Domestic wastewater treatment with Fenton and Constructed Wetlands system

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ABSTRACT

Alternative forms of domestic sewage treatments, such as Constructed Wetlands (WC) systems, are efficient and environmentally friendly. This effect can be intensified by associating two treatments to reduce the pollutant load, in this work, combined the Fenton reaction after a WC system for the removal of Organic Matter (OM). The experimental assay was carried out in a 5 x 5 factorial arrangement, with the factors beingH2O2 and Fe^{2+} at concentrations at both 0, 25, 50, 75 and 100 %, and the variable response was OM at UV 254nm. The data were submitted to exploratory analysis, considering the effects of the factors and their interactions, performing the analysis of variance and statistical models Linear, Linear Plateau, quadratic and quadratic Plateau. There was an interaction between the factors, unfolding Fe^{2+} within H2O2, it was found that in all H2O2 concentrations, the plateau model was the one that best fitted. While in the unfolding H2O2 within Fe^{2+} it was found that in concentrations up to 50% of Fe^{2+} the quadratic model was better adjusted, while in the highest concentrations (75 and 100%) it was the plateau. Modeling demonstrated that the optimal dosage for this study is 25% H2O2 (250 mg L-1) / 33% Fe3+ (165 mg L-1), removing 92.75% OM.

Keywords: Fenton, Constructed Wetlands.

INTRODUCTION

Basic sanitation is of fundamental importance for the well-being of human beings, since it promotes the control of public health, improves the quality of life of a city, eliminates risk factors to its health and, thus, increases the social and environmental conditions favorable to a good survival. However, the guarantee of access conditions and quality of services is growing in the country, still portraying a huge inequality and deficit in the process (BATISTA, 2014). The absence of these treatments can cause numerous environmental damages, including eutrophication. For this reason, several treatment alternatives have been studied with a view to removing pollutants with the use of biological treatments, especially the Constructed Wetlands (WCs) systems have shown promise (Kadlec and Knight, 1996; SOUZA, 2019). And another version of treatment, the hybrids, an association of biological treatments followed by chemical treatments, are a way to increase the efficiency of removing the pollutant load and return the possibility of water reuse, with physicochemical conditions compatible with the environment.

The WC system has low cost of operation, implementation and maintenance compared to conventional systems. The uses of wetlands demonstrate good efficiencies in the removal of suspended solids, BOD and nutrient concentration (Phosphorus and Nitrogen) (Carvalho, 2019; Ferreira & Paulo 2009; SALATI et al., 2009). Within a wetland system, several processes occur that contribute to the improvement of effluent quality, they are: adsorption of ammonium ions and metals by clay minerals, adsorption of metal ions, pesticides and phosphorus-based compounds by organic matter; decomposition of organic matter; removal of pathogens by microorganisms; removal of heavy metals and other toxic substances (within limits) by plants (macrophytes) (CARVALHO, 2019; Kadlec and Knight, 1996; Melo Júnior et al, 2019). In domestic sewage, Organic Matter (OM) is found in solution — represented by dissolved organic solids (rapidly biodegradable) — and in suspension — relative to solids suspended in the liquid medium (slowly biodegradable) (MOREIRA & SIQUEIRA, 2002). but recalcitrant chemicals are removal technologies such as advanced oxidation processes have been scarcely practiced in decentralized areas (Chong et al., 2012). Among the advanced oxidative processes (AOP), the Fenton reaction has been one of the most researched and already commercially adopted in the treatment of recalcitrant effluents characterized by high COD and salinity, low biodegradability and high toxicity such as those from the pharmaceutical or cosmetics industries (CAVALCANTI, 2018; Sires et al., 2014; Rocha, 2014, Xu et al, 2020).

Combining advanced processes as a pre-or post-treatment is generally only intended to transform toxic and/or recalcitrant compounds into biodegradable substances or substances that are easily eliminated (KAMMRADT, FERNANDES, 2004). According to Kunz (2002), combined processes can be used in a complementary way, in such a way that they can overcome deficiencies presented by the processes when applied in isolation. However, Fenton oxidation can be used under more optimal conditions as a pre-treatment prior to biological purification when the main objective is to focus on increasing biodegradability and/or reducing the toxicity of discharges, leaving the task of reducing most of the organic matter to the biological phase. In this case, this association can become more economically attractive (CAVALCANTI, 2018). And/or used as a subsequent treatment in order to remove compounds that by the previous stage had not yet been completely removed, with the character of politeness of that effluent.

The optimization of the dosage of Fenton reagents has been a target for several organic molecules. Experiments using the plateau segmented linear regression model and the plateau segmented quadratic regression model, which use the plateau response technique to models that have minimal levels of regression (Peixoto et al, 2011; Souza et al 2014). Thus, the objective of this study was to evaluate the effect of H2O2/Fe^{2+} concentrations in Fenton after WC system in sewage treatment for removal of organic matter.

MATERIAL AND METHODS

FENTON TREATMENT

The experiment was carried out in a 5x5 factorial arrangement (Table 1), using five dosages of H2O2 and five of Fe^{2+}, with 3 replications. The dosages in % used in both factors were: 0, 25, 50, 75 and 100.

The samples were collected from the WC system located at the Instituto Federal Goiano, Rio Verde Campus, where the effluent generated is characterized as domestic, therefore, Table 1 shows the hydraulic parameters of the WC.

Table 1: Dimensions of the WC system - case study.

Design Parameter (WC)	VA	VC
N (inhab) -	12	--
C (L.hab.d-1)	100	--
T (d) -	1	--
K (d) -	97	--
lf (l.hab-1.d-1)	1	--
Cleaning period (years)-	2	--
Volume Required (L)-	--	3364
Tank geometry -	Prismatic	--
C/L -	2/I	--
Tank depth (m)	1.3	--
Tank length (m)	--	2.2
Tank width (m)	--	1,2
Tank volume (L)	--	3432

VA: Value adopted; VC: Calculated Value; N: number of taxpayers; C: sewage contribution per capita; T: period of detention; K: rate of accumulation of digested sludge; Lf: fresh sludge contribution; C/L: tank length and width ratio
Source: SILVA and SOUZA, 2018.

THE PHYSICOCHEMICAL PARAMETERS WERE QUANTIFIED ACCORDING TO APHA (2012). AND THE PARAMETER EVALUATED AS A CRITERION OF EFFICIENCY OF THE FENTON REACTION WAS THE INDICATOR OF UV ORGANIC MATTER (OM) AT THE WAVELENGTH OF 254 NM

Table 2: Fenton Reaction Reagent Dosages

Fe^{2+} (%)	[Fe+2] mg/L	H2O2 (%)	[H2O2] mg/L
0	0	0	0
25	125	25	250
50	250	50	500
75	375	75	750
100	500	100	1000

Reaction conditions: volume 1 L; pH=3.5; time 120 minutes and rotation 100 rpm. Source: Authors, 2024.

OPTIMIZATION VIA STATISTICAL MODELING, R SOFTWARE:

The data were initially submitted to exploratory and residue analysis considering the effect of peroxide, iron and the interaction between them. Subsequently, they were subjected to analysis of variance and the effects were unfolded, and the adjustment of the linear regression models of first degree, second degree, linear plateau and quadratic plateau was verified. The criteria of Akaike and Bayesian information were used, and the best model was determined to explain the effect of the treatment.

RESULTS AND DISCUSSIONS

Table 3 physicochemical parameters of the effluent before and after fenton treatment.

	Fenton Treatment					
H2O2%/ Fe^{2+}	% UV removal 254 nm					
	0	25	33*	50	75	100
0	----	60,85		66,60	66,52	66,78
25	15,69	85,44		90,85	90,67	89,54
50	---	84,74		90,85	90,84	94,25
75	---	83,43		89,19	90,67	93,72
100	---	82,21		89,36	91,28	93,81
25*			92,79*			

Effluent WC before Fenton		Effluent WC after Fenton*	
pH	6,23	pH	8,5
COD mg/L	8,33	COD mg/L	---
UV(254nm)	0,38233	UV(254nm)	0,0283
Surfactante mg/L	2,18	Surfactante mg/L	0,85

Source: Authors, 2024.

Table 4. Akaike's criterion and Bayesina information of the models adjusted with the unfolding of the factors.

Statistical model	Fe Teor^{2+}%									
	0		25		50		75		100	
	AIC	BIC	AIC	BIC	AIC	BIC	AIC	BIC	AIC	BIC
Linear	97,99	99,56	108,3	110,5	107,3	109,4	106,1	108,2	-61,52	-59,39
Quadratic	76,23	79,06	90,97	93,8	90,99	93,82	90,3	93,13	-85,4	82,57
Quadratic Plateau	76,52	79,35	----	----	----	----	38,71	41,54	-118,9	116,1
Statistical model	**H content$_{2O2}$ %**									
	0		25		50		75		100	
	AIC	BIC	AIC	BIC	AIC	BIC	AIC	BIC	AIC	BIC
Linear	117,1	119,3	138,4	140,5	143,3	145,5	142,6	144,7	142,18	144,3
Quadratic	95,1	97,83	117,9	120,8	125,3	128,2	124,6	127,4	123,16	126
Quadratic Plateau	62,93	65,76	**44,79**	**47,63**	58,39	61,22	62,71	65,54	61,93	64,76

Table 4 shows the observed values of Akaike and Bayesina information of the models adjusted with the unfolding of the factors. It was found that the linear plateau model did not adjust in any of the unfoldings, and that the quadratic plateau only did not adjust in the peroxide unfoldings with contents of 25% and 50% of Fe.

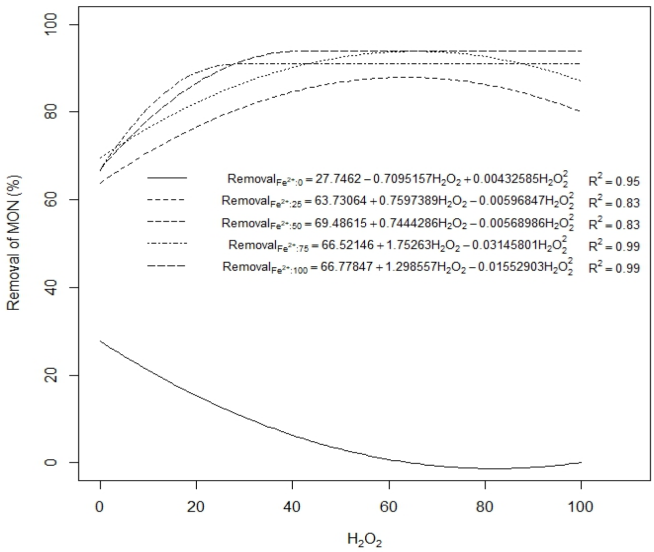
Regarding the results of the dosage of the fenton reagent, among the twenty-five treatments, it is noteworthy that the assays with only dosages of ferrous ions, there was an increase in the removal of OM (UV 254nm), this is due to the coagulant effect that this salt exerts on the matrix, and this effect is recorded in water treatment in the water plant (Matilainen et al., 2010, Sharp et al., 2006).

In the presence of only H2O2, removal was observed only in the condition of 25% of it, peroxide has the effect of oxidant and its efficiency depends on catalyzed conditions for the production of oxidants to degrade organic matter (Pouzarmani et al., 215). On the other hand, at the levels of 25.50, 75 and 100% of H$_{2O2}$/ Fe2+, the best removals occurred in the 1:1 ratio, increasing for ferrous ion dosage, removing 90.85, 94.25, 93.72 and 93.81% of OM, respectively. From the statistical analyses, the levels were optimized, with the best condition being in the proportion of 1:1.5 of$_{H2O2}$/ Fe^{2+}, culminating in a removal of 92.75 % of OM. The stoichiometric ratio of the reactants is the main factor of the Fenton process (Nogueira et al. 2007; Gulkaya et al 2006; Bokare and Choi, 2014). Zhang et al (2005) used the ratio of H2O2/ Fe2 $^{+2 \text{ to } 1.5 \text{ for landfill leachate.}}$

Figure 1 shows the graphs of the effects of peroxide and iron content and the incidence on OM removal. By unfolding H2O2 within iron (Figure 1 a), it was found that within the dosage of ferrous ions 0, 25 and 50 (%), the quadratic model was the one that best adjusted to explain the effect of H2O2. In the absence of ferrous ions, the OM content increased quadratically as the H2O2 content increased, and there was no removal of it. For a dosage of 25% Fe^{2+} , the removal of OM increases quadratically to the content of 63.64% of H2O2, providing the removal of 87.91% of OM. For a dosage of 50 % of Fe2+, the OM is removed in a quadratic manner up to the content of 65.41% of H2O2, equivalent to the removal of 93.84 % of OM. At the dosages of 75 and 100 % of ferrous ions, OM had a quadratic plateau behavior with the addition of H2O2. At 75% of Fe2+, OM reduces quadratically up to 27.86% of H2O2, corresponding to the removal of 90.93% of OM. For the dosage of 100% of Fe2+ (%), OM decreased quadratically until the H2O2 content was equal to 36.68%, equivalent to the removal of 91.48%.

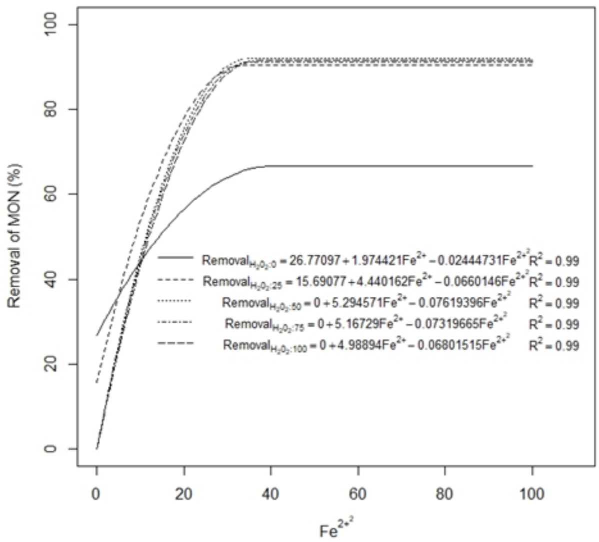
Unfolding the effect of ferrous ion content (%) on H2O2 (Figure 2), it was found that in all treatments the quadratic plateau behavior prevailed in relation to OM removal. At the dosage of H2O2 (%) equal to zero, OM removal increased quadratically plateau as iron content increased, demonstrating that the Fe^{2}+ content equal to 40.38% reaches 66.64% of removal and remains constant thereafter. For the 25% H2O2 content, the removed 90.35% of MON in the presence of 33.63% of ferrous ions, keeping the removal after this content constant. Therefore, for the 50% H2O2 content, the increase was increasing to 91.97% with the 34.74% Fe^{2}+ content, and not changing after this value. In the case of the dosages of 75 and 100 % of H2O2, the % removal had a quadratic plateau behavior with the addition of ferrous ions. Respectively, the OM removal content was above 90% and the limit amount of ions demonstrated by the analysis were 29 and 36.68% of Fe^{2+}.

Figure 1: Effects of peroxide and iron content and incidence on OM removal: unfolding H2O2 within iron, using R software.



Source: Authors, 2024

Figure 2: Effects of peroxide and iron content and incidence on OM removal: unfolding Fe2+ ions within H2O2, using R software



Source: Authors, 2024

CONCLUSION

From this investigation, it is concluded that statistical tools should be used to optimize the dosage of reagents for the Fenton reaction, which demonstrates that there is interaction between the two reagents, iron dosage and peroxide dosage, under fixed conditions of pH equal to 3.5, reaction time of 120 minutes and volume of 1 liter. The best dosage for the proposed treatment is in the ratio of 1.5 H_2O_2/ Fe2+. And there is feasibility of adapting the fenton treatment as a post-treatment in a WC system, promoting this removal of recalcitrant compounds as indicated in the work, the surfactants.

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