{2+} supplied from ferrous sulfate heptahydrate granular ($FeSO_4{\cdot}7H_2O$), was obtained from the ratio H_2O_2: Fe^{2+}, for each 5 a 10 g of H_2O_2 is added 1 g of Fe^{2+} and the doses of oxalic acid resulted from the ratio 1 g of Fe^{2+} per 3 g of $H_2C_2O_4$ [37]. The pH was adjusted with sulfuric acid to 97 % purity according to the predetermined. The experiments were carried out at 167 kJ L^{-1} of accumulated UV energy.

The results of COD reduction and complete experimental design of ferrioxalate-induced solar photo-Fenton experiments with a $FeCl_3$ coagulant pre-treatment are shown in Table 7. The highest reduction of COD (27.2%) was achieved for Exp. 4, with 10.8 g L^{-1} of H_2O_2, 1.97 g L^{-1} of Fe^{2+}, 5.91 g L^{-1} of $H_2C_2O_4$ and pH 4.0.

Table 7. The 3-factor central composite experimental design of solar photo-Fenton experiments for leachate pre-treated with $FeCl_3$ coagulant. Results of % COD reduction.

Exp.	$[H_2O_2]$ (g L^{-1})	$[Fe^{2+}]/[C_2H_2O_4]$ (g L^{-1})	pH	% COD Reduction [a]
1	4.2	0.77/2.32	4.0	11.3
2	10.8	0.77/2.32	4.0	21.2
3	4.2	1.97/5.91	4.0	24.9
4	10.8	1.97/5.91	4.0	27.2
5	4.2	0.77/2.32	6.0	10.4
6	10.8	0.77/2.32	6.0	7.2
7	4.2	1.97/5.91	6.0	4.6
8	10.8	1.97/5.91	6.0	16.5
9	1.95	0.26/0.78	5.0	4.3
10	13.0	0.26/0.78	5.0	9.2
11	7.5	1.30/3.90	5.0	25.6
12	7.5	2.40/7.20	5.0	22.4
13	7.5	0.26/0.78	3.3	24.9
14	7.5	0.26/0.78	6.6	12.5
15	7.5	0.26/0.78	5.0	10.6
16	7.5	0.26/0.78	5.0	11.3
17	7.5	0.26/0.78	5.0	10.6
18	7.5	0.26/0.78	5.0	16.0
19	7.5	0.26/0.78	5.0	13.1
20	7.5	0.26/0.78	5.0	15.1

[a] Average values in experiments.

The ANOVA results show that some factors, except the interactions AC ($[H_2O_2]$-pH) and BC ($[Fe^{2+}]/[C_2H_2O_4]$-pH), are statistically significant (Table 8). The factors in order of importance and contribution were: pH (C), quadratic B, $[Fe^{2+}]/[C_2H_2O_4]$ (B), quadratic C, quadratic A, concentration of H_2O_2 (A) and interaction AB ($[H_2O_2]-[Fe^{2+}]/[C_2H_2O_4]$). All them terms have a p value lower than 0.05 and high F value.

Table 8. ANOVA results for ferrioxalate-induced solar photo-Fenton experiments with leachate pre-treated with $FeCl_3 \cdot 6H_2O$ coagulant.

Factors	Sum of Squares	df [a]	Mean Square	F	Value-*p* [b]
A: $[H_2O_2]$	164.17	1	164.17	12.85	0.0012
B: $[Fe^{2+}]/[C_2H_2O_4]$	203.27	1	203.27	15.91	0.0004
C: pH	584.97	1	584.97	45.80	0.0000
AA	170.03	1	170.03	13.31	0.0010
AB	75.65	1	75.65	5.92	0.0213
AC	3.51	1	3.51	0.27	0.6043
BB	478.98	1	478.98	37.50	0.0000
BC	41.31	1	41.31	3.23	0.0825
CC	180.86	1	180.86	14.16	0.0008
Pure error	370.42	29	12.77		
Total	2352.24	39			

[a] Degree of freedom, [b] Considered significant when $p < 0.05$.

The quality of the fitted model was evaluated based on the determination coefficients, R^2 and R^2_{adj}. The high values of R^2 (83.0%) and R^2_{adj} (77.6%) indicate that Equation (4) present a correlation between the model and observed results. Similarity the Figure 6 demonstrated the concordance between the observed values and the values obtained with the adjusted model.

$$Y = 58.65 - 17.48\,X_1 + 3.98\,X_2 - 12.72\,X_3 + 1.82\,X_1^2 - 0.13\,X_1\,X_2 - 3.35\,X_1\,X_3 - 0.22\,X_2^2 + 0.47\,X_2\,X_3 + 10.26\,X_3^2 \quad (4)$$

where, Y is COD reduction, X_1 is pH, X_2 is H_2O_2 dose and X_3 is Fe^{2+} dose.

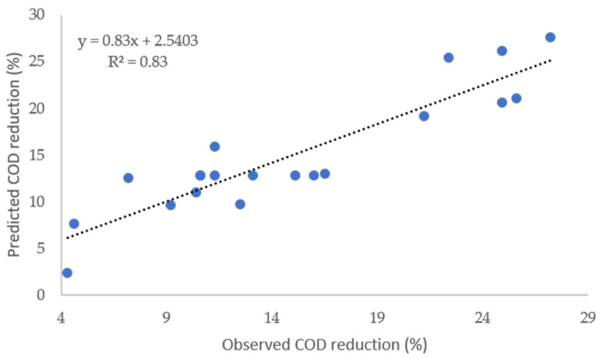

Figure 6. Observed vs Predicted value plot for COD reduction for ferrioxalate-induced solar photo-Fenton experiments in pre-treated leachate with $FeCl_3{\cdot}6H_2O$ coagulant.

Figure 7 shows the optimization of the operation conditions of ferrioxalate-induced solar photo-Fenton experiments in pre-treated leachate with $FeCl_3{\cdot}6H_2O$ coagulant. The COD reduction predicted obtained in the optimization was 37% with 8.95 g L^{-1} of H_2O_2, 1.60 g L^{-1} of Fe^{2+}, 4.8 g L^{-1} of $C_2H_2O_4$ and pH 4.0. The results show that a higher addition of iron doses and H_2O_2 doses promotes the formation of oxidant species to reduce COD. This indicates that with sufficient doses of hydrogen peroxide and $Fe^{2+}/C_2H_2O_4$ to photocatalytic system, the mineralization of pollutants increases, due to the continuous regeneration of Fe (II) from the photo-reduction of Fe (III) by solar light and the generation of additional free radicals (mainly OH•) due to ferrioxalate photochemistry [38–40]. Reducing the pH and increasing the amount of iron in the leachate increases the efficiency of the process to reduce COD, due to the generation of $Fe[(C_2O_4)_3]^{3-}$, similar results were reported by Estrada-Arriaga and co-workers [25]. Low concentrations of Fe^{2+} and H_2O_2 generate a decrease in the removal of organic matter, because it decreases the generation of HO• radicals according to Equations (5) and (6) [41].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO + OH^- \quad (5)$$

$$Fe^{2+} + 3C_2O_4^- + H_2O_2 \rightarrow Fe\,[(C_2O_4)_3]^{3-} + HO\bullet + OH^- \quad (6)$$

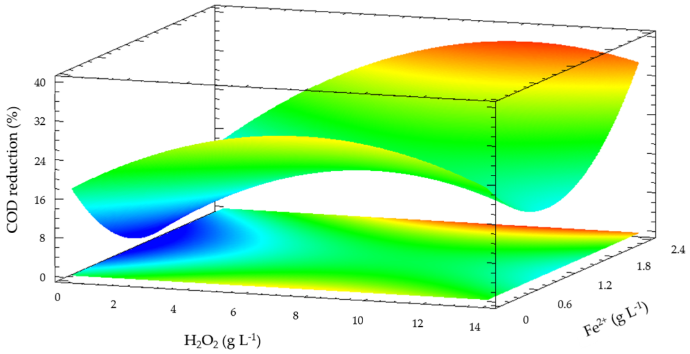

Figure 7. Response surface plot for interactive effect of H_2O_2 dose and Fe^{2+} dose on COD reduction for ferrioxalate-induced solar photo-Fenton experiments in pre-treated leachate with $FeCl_3{\cdot}6H_2O$ coagulant. pH = 4.

3.4. Treatment of Leachate under Optimized Conditions

A preliminary study of the costs per cubic meter of leachate treatment with coagulation followed by solar photo-Fenton process was carried out, in order to compare the costs of the combined treatment and the treatment used in the sanitary landfill located in the Atlantico department, Colombia. The coagulation process is the only treatment used in the treatment of leachates from this sanitary landfill with a removal of organic matter not greater than 20%. Currently, the operational conditions used in the sanitary landfill are 1.5 g L^{-1} of PAC, pH 8.0, fast mixing of 300 rpm for 2 min and slow mixing of 40 rpm for 30 min, for a total unitary cost of 2.60 €/m^3 [42].

(i) Treatment 1: coagulation/sedimentation using PAC followed by solar photo-Fenton process. The treated leachate with the optimal operational conditions of each of the processes (Sections 3.1 and 3.2) obtained a 73% reduction of COD (COD final 1674 mg L^{-1}, 0.615 g L^{-1} of PAC) with a total unitary cost of 3.00 €/m^3. By comparing these results, optimized treatment 1 allowed to substantially improve the reduction of COD in the leachate landfill, with only an increase of 13.3% in the total unitary cost. In addition, the use of the PAC coagulant was reduced by 59%.

(ii) Treatment 2: coagulation/sedimentation using $FeCl_3{\cdot}6H_2O$ followed by ferrioxalate-induced solar photo-Fenton process. The treated leachate with the optimal operational conditions of each of the processes (Sections 3.1 and 3.3) obtained a 80% reduction of COD (COD final 1240 mg L^{-1}, 2.5 g L^{-1} of $FeCl_3{\cdot}6H_2O$) with a total unitary cost of 4.30 €/m^3. By comparing these results, optimized treatment 2 allowed to substantially improve the reduction of COD in the leachate landfill, with only an increase of 39.5% in the total unitary cost.

Treatments 1 and 2 increased the removal of organic matter (final COD of 1674 mg O_2 L^{-1} and 1240 mg O_2 L^{-1}, respectively) compared to the process used in the landfill sanitary (final COD of 4960 mg O_2 L^{-1}). Under these conditions, the effluent obtained with the alternative treatments presents high values of COD, therefore it cannot be discharged into natural water streams, to Colombian legislation the concentration of COD for the final leachate effluent is set at $<$ 180 mg O_2 L^{-1} [32]. However, the effluent improves enough to be released into public wastewater where the COD legal limit is 2000 mg O_2 L^{-1} [32].

This means that in terms of costs, treatment 1 would be the most competitive to implement in the landfill. However, the PAC coagulant has the disadvantage that the aluminum contents present in the final effluent ($Al_{inicial}$ 1595 mg L^{-1} and Al_{final} 2485 mg L^{-1}) may require an additional process for their removal. Also, in the Caribbean region of Colombia where the sanitary landfill is located and treatment 1 would be implemented, it has a great potential for the use of photo treatment with UV energy, because the climate is tropical dry, it is hot all-year-round, therefore a renewable and sustainable source would take the maximum advantage.

4. Conclusions

Two alternative combined treatments were assessed for reduction of COD in leachate from the sanitary landfill located in Atlantico-Colombia. At the sanitary landfill located in Atlántico-Colombia, coagulation with PAC is currently used, obtaining a 20% reduction of COD (final COD of 4960 mg O_2 L^{-1}). Under these conditions, the effluent from the treated leachate cannot be discharged into public wastewater (COD legal limit is 2000 mg O_2 L^{-1}).

In optimum conditions for Treatment 1 (coagulation/sedimentation using PAC followed by solar photo-Fenton process) and Treatment 2 (coagulation with $FeCl_3{\cdot}6H_2O$ followed by ferrioxalate-induced solar photo-Fenton process), COD was reduced by 73% and 80%, respectively (final COD of 1674 mg O_2 L^{-1} and 1240 mg O_2 L^{-1}, respectively). Under these conditions, the effluent from the treated leachate can be discharged into public wastewater.

The combined treatments could be a promising alternative for the reduction of COD in landfill leachate, particularly Treatment 1 with an increase of 13.3% in total unitary cost and a PAC coagulant reduction of 59%. In addition, the potential of solar radiation as a sustainable and renewable energy resource could be exploited.

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