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REMEDIATION

WASTEWATER TREATMENT OF INDUSTRIAL LOADS WITH ADVANCED OXIDATION IN CONVENTIONAL SYSTEMS

TRATAMIENTO DE AGUAS RESIDUALES DE CARGAS INDUSTRIALES CON OXIDACIÓN AVANZADA EN SISTEMAS CONVENCIONALES

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Abstract

In the rural regions of Latin America, wastewater treatment systems are based on conventional technologies such as the septic tanks. These treatment systems do not support biodegradability indexes lower than 0,4 measured in the form of BOD_5/COD, values obtained when refractory contaminants are found in water; which in turn are associated in most cases with the intrusion of industrial wastewater. In these cases, the conventional treatment systems do not meet the regulations for which they were designed; and therefore public investment is lost to build them. This is why in the present investigation the biodegradability index of this type of effluents was increased, for which domestic wastewater mixed with leachate and industrial effluent obtained from the Chasinato creek in the Tungurahua province of Ecuador was used, in which a biodegradability index of 0,22 was obtained in BOD_5/COD. An advanced oxidation process of modified Fenton was applied to this effluent, which increased the biodegradability index and avoided reducing the pH, since in large volumes this is very expensive. The optimal concentrations of reagents were $FeSO_4/H_2O_2 = 1$ and $C_6H_8O_7/H_2O_2 = 2$; with the addition of 10 mg/L of H_2O_2, which increased the biodegradability index to a value of 0,46, which is a satisfactory value to be treated in conventional systems such as septic tanks; in addition to a reduction of BOD_5 and COD in efficiencies of 12.54 %; 44.4 % respectively.
Keywords: Advanced oxidation, modified Fenton, refractory contaminants, leachate treatment, septic tank.

Resumen

En las regiones rurales de América Latina los sistemas de tratamiento de agua residuales se basan en tecnologías convencionales como las fosas sépticas. Estos sistemas de tratamiento no soportan índices de biodegradabilidad menores a 0,4 medidos en forma de DBO_5/DQO, valores que se obtienen cuando en el agua se encuentran contaminantes refractarios; que a su vez se los asocia en la mayoría de los casos con la intromisión de agua residual industrial. En estos casos los sistemas de tratamiento convencionales no cumple las normativas para los cuales fueron diseñados; y por tanto se pierde la inversión pública para construirlos. Es por esto que en la presente investigación se elevó el índice de biodegradabilidad de este tipo de efluentes, para lo cual se usó agua residual doméstica mezclada con lixiviado y efluente industrial obtenida de la quebrada Chasinato en la provincia de Tungurahua en Ecuador, en la cual se obtuvo un índice de biodegradabilidad de 0,22 en DBO_5/DQO. A este efluente se le aplicó un proceso de oxidación avanzada de Fenton modificado, con lo cual se incrementó el índice de biodegradabilidad y se evitó reducir el pH, ya que en grandes volúmenes esto resulta muy costoso. Las concentraciones óptimas de reactivos fueron de $FeSO_4/H_2O_2$ = 1 y $C_6H_8O_7/H_2O_2$ = 2; con la colocación de 10 mg/L de H_2O_2, con lo cual se aumentó el índice de biodegradabilidad a un valor de 0,46 que es un valor satisfactorio para tratarse en sistemas convencionales como son las fosas sépticas; además de una reducción de la DBO_5 y DQO en eficiencias de 12,54 %; 44,4 % respectivamente.
Palabras claves: Oxidación avanzada, Fenton modificado, contaminantes refractarios, tratamiento de lixiviados, fosa séptica.

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1 Introduction

In the rural regions of Latin America and the Caribbean, the coverage of sewerage systems was 64% by 2015 (Lentini, 2015), with residual water being treated by 34% (UNESCO, 2017). Most of these treatment systems are conventional plants built in the final stages of sewerage systems, which are located before a discharge to bodies of water. These treatment systems are based on technologies for the removal of low pollutant load and low cost of construction and operation. The most used technology is the septic tank, generally built of concrete or plastic (Jouravlev, 2004).

Septic tanks are used as primary treatment systems (Metcalf y Eddy, 2003) that remove oils, fats and suspended solids by 50% (Méndez *et al.*, 2012), converting volatile suspended solids to fixed solids. The efficiency in the removal of biochemical oxygen demand (BOD_5), total suspended solids (TSS), and total coliforms range from less than 50% to 80% as a function of temperature (Lucho-Constantino *et al.*, 2015).

The biodegradability index is a factor influencing the efficiency of a septic tank, which must be greater than 0.4 calculated with the factor DBO_5/COD (Ortiz de Zárate y Aguila Apodaca, 1997), which is not met when wastewater has refractory pollutants , which are related to the mixing of domestic wastewater and industrial wastewater without treatment. These pollutants are increased in wastewater from rural areas by the increase in the use of chemical products in homes, domestic industry or other productive activities. Among the refractory contaminants present in domestic wastewater are pesticides, medicines, personal hygiene compounds, household waste, among others (Gil *et al.*, 2013); and when their concentrations are very high, their biodegradability indexes are reduced to levels in which the efficiencies of conventional treatment plants fail to meet discharge regulations, becoming unusable infrastructure (English, 2010).

That is why in the present investigation the increase of a stage of advanced wastewater treatment at the beginning of conventional systems with a septic tank is proposed, to increase the biodegradability of the waters and allow the subsequent treatment to treat the wastewater with the modified biodegradability index.

The advanced oxidation treatment was initially described by Glaze, Kang y Chapin (1987), based on the generation of strong oxidants such as the ·OH radicals for the degradation of soluble non-biodegradable compounds present in the wastewater. The advanced oxidation process chosen is the Fenton method, which forms ·OH radicals according to the following equation (Somich, Muldoon y Kearney, 1990; Martiínez-Huitle *et al.*, 2008):

$$Fe_{2+} + H_2O_2 \rightarrow Fe_{3+} + \cdot OH + OH^-$$

As shown, a reagent in the Fenton process is hydrogen peroxide (H_2O_2), but this by itself does not oxidize certain refractory contaminants; requiring the addition of iron salts for the formation of hydroxyl radicals ·OH. With the presence of ·OH, they will oxidize non-specific organic compounds at high speeds (Pawar y Gawande, 2015).

In a Fenton reaction the pH is controlled in a range of 3 to 5 (Pawar y Gawande, 2015), but having residual water with pH close to 7, the decrease and subsequent increase in pH would become very costly. That is why we have opted for the addition of an additional reagent, a chelator to induce the formation of a complex; and in this way produce the Fenton reaction at a neutral pH or close to this value (Isch Zambrano, 2016).

One of the most used compounds for the formation of chelates is EDTA, however, the colloids formed by this reagent are very stable, and their degradation would be complex in subsequent biological systems (Oviedo y Rodríguez, 2003). This is why citric acid will be used, which is considered as a chelating agent that can sequester iron in the presence of ammonia, in addition to having numerous applications due to its capacity to form soluble complexes (REPAMAR, 1998).

For the present investigation, as a sample of wastewater, a discharge has been chosen in the Çhasinato"stream in the Ambato canton, Tungurahua province in Ecuador, whose location is shown in Figure 1. This water discharge has low biodegradability due to that domestic wastewater in the upper levels is mixed with leachate from the sanitary landfill of the city of Ambato, wastewater from the city's Industrial Park, an animal slaughterhouse, among other residential and industrial settlements.

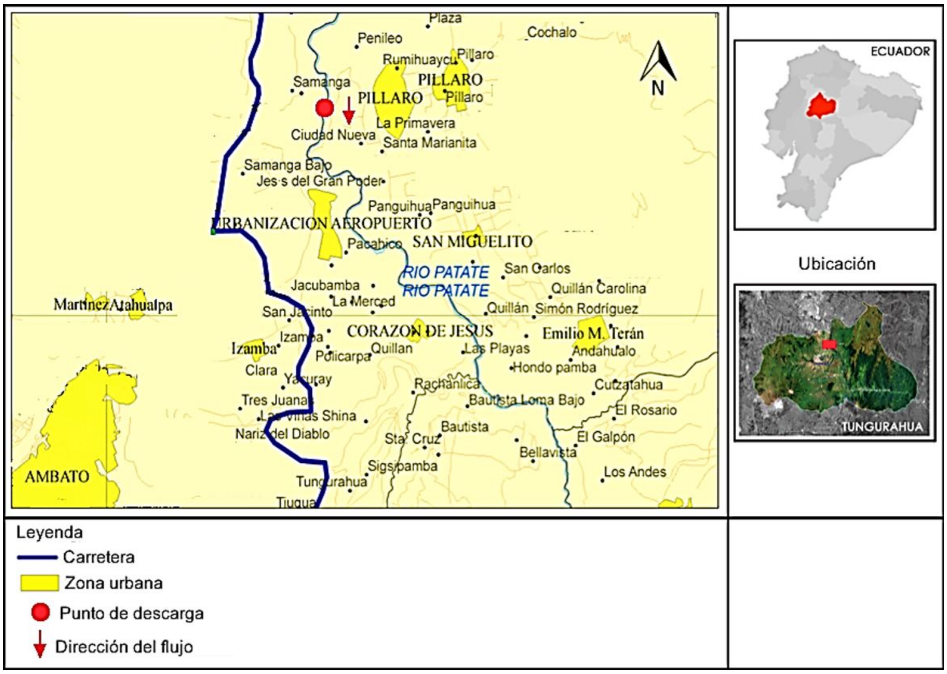

Figure 1. Location of sampling point for domestic wastewater combined with industrial water and landfill leachate. (MTOP, 2010)

Once the waste water from the body of water from which the sample was taken for the present investigation is poured into the Chasinato stream, it flows into the Cutuchi river; which downstream is used to irrigate crops in the Quillán Playas, Chiquicha, Bellavista, Los Andes, etc. areas, until reaching the Pastaza River.

2 Materials and methods

2.1 Wastewater

The samples of residual water were obtained in the Chasinato creek in March 2016; for the analysis, 40 liters of wastewater were taken in two sealed 20 liter plastic containers, transported to the laboratory to be analyzed.

2.2 Analysis protocols

The analysis protocols were carried out according to the Standard Methods (Pawlowski, 1994) for the parameters of Chemical Oxygen Demand (COD), with the technique of closed reflux and volumetry (Standard Methods 5220C), the Oxygen Biochemical Demand (BOD_5) with the technique of incubation in 5 days and use of oximeter (Standard Methods 4500), pH and electrical conductivity.

2.3 Fenton reaction

The procedure chosen for the experimental decontamination is the advanced oxidation reaction type modified Fenton. The Fenton reaction was carried out at 20°C and at the atmospheric pressure of the city of Quito (546 mm Hg).

The optimal conditions of the Fenton reagent are obtained at acid pH values (Méndez *et al.*, 2010). The reduction of the pH in the effluents of domestic wastewater is very expensive due to the large flow rates to be treated; therefore, as indicated above, a modified Fenton technique has been chosen through the use of a chelating agent, citric acid being chosen, since it can form more stable Fe^{3+} chelates than with Fe^{2+}. The activity of Fe^{3+} chelates formed with chelating agents is low to dissociate H_2O_2, thus forming less stable complexes (Seol y I., 2008); which can be degraded better in the next stage of the wastewater treatment plant, which is the biological system.

The stability of the chelates is inversely proportional to the increase in stability constants (log k), which are 7.49; 9.4 and 11.85 for tartaric, oxalic and citric acids respectively (Furia, 1973). In this way the strong chelates of citric acid-Fe^{3+} by giving a low Fe^{3+} activity inhibit the iron species from being reduced again to Fe^{2+} by cutting the catalytic cycle of the Fenton reaction (Seol y I., 2008). The presence of nitrogen in the form of ammonia due to the contribution of domestic wastewater improves the capacity of citric acid to sequester iron and form soluble complexes (REPAMAR, 1998), this can occur in well-built septic tanks where anaerobic processes are generated.

For the experimental treatment, several mixtures of H_2O_2, $FeSO_4$ and citric acid ($C_6H_8O_7$) were carried out in the proportions indicated in Table 1 (Zazouli *et al.*, 2012; Mashal *et al.*, 2012; **?**). The pH of the residual water was not modified, so this parameter for all the mixtures made before the Fenton reaction was 7.21. As an initial treatment to the Fenton mixtures, a decanting of the residual water was carried out for one hour to remove the suspended solids. The assays were performed in duplicate by mixing the wastewater, $FeSO_4$, H_2O_2 and $C_6H_8O_7$ at 100 rpm for one minute and subsequently at 30 rpm for four minutes in a jar-mixer (Figure 2). The BOD_5 and COD analyzes were performed one hour after the mechanical mixing stopped, since this method requires relatively short reaction times and uses easy-to-handle reagents (Bautista *et al.*, 2008).

Table 1. Mixtures of H_2O_2, $FeSO_4$ and $C_6H_8O_7$ for modified Fenton reaction

Mixture	Modified Fenton Reagent (mg/L)		
	H_2O_2	$FeSO_4$	$C_6H_8O_7$
1	10	10	10
2	10	10	20
3	10	20	10
4	10	20	20
5	20	10	10
6	20	10	20

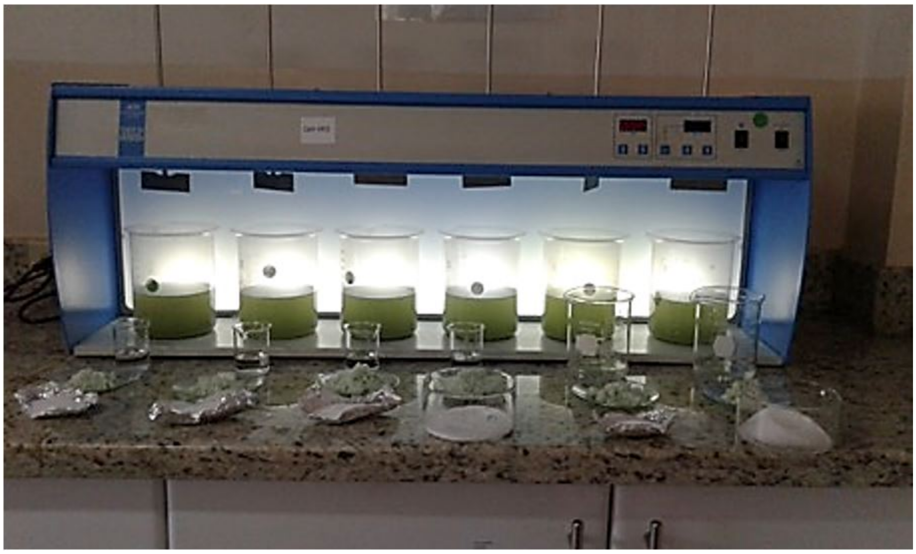

Figure 2. Photograph of a jar test performed with different concentrations of the modified Fenton reagents: H_2O_2, $FeSO_4$ and $C_6H_8O_7$; made to the residual water of the sample.

3 Results

The results of the initial water quality analyzes are shown in Table 2.

Table 2. Results of initial quality of residual water

pH	DQO	DBO_5	Relation DBO_5/DQO
7,21	11750 mg/L	2606 mg/L	0,22

The results of each mixture are shown in Table 3. As expected, the values of BOD_5 and COD remain high. However, biodegradability values of organic matter increased, being the optimum value in a mixture 6 with 20 mg/L of H_2O_2, 10 mg/L of $FeSO_4$ and 20 mg/L of $C_6H_8O_7$ despite having a value of Non-optimal pH for the classic Fenton reaction. It should be noted that in mixtures 3 and 4 precipitates of iron oxides were observed, possibly due to a co-precipitation accompanied by a decrease in the removal of the COD; therefore no mixtures were made in greater proportions.

Table 3. COD, BOD_5 and biodegradability index of the H_2O_2, $FeSO_4$ and $C_6H_8O_7$.

Mixture	DQO (mg/L)	DBO_5 (mg/L)	DBO_5/DQO
1	7598	2279	0,3
2	6536	3007	0,46
3	11331	4079	0,36
4	11532	5420	0,47
5	8257	3055	0,37
6	9716	4761	0,49

4 Discussion

The results obtained show that the Fenton reaction improves the biodegradability ratio until a treatment can be achieved in a conventional system; but, the modified Fenton reaction by itself does not reach the reduction of the BOD_5 and the COD to be below the Ecuadorian regulations in force to date; which, for discharges into bodies of fresh water, indicates maximum values of 100mg/L of BOD_5 and 200 mg/L for COD (MAE, 2015). The maximum removal of COD is given in mixture 2, whose efficiency is 44.4 %, the maximum removal of BOD5 in 12.54 % and the optimum increase in biodegradability in mixture 6, reaching an index of 0, 49.

For all other mixtures there is an increase in BOD_5 as a function of a decrease in COD, due to a decomposition and reorganization of structures in organic molecules from refractory compounds to more biodegradable compounds. In this particular case, obtaining greater efficiencies in COD removal is probably due to the fact that in the wastewater there are preferential biodegradable organic compounds for the Fenton reaction, similar to that obtained in studies with mature leachates (Lopes de Morais y Peralta Zamora, 2005).

The domestic wastewater with industrial load can enter the wastewater treatment plant with a modified oxidation stage of Fenton at the beginning of the system; that with the data taken in the field they would enter with a COD and BOD_5 of 11750 mg/L and 2606 mg/L respectively; and when going through the modified Fenton oxidation stage, these data would decrease to a COD and BOD_5 of 6536 mg/L and 3007 mg/L respectively (Figure 3).

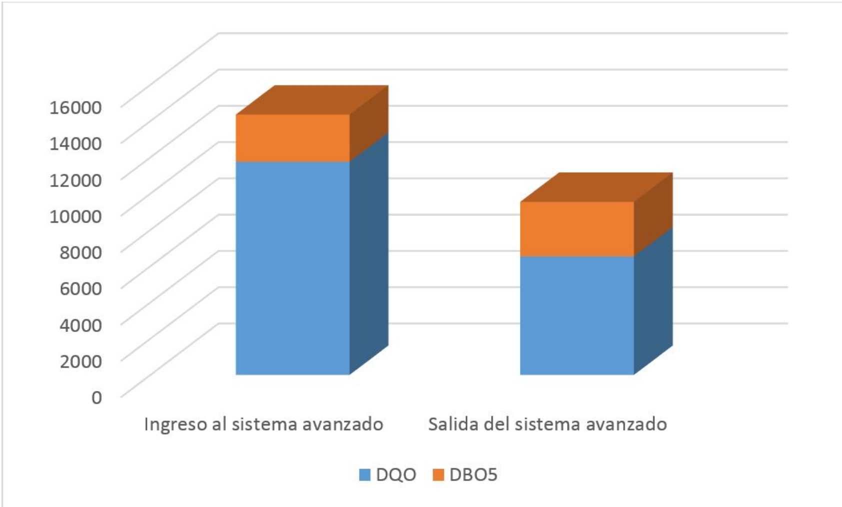

Figure 3. Graph of COD decrease, increase of BOD_5 measured in mg/L at the optimum concentration of modified Fenton reagent.

In summary, the results of this work demonstrate the suitability of the Fenton process to improve the biodegradability index of domestic wastewater with industrial load. The results show that domestic wastewater mixed with industrial and leached waters have low BOD_5/COD ratios; so the advanced oxidation process should not be done as a final treatment to a biological treatment system; but on the contrary, prior to an aerobic or anaerobic treatment (Lopes de Morais y Peralta Zamora, 2005). The location of the advanced oxidation treatment system will be between the physical treatment system and the biological treatment, as indicated in Figure 4; this avoids the use of reagents for the oxidation of solid material that is not suspended and that is separated in the physical treatment system of screening and de-sanding.

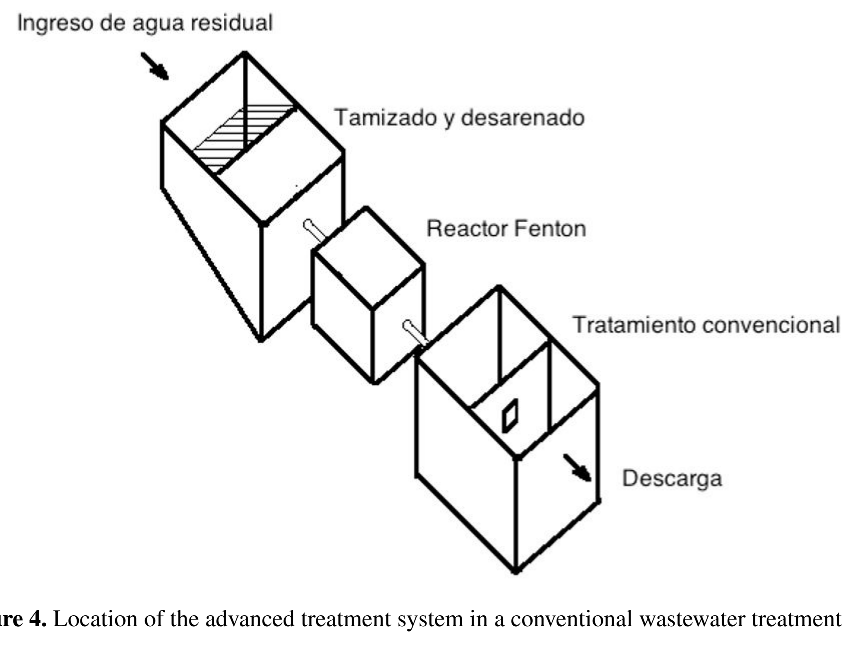

Figure 4. Location of the advanced treatment system in a conventional wastewater treatment plant.

5 Conclusions

With the data presented, it can be concluded that: Optimal conditions for the Fenton reaction were $FeSO_4/H_2O_2$ = 1 and $C_6H_8O_7/H_2O_2$= 2; with the placement of 10 mg/L of H_2O_2. With these relationships, the organic load of the residual water was reduced in the parameters of the COD and the BOD_5 in efficiencies of 44.4% and 12.54% respectively.

Also, it was found that the modified Fenton reaction oxidized preferentially to the non-biodegradable organic matter of the wastewater; which increased the BOD_5/COD index from 0.22 to 0.46, and therefore the wastewater can be treated in a conventional system.

Finally, the implementation of an advanced oxidation treatment process with modified Fenton can be located between the physical treatment system and the biological treatment system, allowing prolonging the useful life of conventional purification systems and thereby maintaining the public investment disbursed in build them.

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