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STUDY OF THE CORRELATION BETWEEN VOLATILE SOLIDS AND CHEMICAL OXYGEN DEMAND AS INDICATORS OF THE TIME OF DEGRADATION OF CIGARETTE BITUCAS IN THE ENVIRONMENT

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Abstract: Municipal solid wastes are one of the responsible of the soil and water degradation at the environment, among these wastes, the cigarette butt's appears. The cigarette butt's are classified as dangerous solid microwastes and corresponds about 25 to 50% of the collected trash at roads and streets. The butt's are of hard degradation, due possible of the cellulose acetate (CA) presence, a recalcitrant polymer present in about 95% cigarette filters. So, it's necessary the physico-chemicals parameters monitoratoration with the intent of describe the conditions of the degradation phenomena processess. Therefore, in that case, the research inserts itself aiming to correlate the volatile solids (VS) content with the chemical oxygen demand (COD), to stablish it as cigarette butt's degradation time indicators at the environment. For the methodological proceeds, cigarette butt's samples were collected randomly at Campina Grande city, from Paraíba state. The physico-chemical monitoring from the VS and COD parameters was made, of which were used the gravimetric and closed reflux, in a digester block, respectively. After that, the data were tabulated and computed in a statistical software with the intent to verify the correlation existence between these parameters. As result, a positive linear correlation (r = 0,9764) and a probability p = 0,000 with 5% of meaningfulness was observed, showing that the VS decay shape along the time it's also followed by the COD, showing the possibility establishing those parameters as degradation time for the cigarette butt's indicators.

Keywords: Microwastes, butts, chemical oxygen demand.

INTRODUCTION

The cigarette filter has the function of reducing the smoker's inhalation of tar and other toxic substances present in the smoke (JUNG, TOCCHETTO and GONÇALVES, 2014). After use, cigarette filters are discarded and called a butt. The butt contains the filter, a part of unburned smoke and the residue from the burning of the cigarette. The filter accumulates the numerous chemical substances present in the smoke and those resulting from its burning.

According to Kist et al. (2020), approximately 5.26 trillion units of tobacco were consumed in the world in 2019, and considering that one butt is equivalent to 0.5 g, about 2.63 million tons of cigarette butts were generated and discarded in the environment. environment in a single year.

In addition to being a consumer, Brazil is also a major tobacco producer. In 2019, Kist et al. (2020) showed that world tobacco production was 4,483,509 tons (T), in which Brazil contributed with the production of 663,909 T. Of this production, Brazil exported 548,916,000 T, then characterized as the largest tobacco exporter in the world. world.

In addition, the tobacco production chain in Brazil generated BRL 28,142,630,150.00, with BRL 19,683,871,420.00 from domestic consumption of cigarettes and BRL 8,459,821,730.00 from the export of tobacco and derivatives, in which this the latter presents 51.7% related to government taxes, 21.3% to producers, 21.3% to industries and 5.9% to retailers (KIST et al., 2020).

The butts randomly discarded in the environment, specifically in the soil, become urban solid waste (MSW), which is difficult to degrade due to cellulose acetate (CA), a basic constituent of cigarette filters. CA is a neutral polymer of organic esters derived from cellulose, has high hardness and low cost (CERQUEIRA et al., 2010).

According to the Solid Waste Management Plan (BRASIL, 2010), cigarette butts are classified as class I solid micro-waste - hazardous, that is, those whose physical, chemical or infectious properties can cause risks to public health and /or risks to the environment when the waste is improperly disposed of. For a waste to be classified as class I, it must be contained in the annexes of the Brazilian Standard NBR 10.004 of the Brazilian Association of Technical Standards (ABNT, 2004) or have one of the following characteristics: flammability, corrosiveness, reactivity, toxicity and/or pathogenicity.

Therefore, because the butts absorb part of the numerous chemical substances contained in tobacco such as nicotine and chemical compounds that have characteristics of flammability, toxicity and pathogenicity, the butt is characterized as a hazardous waste. Therefore, they must not be discarded in the common waste, as their disposal includes, at least, decontamination and disposal in controlled industrial landfills (BRASIL, 2010).

According to Trigueiro (2005) and Marchi et al. (2016), butts can take up to 15 years in a dry environment (such as asphalt) and between 5 – 7 years in favorable environments (such as dumps) to decompose, precisely because of the AC, present in about 95% of the filters. cigarettes.

According to the National Solid Waste Policy (Law N0 12.305/2010), it is necessary to create goals for the elimination of dumps and to adopt adequate forms of treatment and disposal of MSW (BRASIL, 2010). Therefore, for the correct treatment and disposal of MSW, physical-chemical characterization is necessary to establish the best way to treat and dispose of them.

According to Ribeiro et al. (2016), the monitoring of physical-chemical parameters is of great importance because they describe the conditions in which the degradation phenomena take place. Thus, from the knowledge of these parameters, it is possible to evaluate the decomposition of solid waste over time and what are the peculiar characteristics of each phase of MSW degradation, especially for the choice of a form of treatment for them.

The disposal of MSW in the soil will suffer the action of biotic media, that is, they will undergo biodegradation. To promote biodegradation, microorganisms promote the degradation of physical, chemical and biological aspects in the MSW mass, varying, for example, SV and COD. The SV and COD allow monitoring the process of decomposition of MSW in the soil, indicating the evolution of the microbiological degradation of organic matter and the global evolution of the process of stabilization of the mass of residues (RIBEIRO et al., 2016; FOLLMANN et al., 2017).

Studies carried out by Firmo (2013) indicated that the SV content decreases as the decomposition period increases, with values found for new residues (82.97%), residues of 2.5 years (57.35%), 3.5 years (46.78%) and 5 years (14.57%). Also according to Firmo (2013), a high content of SV can indicate considerable existence of materials subject to degradation. However, the use of this parameter only to analyze the biodegradability of a material can lead to misinterpretations, as some materials, such as paper/cardboard, textiles, plastics, vegetable fabrics, rubber and leather, have a high content of volatile solids and, on the other hand, are classified as moderately or slowly or non-biodegradable, and may still contain a high fraction of organic substances, but not biodegradable.

Ribeiro et al. (2017) developed MSW monitoring surveys in a landfill. At first, they observed that MSW had high concentrations of SV and COD. During the monitoring, there was a decrease in the SV content and a reduction in COD concentrations. The authors suggest a possible correlation between the values of COD and SV, where the decay of SV can imply in the almost total removal of the COD, this for the study of the temporal variation of MSW in a sanitary landfill.

Moreira, Braga and Fries (2009) state that the dissolved organic matter expressed in COD tends to decrease as a degradation process and mention that the COD concentrations of MSW leachates decreased according to the age of the residues, obtaining 15,000 to 40,000 mg. L-1 (age 0 to 5 years), 10,000 to 20,000 mg.L-1 (age 5 to 10 years), 1,000 to 5,000 mg.L-1 (age 10 to 20 years) and less than 1,000 mg. L-1 (age over 20 years old).

Therefore, it is in this context that the present research is inserted, given that the butt is a solid micro-waste that is difficult to biodegrade. This difficult biodegradation occurs because the butt presents AC, a polymer with a complex chain. Thus, seeking research that allows the study of the physical-chemical mechanism of this type of solid waste is pertinent to the development of studies that minimize the impacts of these micro-waste on soil and water. Thus, this research aimed to correlate the volatile solids content with the chemical oxygen demand, in order to establish them as indicators of the degradation time of cigarette butts in the environment.

MATERIALS AND METHODS

The present research was carried out at the Laboratory of Environmental Management and Waste Treatment (LABGER), at the Academic Unit of Chemical Engineering (UAEQ), at the Science and Technology Center (CCT), Campus Headquarters, of the Federal University of Campina Grande (UFCG), Campina Grande, Paraíba, Brazil.

MATERIALS

CIGARETTE BUTTS

For the development of the proposed objectives, butts were acquired at the UFCG Headquarters Campus, by simple random probabilistic sampling, according to Montgomery and Runger (2009). Figure 1 shows discarded butts on the ground of the

UFCG Headquarters Campus.

METHOD

EXPERIMENTAL PLANNING

The experimental design followed a simple linear regression model at 5% significance, according to Montgomery and Runger (2009), through the statistical test of hypotheses in relation to the model parameters, SV (x) and COD (Y) content:

- Null hypothesis (H_0): $\beta_1=0$;
- Alternative hypothesis (H_1): $\beta_1 \neq 0$.

With a probability of 5% of significance, these hypotheses regarding the significance of the regression were observed, where the null hypothesis (H_0: $\beta_1=0$) is equivalent to concluding that there is no linear relationship between X and Y. While the alternative hypothesis (H_1: $\beta_1 \neq 0$) it is equivalent to affirm that there is a linear relationship between x and Y, that is, the expected value of Y is affected by the values of X.

In this work, the Computer Program MINITAB® 17.0 (2014) and the recommendations for simple regression analysis were used, according to Montgomery and Runger (2009).

VOLATILE SOLIDS CONTENT (SV)

The gravimetric methodology adopted was from the American Public Health Association (APHA, 2005), which consists of calcining the samples in a muffle furnace (Marca Magnu's®) at a temperature of 500 (+ 50) 0C for a period of 1 h. Subsequently, the gravimetric steps were followed until constant weight was reached.

DETERMINATION OF COD

The COD determination followed the recommendation of APHA (2005), using the closed reflux method, in a Dry-Block® Digester Block for a period of 2 h (± 5 min) at 150 °C. For the digestion of the sample, a digester solution, 2.5 mL of the diluted butt solution and a catalytic solution were used. After the necessary time in the digester block, the samples were taken for titration with the titrating solution of 0.025N ferrous ammonium sulfate in the presence of the ferroin indicator solution until the turning point.

The results obtained were expressed in milligrams of oxygen per kilogram of butt, as well as in milligrams of oxygen per kilogram of butt and as a percentage.

STATISTICAL ANALYSIS OF THE RESULTS OBTAINED

In the analysis of the results, regression analysis was performed to observe the correlation between the SV and the COD, the validation of the model was observed through Table 1, which presents the output of the MINITAB® 17.0 (2014) software for regression analysis in ANOVA.

The quantity R2 is called the coefficient of determination, it is the ratio between the quadratic sum explained by the regression and the total quadratic sum. The sum:SQ_T (Sum of the Total Square) represents the total variation of the SV and COD contents around its own mean, that is, it is the corrected total square sum of y, being given by $y=\sum^{n}_{i=1}(yi-\bar{y})^2$. The term SQ_E (Error Square Sum) is the portion of this variation that the model found is able to describe. SQ_E deals with the deviations of the observed values in relation to the values given by the model, and is given by $SQ_E=\sum^{n}_{i=1}[(yi-\bar{y})/\sigma_i]^2$; where σ_i is the standard deviation at point i and n is the number of samples analyzed (MONTGOMERY and RUNGER, 2009).

RESULTS AND DISCUSSIONS

Table 2 shows the SV results in percentage and also the COD results in $mg.L^{-1}$, $mg.kg^{-1}$ and in percentage.

Figure 1. Bitucas in the soil of the collected in the Campus headquarters of UFCG.

Source: Author himself (2020).

Regression equation: $y=\beta_0+\beta_1+\varepsilon$					
Sources of variation	**Degrees of freedom (G.L.)**	**Sum of squares (SQ)**	**Medium square (QM)**	**F**	**Value p[1e2]**
Regresion	1	SQ_R	QM_R	QM_R/QM_E	-
	n – 2	SQ_E	QM_E	-	-
Total Mistake	n – 1	SQ_T	-	-	-
		R^2	**R^2_{pred}**	**R**	

Note: 1 – significantly different (p<0.05); 2 – not significant (p> 0.05).

Table 1. MINITAB output for regression analysis.

Source: MONTGOMERY and RUNGER (2009) and MINITAB 17.0® (2014).

N	SV (%)	DQO ($mgO_2.L^{-1}$)	DQO ($mgO_2.kg^{-1}$)	DQO (%)
1	93,78	13.815,26	276.305,22	27,63
2	93,60	11.755,23	235.104,67	23,51
3	93,35	10.950,08	219.001,61	21,90
4	93,01	10.950,08	219.001,61	21,90
5	92,39	7.925,93	158.518,52	15,85
6	92,06	6.119,16	122.383,25	12,24
7	91,99	5.783,13	115.662,65	11,57
8	91,86	5.703,70	114.074,07	11,41
9	91,46	5.703,70	114.074,07	11,41
10	91,33	4.962,96	99.259,26	9,93
11	91,16	4.222,22	84.444,44	8,44
12	90,65	4.176,71	83.534,14	8,35
13	90,61	1.767,07	35.341,37	3,53
14	90,41	963,86	19.277,11	1,93
Average	**91,98**	**6.771,36**	**135.427,29**	**13,54**
Standard deviation	**1,12**	**3.819,63**	**76.392,58**	**7,64**

Table 2. Percent SV magnitudes determined on cigarette butts and COD magnitudes determined on cigarette butts.

Source: Prepared by the Author (2020).

Also for Firmo (2013), a high SV content indicates the presence of materials susceptible to degradation. However, the author emphasizes that only the SV content as a parameter for evaluating biodegradability can lead to a mistake in the interpretation of the result, as materials such as paper/cardboard and leather have high SV, but may be moderately or even non-biodegradable, despite having high organic load.

Regarding COD, the results presented in Table 2, demonstrate agreement with the statement by Moreira, Braga and Fries (2009), that the dissolved organic matter expressed in COD tends to decrease with the degradation process and that the COD concentrations of leachate of MSW decrease according to the age of the waste, obtaining 10,000 to 20,000 mg.L-1 (age from 5 to 10 years), 1,000 to 5,000 mg.L-1 (age from 10 to 20 years) and less than 1,000 mg.L-1 (age over 20 years old). In the results obtained, it was actually observed a decrease in COD according to the storage time of the butts.

Table 3 presents the results of the regression analysis in ANOVA at 5% of significance for percentage of SV and COD, respectively.

The results in Table 3 show that the percentage of solids SV influenced the responses of the percentage of COD, since the value of p = 0.000 was less than 0.05 ($p \leq 0,05$ significant at 5%), that is, the alternative hypothesis (H1) was proved, with $\beta_1 \neq 0$ regarding the significance of the regression, demonstrating that there was a linear relationship between the percentage levels of SV and COD. Thus, the expected COD value was affected by the SV values. Linearity is observed in the linear equation (Equation 1):

$$DQO(\%)=6,632*SV-596,4 \qquad (1)$$

The coefficient of determination (R^2) obtained for Equation (1) was 95.33%, showing that the model fits the data very well and indicating that about 95% of the results found can be explained by the regression analysis. The predicted coefficient (R^2_{pred}) 93.33% determined that the model predicts responses to new observations well. Finally, the correlation coefficient (r) of 0.9764 showed that the positive linear correlation between the variables is very strong, as seen in the graph in Figure 2.

Thus, the suggestion by Ribeiro et al. (2017) of a possible correlation between the values of COD and SV, where the decay of SV can imply in the almost total removal of the COD, could be confirmed, demonstrating that, in fact, the decay of the SV content occurs according to the time of storage of butts and that it is correlated with the COD content, that is, as time passes, the SV and COD content decrease.

CONCLUSION

In view of the foregoing, it can be concluded that:

- The average result of 91.98 (± 1.13) % indicates high levels of SV. However, this high percentage is not necessarily related to the biodegradation of butts in the soil, since, according to the literature, the fact that many materials have a high organic load does not guarantee that they are biodegradable.
- The average result of 6,771.36 (± 3,819.63) mg.L-1 of the COD of cigarette butts reinforces the need for previous treatments before being discarded, because when in contact with the biotic media of the soil and water, it will require high oxygen content, causing great impacts to the environment as a whole.
- The regression analysis showed an Fcalculated = 245.14 greater than the Ftabulated = 2.263 and a probability p

Regression equation: DQO(%)=6,632*SV-596,4

Sources of variation	Degrees of freedom (G.L.)	Sum of squares (SQ)	Medium square (QM)	*F*	Value p^{1e2}
Regression	1	723,25	723,253	245,14	0,000
SV (%)	1	723,25	723,253	245,14	0,000
Total Mistake	12	35,40	2,950	-	-
	13	758,66	-	-	-

R^2 = 95,33% R^2_{pred} = 93,33% r = 0,9764

Note: 1 – significantly different (p<0.05); 2 – not significant (p> 0.05).

Table 3. MINITAB output for 5% ANOVA regression analysis.

Source: Data obtained by the author in the MINITAB software (2020).

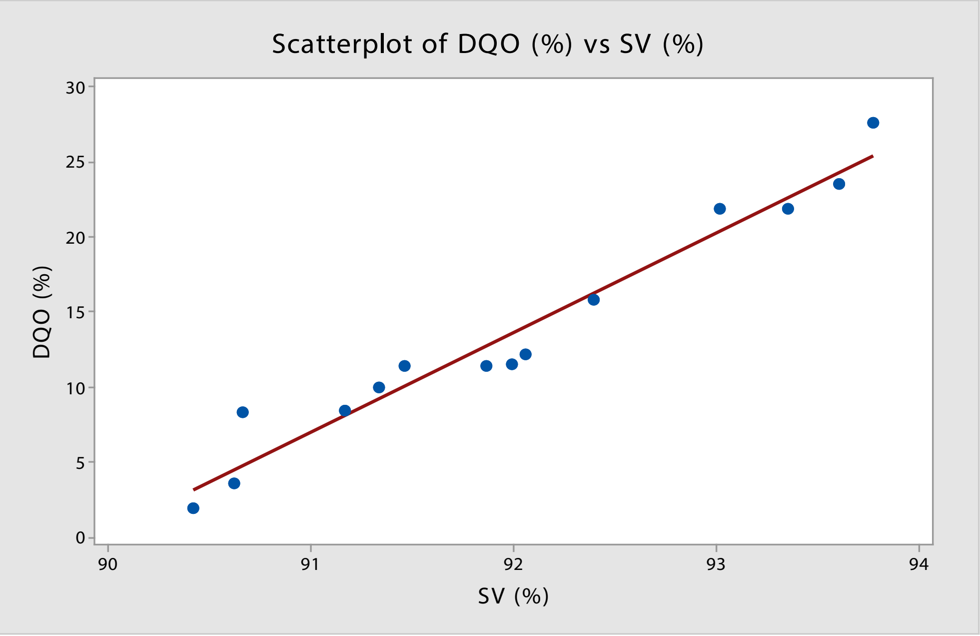

Figure 2. Positive linear correlation graph between percentage of SV and COD.

Source: Data obtained by the author in the MINITAB® software (2020).

obtained of 0.000 (less than 0.05 to 5% of significance), proving the alternative hypothesis, regarding the significance of the regression, demonstrating that there was a linear relationship between the percentages of SV and COD. Thus, the expected value of COD was affected by those of SV.

- The decay profile of the SV content over time accompanied by the same decay profile of the COD reached a positive linear correlation with a correlation coefficient (r) of 0.9764; demonstrating the possibility of establishing them as indicators of the degradation time of cigarette butts in the environment.

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