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## Design of a methodology to monitor the organic matter in industrial ceramic wastewaters and sewages

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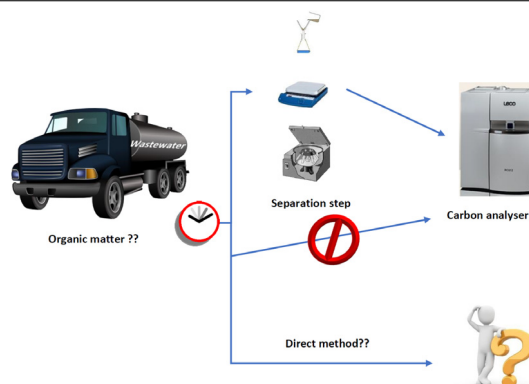
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### HIGHLIGHTS

- Methodology to monitor the organic matter in ceramic wastewaters and sewages.
- Direct relationship between the organic carbon and COD value.
- Design of less time-consuming control method to accept or reject wastewater reuse.
- Elimination of hazardous chemicals makes the method more environmentally friendly.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A rapid, simple, and accurate methodology for the control of the organic matter present in the industrial ceramic wastewaters and sewages reused in the ceramic industry was designed by studying the relationship between COD value and the carbon at 490 °C content. The presence of organic matter in wastewater and sewages used in the ceramic industry is undesirable as it can result in the appearance of black core in the final product when these waters and sewages are reused in the spray-drying process. That is the reason why the organic matter content present in the wall and floor tile compositions is an important variable to be considered. The actual method for the determination of organic matter implies a prior treatment of the sample, which make it time-consuming to be used as a control method. The setting up of the methodology has been undertaken by studying the relationship between carbon at 490 °C (organic matter) and COD and by modifying the current COD test to make it faster (reducing the digestion time) and more environmentally friendly (eliminating hazardous chemicals from the determination process).

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## 1. Introduction

In the ceramic process, the preparation of wall and floor tile compositions destined to pressing can be done either by wet or dry processing. In the “wet process”, clays and other raw materials are mixed with water and milled in order to achieve an appropriate particle size distribution for their subsequent spray-drying process.

If organic matter is contained in these tile compositions, dark zones, known as black core, can appear in the interior of the fired ceramic tiles. This phenomenon is related to the organic carbon concentration present in the compositions used in tile preparation. The occurrence of black core during the firing process is favored by short firing cycles or the production of large pieces whose compactation is increased and whose diffusion coefficient is, consequently, decreased.

Black core is undesirable as it can produce a reduction in mechanical strength, swelling of the fired ware, pyroplastic deformations, color changes in the body and/or the glaze, etc. Therefore, it is necessary to find a way of elimination or prevention. That is the reason why, apart from controlling process variables such as temperature, firing cycle, apparent density, etc., the organic carbon content present in the wall and floor tile compositions is an important variable to be considered (Gazulla et al., 2002; Negre, 1989).

Wall and floor tile composition preparation by spray-drying involves the use of water. Growing water demands for industrial use and stricter pollution control regulations have led to a constant rise in industrial water supply and effluent treatment costs. This led to consider the possibility of wastewater reuse in the same manufacturing process or in other ceramic processes (Enrique et al., 2000). Consequently, industrial wastewaters from different sources (different ceramic processes and/or different suppliers from the ceramic sector) are commonly used in the spray-drying process and can contain considerable amounts of organic matter from the use of organic vehicles, defloculants, plasticizers, and other organic compounds used in glazing and decoration operations, which will subsequently be part of the spray-dried powder.

Nowadays, there is not a real-time monitoring of organic matter in industrial wastewater to accept or reject them to be used in industrial spray-driers. It is known that conductivity and solid content are the only parameters controlled because of the test simplicity, but these parameters have no relationship with organic matter. Consequently, when some wastewater has high organic matter contents, black core problems arise and they are only detected when the final product is submitted to the firing process, which is the last step of the production process.

There are several standards (EN 13137, 2001; ASTM D7573, 2017; UNE 77321, 2003) for the determination of organic carbon (OC). These standards present two methods for the determination of organic carbon: both an indirect and a direct method. The indirect method is based on the determination of inorganic carbon (IC) (defined as the carbon from carbonates, bicarbonates, and graphite) and total carbon (TC) (defined as the sum of inorganic and organic carbon), the organic carbon calculated as the difference between TC and IC. The direct method is based on the prior elimination of IC and subsequent determination of TC, which is assigned to organic carbon (as all inorganic carbon is supposed to be eliminated). These methods can lead to erroneous results since elemental carbon (EC), which is the one that comes from graphite or coal, for example, will be detected as organic. There are several studies in which the determination of organic carbon is carried out submitting the sample to a heating process at a certain temperature. The key point is the establishment of the temperature at which the organic carbon has completely decomposed and carbonates have not started yet. Different temperatures have been stated between 450 °C and 700 °C. Although almost all carbonates decompose at temperatures higher than 700 °C, siderite (FeCO<sub>3</sub>) decomposes at 550 °C. Consequently, the determination of organic carbon must be carried out at lower temperatures, and a temperature of 490 °C was set up.

DIN 19539 (2016) differentiates between inorganic carbon, organic carbon, and elemental carbon (EC) and proposes a method for the determination of the different carbon species based on the combustion of the sample at different temperatures in an oxygen atmosphere and IR detection. In accordance with this standard, organic carbon would be the one that is obtained at a temperature of 400 °C, while elemental carbon would be released at a temperature of 600 °C. Total carbon would be the one obtained at a temperature of 900 °C, the inorganic carbon obtained by difference between TC and (OC + EC).

However, a temperature of 400 °C can be too low to decompose certain type of organic matter, and the determination could be carried out at a temperature of 490 °C to assure the complete decomposition of the carbon from the organic matter.

Since there is not an agreement about the analysis temperature of organic carbon, in this study the organic carbon will be referred as “carbon at a certain temperature” rather than “organic carbon”.

In liquid samples the organic matter can be controlled determining the chemical oxygen demand (COD), that is, the total concentration of substances that can be chemically oxidized to inorganic final products (Pisarevsky et al., 2005). This parameter is an indicative measure of the amount of oxygen that is consumed by reactions in a measured solution, an indicative of the concentration of substances that can be chemically oxidized, so it can be used to quantify the amount of organics in waters. In the case of industrial wastewaters and sewages, which is composed by a solid and a liquid fraction, the organic matter could be controlled by analyzing the amount of carbon at 490 °C in the dried sample, which would imply the prior sample treatment. This test has the disadvantage that takes too long to be used as a control method. If there was a direct relationship between COD value and carbon at 490 °C, COD test could be an alternative method to control the organic matter in industrial wastewaters and sewages.

Ronzano and Dapena (Ronzano and Dapena, 2017) studied the different methods to control the organic matter in waters and stated the following equation that correlates the organic carbon with the COD value:

$$\text{COD} = n(1.87 - \text{OC} - 17)$$

where  $n$  depends on the degradability of the sample and it normally comprises values between 1 and 3.

Standard COD method (UNE 77-004, 2002) is rather tedious as it requires a relatively long digestion with sulfuric acid and the use of different chemicals such as silver sulfate and mercury sulfate which are hazardous and/or expensive (Jirka and Carter, 1975; Stenger and Van Hall, 1967). However, the initial equipment cost is quite cheap, which makes it worth trying to modify this test to obtain a rapid and accurate control method for the organic matter in industrial ceramic wastewaters, if it does exist a direct relationship between COD value and carbon at 490 °C.

The aim of this study is the setting up of a simple, fast, and accurate control method for the determination of the amount of organic matter in industrial ceramic wastewaters and sewages to be used to accept or reject these wastewaters in the industrial spray-driers, by studying the relationship between carbon at 490 °C and COD and modifying the current COD test to make it faster and more environmentally friendly.

## 2. Experimental

The present study was approached in two different steps: a first research to find a relationship between the amount of carbon at 490 °C and the value of COD, and, in a second stage, the design of a rapid method for the determination of COD more environmentally friendly.

### 2.1. Instrumentation

For the determination of COD, samples were digested in a model VELP-ECO 6 6-position thermoreactor from VELP SCIENTIFICA with settable temperature (up to 200 °C).

The determination of carbon at 490 °C was carried out in a model RC-412 elemental analyzer from LECO, provided with a tubular furnace capable of working at different temperatures in an oxidizing atmosphere, and an infrared cell detector.

A model ICS-1000 ionic chromatograph from DIONEX was used for the determination of the chloride content in the samples.

### 2.2. Reagents and reference materials

Unless otherwise noted, all reagents were ASC reagent grade. All reagent water was pure, with a conductivity less than 3  $\mu\text{S cm}^{-1}$ .

The following reagents were prepared for the determination of COD as indicated in the standard (UNE 77-004, 2002):

- Dichromate standard solution 0.250 N (Digestion solution)
- Silver sulphate–sulphuric acid solution (Catalyst solution)
- Ammonium ferrous sulphate standard solution 0.125 N (Titration solution)
- Solution of ferroin (indicator).
- Potassium hydrogen phthalate standard solution 2.0824 mM (Verification material)

The following reference materials were used for the determination of the amount of carbon at 490 °C:

- Calibration standard: GBW 07406 Soil from the National Research for Certified Reference Materials GBW.
- Validation standards: GBW 07401 Soil, GBW07404 Soil, and GBW07407 Soil from the National Research for Certified Reference Materials GBW.

### 2.3. Samples

Seven industrial wastewaters and sewages from different ceramic sources were selected to carry out the study. The samples were identified as follows: Wastewater A, Wastewater B, Sewage A, Sewage B, Sewage C, Sewage D, Sewage E, Sewage F. These samples were provided from different ceramic industries from their own productive process.

### 2.4. Experimental procedure

#### 2.4.1. Study of the amount of organic matter present in both the solid and the liquid fractions in the ceramic wastewaters and sewages

The standard COD procedure can be undertaken either in the overall sample or in the settled sample. In industrial wastewater and sewages, settling the sample can lead to erroneous results if the organic matter is present in the solid fraction.

To investigate whether the organic matter is mainly in the liquid or the solid fraction, COD determinations in the overall wastewaters (liquid + solid fractions) and determinations in the liquid fractions following the standard procedure were carried out in three of the selected samples. Table 1 shows the results obtained, together with the standard deviation ( $\sigma$ ).

From the results obtained, it can be concluded that the major part of COD content derives from the solid, as the amount of COD obtained in the liquid fraction is insignificant compared with the amount of COD of the overall sample.

**Table 1**

Determination of COD content in the overall sample (liquid and solid fractions) and liquid fraction in three of the samples selected for this study.

	COD (mg O <sub>2</sub> L <sup>-1</sup> ) (liquid + solid)	COD (mg O <sub>2</sub> L <sup>-1</sup> ) (liquid)
Sewage A	1200 ± 20	53 ± 3
Sewage C	2368 ± 40	428 ± 10
Sewage D	829 ± 13	106 ± 5

In a previous work, [Aghasadeghi et al. \(2018\)](#) studied the correlation between conventional COD determination and the determination of COD via a photoelectrochemical measurement. COD values obtained with the photoelectrochemical method were lower than those obtained with the reference method and they attributed it to the fact that the sample must be filtered prior to the photoelectrochemical measurement as it is a colorimetric method. In that case, they found a good agreement filtering also the samples to carry out the reference COD determination, but as it has been demonstrated in this study, wastewaters and sewages cannot be filtered as the organic matter is mainly in the solid fraction, which would result in an error in the determination and bring about unexpected problems in the industrial process.

#### 2.4.2. Relationship between the amount of carbon at 490 °C and the value of COD

COD value and carbon at a temperature of 490 °C were analyzed in the samples selected in this study.

COD determination was carried out following the standard method which involves the boiling of a sample in a strong acidified medium with sulfuric acid, with the introduction of  $K_2Cr_2O_7$  (as the oxidant agent),  $HgSO_4$  (to eliminate the chloride interference), and  $Ag_2SO_4$  (as catalyst) for a certain period during which part of dichromate is reduced by the oxidable matter present in the sample. The excess or unreacted  $Cr_2O_7^{2-}$  is titrated with Mohr's salt and COD value is obtained from the amount of dichromate reduced (back titration).

The determination of  $C_{490\text{ °C}}$  was conducted in an elemental analyzer submitting the dried sample to a heating process from a temperature of 25 °C to a temperature of 490 °C in an oxygen atmosphere, the carbon released being analyzed in an infrared cell ([Gazulla et al., 2012](#)).

#### 2.4.3. Design of a rapid and environmentally friendly method for the determination of COD

##### A. Optimization of the digestion time

In accordance with standard [UNE 77-004, 2002](#), samples must be in continuous boiling at a temperature of 148 °C for 110 min to carry out the test ([UNE 77-004, 2002](#)).

The first approach to get the proposed objectives was the reduction of the time needed to carry out the test by studying the digestion time necessary to oxidize all the compounds present in the samples of wastewater and/or sewage. For that, several tests were carried out at different digestion times and the results obtained were compared with the one obtained with 110 min digestion time.

##### B. Study of the necessity of the use of $HgSO_4$ . Interference of chlorides

According to different literature consulted, chlorides are an important interferent in COD determination as they are reducing agents and react with the dichromate increasing the COD value. The addition of  $HgSO_4$  reduces this interference by the formation of the soluble complex chloromercuriate (II). The standard test method only applies to samples with a maximum value of 1000 mg Cl L<sup>-1</sup>. Different books of wastewater analysis state disparate maximum chloride values of 2000 mg L<sup>-1</sup> and 3000 mg L<sup>-1</sup> ([Apha et al., 1992](#); [Rodier, 1989](#)). [Dobbs and Williams \(1963\)](#) propose a modification in the procedure to be able to analyze samples with higher chloride concentrations, but all them agree on the use of  $HgSO_4$  to eliminate this interference.

Mercury sulphate is a toxic reagent, so its use is not desirable. Therefore, a study of the necessity of using this reagent was also carried out in the present research. For that, the chloride content of all the samples analyzed in this study was determined by ionic chromatography and COD determination was undertaken with and without the addition of  $HgSO_4$ . As all samples selected for this study presented low chloride contents (below 300 mg L<sup>-1</sup>), one of the samples was also spiked with different amount of chlorides (from 50 to 500 mg Cl L<sup>-1</sup>) to study the need of the use of mercury sulphate with higher chloride concentrations.

##### C. Study of the necessity of the use of $Ag_2SO_4$

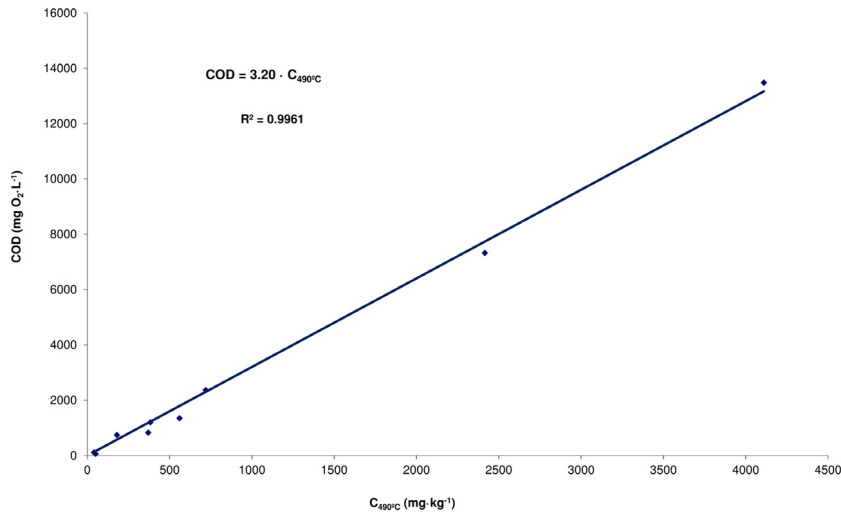
Silver sulphate is used as a catalyst to increase the oxidation speed of some organic components such as alcohols, organic acids, and aliphatic hydrocarbons of non-ramified chain ([UNE 77-004, 2002](#)). This is an expensive and toxic reagent, so it was thought that it would be worth studying the real need of using this catalyst in the type of samples that were under study.

Several COD determinations with and without the addition of silver sulphate were undertaken to study if there were differences in the results obtained.

**Table 2**

Results of COD and carbon at 490 °C obtained in the wastewaters and sewages selected for this study.

	COD (mg O <sub>2</sub> L <sup>-1</sup> )	C <sub>490 °C</sub> (mg kg <sup>-1</sup> )
Wastewater A	114 ± 4	41 ± 5
Wastewater B	60 ± 3	50 ± 5
Sewage A	1200 ± 20	383 ± 15
Sewage B	13 485 ± 110	4110 ± 100
Sewage C	2368 ± 40	720 ± 20
Sewage D	742 ± 12	180 ± 9
Sewage E	829 ± 13	370 ± 12
Sewage F	7328 ± 45	2415 ± 50

**Fig. 1.** Relationship between COD value and carbon at 490 °C.

### 3. Results

#### 3.1. Relationship between the amount of carbon at 490 °C and the value of COD

Table 2 shows the results of COD and carbon at 490 °C obtained in the wastewaters and sewages analyzed in this study, together with the standard deviation ( $\sigma$ ).

Fig. 1 shows the correlation between both parameters studied, together with the equation of the linear adjust and its regression ( $R^2$ ).

Data show good correlation between them as the linear adjust regression is higher than 0.99. From the equation obtained for the relation between both parameters, the value of  $n$  can be calculated, obtaining a value of 1.7, which is between the range stated by Ronzano and Dapena. Therefore, the correlation obtained agrees with that find in the literature which, together with the good regression coefficient obtained, make the method proposed appropriate to be used in the control of organic matter in industrial ceramic wastewaters and sewages.

#### 3.2. Design of a rapid and environmentally friendly method for the determination of COD

Generally, a method that is intended to be used for controlling the specifications of a product must be quick as the unloading of the product mostly depends on the results obtained. Related to the reuse of industrial wastewaters and sewages, they are normally transported by truck and the wastewater or sewage cannot be unloaded until it is checked. That is the reason why it is important to have a rapid method.

COD test as it is established in the standards takes too long to be used as a control method so, once the correlation between COD and  $C_{490 °C}$  was found, some modifications were undertaken in the standard procedure to reduce the analysis time and to have also a more environmentally friendly method, as the standard one uses hazardous and expensive chemicals.

##### 3.2.1. Optimization of the digestion time

Several tests with different digestion times were undertaken to study if it could be reduced. Table 3 shows the results obtained in the analysis of Sewage D together with the results obtained in the analysis of the verification material.

**Table 3**  
Determination of COD content with different digestion times.

COD (mg O <sub>2</sub> L <sup>-1</sup> )		
Digestion time (min)	Sewage D	Verification material (500 mg O <sub>2</sub> L <sup>-1</sup> )
120	829 ± 13	504 ± 10
10	710 ± 12	452 ± 11
20	790 ± 14	465 ± 9
30	840 ± 13	500 ± 10
35	835 ± 14	497 ± 10

**Table 4**  
Determination of COD content using the shortened digestion time.

COD (mg O <sub>2</sub> L <sup>-1</sup> )		
Sample	In accordance with UNE 77-004 (2002) (158 min digestion time)	30 min digestion time
Sewage C	2368 ± 40	2310 ± 38
Wastewater A	60 ± 3	65 ± 2
Verification material (500 mg O <sub>2</sub> L <sup>-1</sup> )	495 ± 10	498 ± 11

**Table 5**  
Determination of COD content with and without the addition of HgSO<sub>4</sub>.

	Cl <sup>-</sup> (mg L <sup>-1</sup> )	COD (mg O <sub>2</sub> L <sup>-1</sup> ) (with HgSO <sub>4</sub> )	COD (mg O <sub>2</sub> L <sup>-1</sup> ) (without HgSO <sub>4</sub> )
Sewage B	252 ± 5	13485 ± 110	13504 ± 105
Sewage C	284 ± 4	2368 ± 40	2347 ± 42
Sewage D	153 ± 4	730 ± 14	742 ± 12
Sewage E	104 ± 5	829 ± 13	809 ± 14

**Table 6**  
Determination of COD content with and without the addition of HgSO<sub>4</sub> in Sewage C with different additions of chloride.

Spiked Cl <sup>-</sup> content (mg L <sup>-1</sup> )	Cl <sup>-</sup> content in the sample (mg L <sup>-1</sup> )	COD (mg O <sub>2</sub> L <sup>-1</sup> ) (with HgSO <sub>4</sub> )	COD (mg O <sub>2</sub> L <sup>-1</sup> ) (without HgSO <sub>4</sub> )
0	284 ± 4	2368 ± 40	2347 ± 45
50	334 ± 5	2379 ± 37	2309 ± 38
100	384 ± 3	2396 ± 35	2379 ± 37
200	584 ± 3	2379 ± 42	2414 ± 40
500	784 ± 5	2361 ± 41	2379 ± 42

Different digestion times were tested, the results compared with the one obtained following the standard methodology. The results showed that with a total digestion time of 30 min, COD value was the same than that obtained with a digestion time of 120 min, which supposed that for the sample used a maximum time of 30 min was enough to completely oxidase all the oxidable compounds present in it. This behavior was also observed in the verification material. After that, samples with different COD content and different matrices were tested using the shortened digestion time and the results were compared with the ones using the standard method. Table 4 shows the results obtained for a wastewater and a sewage together with the result obtained in the analysis of the verification material.

No significant differences were found between the results obtained using the standard method (120 min digestion time) and reducing the digestion time to 30 min, which assure that the digestion time can be reduced to 30 min to analyse wastewaters and sewages from the chemical and ceramic industries. Besides, the verification material, which is a synthetic sample prepared from potassium hydrogen phthalate to have a COD value of 500 mg O<sub>2</sub> L<sup>-1</sup>, assured the accuracy of the test in both cases.

Consequently, the reduction in time will permit this test to be used as a control method in the determination of organic matter in industrial ceramic wastewaters and sewages.

### 3.2.2. Study of the necessity of the use of HgSO<sub>4</sub>. Interference of chlorides

Table 5 shows the results of the chloride content together with the results of COD, with and without the addition of mercury sulphate.

No significant differences were obtained between the COD content obtained with and without the addition of HgSO<sub>4</sub> in samples with a chloride content lower than 300 mg L<sup>-1</sup>.

As chloride content present in the samples analyzed is low, different chloride concentrations were added to SEWAGE C to design a robust method. Table 6 shows the results obtained.

**Table 7**

Determination of COD content with and without the addition of  $\text{Ag}_2\text{SO}_4$  in different sewages selected for this study.

Sample	COD ( $\text{mg O}_2 \text{ L}^{-1}$ ) With $\text{Ag}_2\text{SO}_4$	COD ( $\text{mg O}_2 \text{ L}^{-1}$ ) Without $\text{Ag}_2\text{SO}_4$
Sewage A	$1200 \pm 20$	$1280 \pm 18$
Sewage B	$13560 \pm 100$	$13501 \pm 109$
Sewage C	$2368 \pm 40$	$2395 \pm 39$

According to the results obtained, chloride in concentrations up to  $800 \text{ mg L}^{-1}$  do not interfere in COD determination in the type of samples selected for the study, contrary to what is stated in the consulted literature COD determination in the type of samples selected for the study, contrary to what is stated in the consulted literature (UNE 77-004, 2002; Apha et al., 1992; Dobbs and Williams, 1963; Rodier, 1989). Thus, the addition of mercury sulphate would not be necessary for COD determination in ceramic wastewaters and sewages from the ceramic industry and can be eliminated from the analysis procedure.

### 3.2.3. Study of the necessity of the use of $\text{Ag}_2\text{SO}_4$

Table 7 shows the results of COD content of different sewages, the assay carried out with and without the addition of silver sulphate.

As can be seen from the results obtained, there are no significant differences between the results obtained with and without the addition of silver sulphate in the analyzed samples. The no need of this catalyzer is probably due to the more simplicity of the organic components present in the ceramic industrial wastewater and sewages.

## 4. Conclusions

A direct and lineal relationship between the COD value and the organic matter content was found, so COD measurement can be used as the quality control method for the determination of the organic matter of industrial ceramic wastewaters and sewages reused in the spray-driers.

Total analysis time of COD was reduced to 30 min plus the time needed for back-titration which makes the determination fast enough to be used as a control method, prior to the unloading of the truck, which will result in a decrease of the risk of obtaining defects in the final product, and leading in an increase of the productivity and an improvement in the final product quality.

The methodology is more environmentally friendly as it has been demonstrated that the use of hazardous chemicals such as  $\text{Ag}_2\text{SO}_4$  and  $\text{HgSO}_4$  is not necessary in the determination of COD content in industrial ceramic wastewaters and sewages. These actions eliminate the use of 6.4 g of  $\text{HgSO}_4$  and 2.4 of  $\text{Ag}_2\text{SO}_4$  per day, supposing that 8 trucks are controlled per day, which is a considerable reduction in the generation of toxic residues.

Organic matter is mainly present in the solid fraction, thus not being possible the filtering of the sample prior to the COD determination.

The proposed method is appropriate to be used to accept or reject the use of industrial ceramic wastewaters and sewages in the spray-driers in a relatively short time.

## 5. Acknowledgments

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## Conflicts of interest

There are no conflicts to declare.

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