REAL-TIME CONTROL OF ORGANIC MATTER CONTENT IN INDUSTRIAL WASTEWATER

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ABSTRACT

In the ceramic body preparation process by the wet method, using spray drying, the clays and other raw materials are mixed with water and ground in industrial mills to an appropriate particle size distribution. The presence of organic matter in these bodies can give rise to so-called black core inside the tiles during the tile firing process.

In ceramic body preparation by spray drying, industrial wastewater, which can contain considerable quantities of organic matter, is customarily used.

At present there is no method for real-time monitoring of the amount of organic matter contained in wastewater or sludge, which allows their acceptance or rejection for use in the spray-drying process. There are different standard test methods for

determining organic carbon, but all require previous drying treatment of the sample, as the test needs to be performed on a solid sample, which makes the process too time consuming for use as a control method.

Since chemical oxygen demand (COD) is a parameter that determines the amount of oxygen consumed for total chemical oxidation, the possibility was studied of finding a relationship between COD and organic matter content in industrial wastewater.

Industrial wastewater from different sources was analysed and a linear relationship was found between COD and organic matter content. The different variables such as chloride content, which might affect this determination, were studied and the method was optimised to make it rapid and more respectful of the environment, shortening digestion time and eliminating the hazardous reagents used in the standard method.

A method has thus been developed for real-time control of organic matter content in industrial wastewater.

1. INTRODUCTION

Industrial wastewater is typically used in preparing ceramic bodies when they are prepared by the wet method, using spray drying. Such water can contain organic matter that may subsequently generate black coring in the tile firing process if there is a significant amount of organic matter. Industrial wastewater reuse in the spray-drying process is due to the steady growth in industrial demand for water and strict regulations on environmental dust control, which have led to a constant increase in water supply and wastewater treatment costs [1]. A key variable that needs to be controlled is, therefore, organic carbon concentration [2,3].

There are several standard methods for determining organic carbon, such as EN 13137, ASTM D7573, UNE 77321, and DIN 19539. This last standard differentiates between inorganic carbon, organic carbon, and elementary carbon and sets out a method for determining different carbon species based on sample combustion at different temperatures in oxygen atmosphere and IR detection.

Organic matter can also be controlled by determining the chemical oxygen demand (COD), i.e. the concentration of substances liable to chemical oxidisation [4].

In the case of industrial wastewater and sludge, which are made up of a liquid and a solid fraction, organic matter can be controlled by analysing carbon at an appropriate temperature in the dried sample, a temperature of 490ºC being used, which requires previous sample preparation.

This test entails the drawback of requiring too much time to enable it to be used as a control method. Therefore, if a direct relationship could be established between the value of the COD and the value of carbon at 490ºC, the COD determination might be an alternative method for controlling organic matter in this type of material.

Ronzano and Dapena [5] studied the different methods for controlling organic matter in wastewater and found the following experimental equation that relates organic carbon to the COD value:

$$COD=n\cdot(1.87\cdot Corg-17)$$

Where n depends on sample degree of degradation and usually lies between 1 and 3.

The standard test method for determining COD (UNE 77-004) is quite tedious and requires a relatively long digestion process with sulfuric acid and the use of different chemical reagents such as silver sulphate and mercury sulphate, which are hazardous and/or expensive [6]. However, as the initial outlay in equipment is quite low, in this study, it was sought to modify this test to develop a rapid and accurate control method for determining organic matter in ceramic industry wastewater, provided a direct relationship between the value of the COD and carbon at 490ºC could be found.

The study was undertaken to develop a method of simple, rapid, and accurate control for determining organic matter content in ceramic industry wastewater and sludge, which would allow a particular industrial water for industrial spray dryers to be accepted or rejected, examining the relationship between carbon at 490ºC and the COD value and modifying the current approach for determining this parameter to make the method faster and more respectful of the environment.

2. EXPERIMENTAL

The study was conducted in two stages: the relationship between the amount of carbon at 490ºC and the COD was studied first, followed by design of a rapid and more environmentally respectful method for determining the COD value.

2.1. RELATIONSHIP BETWEEN CARBON AT 490ºC AND THE COD VALUE

The COD was determined according to the standard method, which involves boiling the sample in a strongly acid medium (H_2SO_4) for a set time, adding $K_2Cr_2O_7$ (as oxidising agent), $HgSO_4$ (to eliminate any interference from the presence of chloride), and Ag_2SO_4 (as a catalyst). Part of the dichromate was reduced, owing to the oxidisable matter present in the sample, and the excess $Cr_2O_7^{2-}$ was titrated with Mohr's salt.

The tests were carried out in a VELP-ECO 6 digester supplied by VELP SCIENTIFICA. The results were validated by analysing a standard solution of potassium hydrogenophthalate together with the samples.

Carbon was determined at 490ºC in a LECO RC-412 elemental analyser, equipped with a tube furnace that worked at different temperatures in an oxidising atmosphere, subjecting the dried sample to heating from 25ºC to 490ºC, carbon release being analysed in an infrared cell [7]. The following reference materials were used to calibrate and validate the measurements: GBW07406 Soil as calibration standard and the materials GBW 07401 Soil, GBW 07404 Soil, and GBW 07407 Soil as validation standards, all supplied by National Research for Certified Reference Materials.

The study was performed on six samples of wastewater and sludge, from different ceramic industry companies, referenced as follows: Wastewater 1 (RS1), Wastewater 2 (RS2), Sludge 1 (L1), Sludge 2 (L2), Sludge 3 (L3), Sludge 4 (L4), and Sludge 5 (L5).

2.2. DESIGN OF A RAPID AND ENVIRONMENTALLY RESPECTFUL METHOD OF COD DETERMINATION

The design of a rapid and environmentally respectful method of COD determination was addressed by studying and/or optimising three variables: digestion time, to make it sufficiently fast for use as a control method; the need to use mercury sulphate (II) ($HgSO_4$); and the need to use silver sulphate (Ag_2SO_4), suppression of both of which would make the test method more respectful of the environment.

Optimisation of digestion time

The test method in standard UNE 77-004 [8] requires keeping the samples boiling at 148ºC for 120 minutes.

The first tests were conducted with a view to reducing test time, shortening the digestion time needed to oxidise all compounds contained in the test samples. To do so, COD tests were performed at different digestion times (between 10 and 35 minutes), the results then being compared with those obtained after 120-minute digestion.

Study of the need to use $HgSO_4$.

According to the literature, chlorides interfere significantly in determining the COD value, as they act as reducing agents that react with dichromate and, hence, raise the resulting COD value. Adding $HgSO_4$ diminishes this interference by forming soluble chloromercuriate. Dobbs and Williams [9] proposed a modification to the method to enable analysis of samples with chloride contents up to 2000 mg Cl-·L-1, using $HgSO_4$ to eliminate this interference.

Mercury sulphate (II) is a toxic reagent, which makes its use inadvisable. The need to use it in testing the materials at issue was therefore examined by determining the chloride content in all test samples, using ion chromatography, and determining the COD with and without the addition of $HgSO_4$. As all test samples exhibited relatively low chloride values (below 300 mg Cl-·L-1), different amounts of chlorine were added to one the samples (from 50 to 500 mg Cl-·L-1) to study whether this reagent needed to be used in the presence of higher chlorine concentrations.

Study of the need to use Ag_2SO_4

Silver sulphate is used as a catalyst to increase the oxidation rate of some organic compounds such as paraffin hydrocarbons (alcohols and acids) [6]. This reagent is quite expensive, in addition to being toxic, so that the need for its use in the type of samples being studied was also examined. To do so, tests were conducted to determine the COD with and without adding Ag_2SO_4 and the results were compared.

3. RESULTS

3.1. RELATIONSHIP BETWEEN CARBON AT 490ºC AND THE COD VALUE

Table 1 details the results obtained, together with their uncertainty (I), in the determination of the COD value and carbon at 490ºC of the test samples.

	COD (mg $O_2 \cdot L^{-1}$)	$C_{490ºC}$ (mg·kg^{-1})
AR1	108 ± 10	72 ± 10
AR2	63 ± 10	42 ± 10
L1	1420 ± 22	405 ± 15
L2	8749 ± 60	2758 ± 90
L3	2499 ± 40	910 ± 20
L4	5328 ± 40	1815 ± 40
L5	611 ± 15	141 ± 10

Table 1 *Results of COD and $C_{490ºC}$ obtained in the studied samples*

The relationship between the two studied parameters, together with the equation of the linear fit and the regression curve value (R), is shown in Figure 1

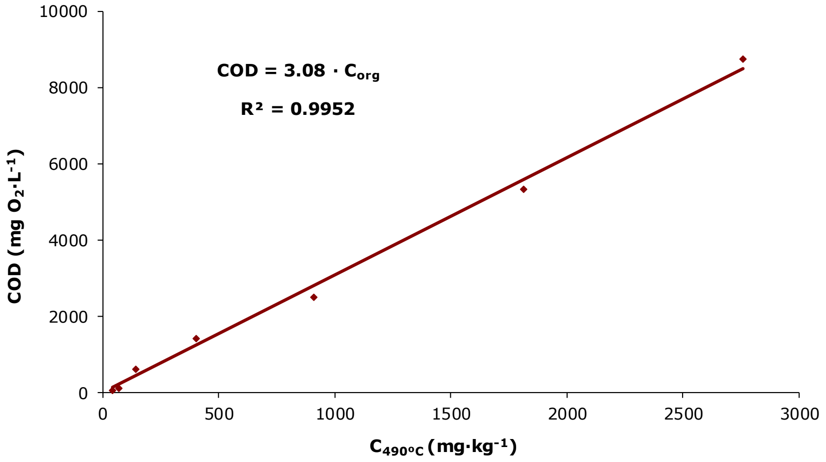

Figure 1 *Relationship between the COD value and carbon at 490ºC*

The results exhibited good linear correlation, as the value of R was above 0.99. The equation obtained of the relationship between both parameters was used to calculate the value of n, a value of 1.6 being obtained, which lay within the range reported by Ronzano y Dapena [5] on measuring organic pollution in wastewater. The relationship obtained between both parameters therefore coincided with that found in the literature, which, together with the good regression coefficient obtained, indicated that the proposed method was appropriate for use in controlling organic matter in ceramic industry wastewater and sludge.

3.2. DESIGN OF A METHOD FOR RAPID AND ENVIRONMENTALLY RESPECTFUL COD DETERMINATION

Any method to be used in controlling product specifications usually needs to be rapid. Industrial wastewater and sludge are generally transported by tank truck and cannot be unloaded until they have been duly checked. It is therefore important to have an appropriate control method.

Optimisation of digestion time

Table 2 details the results obtained on analysing sample L5, together with those obtained in the validation material (with a known COD value of 500 mg $O_2 \cdot L^{-1}$), at different digestion times.

Digestion time (min)	*COD (mg $O_2 \cdot L^{-1}$)*	
	L5	***Validation material***
120 (according to UNE 77-004)	611 ± 15	504 ± 10
10	494 ± 15	450 ± 9
20	568 ± 16	472 ± 10
30	614 ± 14	502 ± 11
35	610 ± 15	499 ± 10

Table 2 *Determination of the COD value at different digestion times in sample L5*

The table shows that the COD value obtained after 30-minute digestion was the same as that the obtained after 120 minutes, both in sample L5 and in the validation material, indicating that, for the studied sample, 30 minutes sufficed to oxidise the organic compounds in the sample. Samples were then therefore selected with high and low COD values and tested at 30-minute and 120-minute digestion times to verify whether they also exhibited the same behaviour. The results are listed in Table 3.

Sample	*COD (mg $O_2 \cdot L^{-1}$)*	
	120 min (according to UNE 77-004)	***30 min***
L3	2499 ± 40	2475 ± 38
AR1	108 ± 4	110 ± 7
Validation material (500 mg $O_2 \cdot L^{-1}$)	494± 12	501 ± 10

Table 3 *Determination of the COD value at 30-min and 120-min digestion times*

There were no significant differences in any test sample on shortening digestion time, confirming that digestion time could be reduced to 30 minutes for ceramic industry wastewater and sludge COD analysis. In addition, the validation standard, a synthetic sample prepared from potassium hydrogenophthalate to exhibit a COD value of 500 mg $O_2 \cdot L^{-1}$, assured method accuracy.

Therefore, the shorter test time would allow this method to be used as control method in determining the organic matter content in industrial wastewater and sludge.

Study of the need to use $HgSO_4$.

Table 4 details the results of the chloride determination, together with the COD results, with and without mercury sulphate addition, in four of the test samples with different COD and chloride values.

	Cl^- ($mg \cdot L^{-1}$)	COD (mg $O_2 \cdot L^{-1}$) (with $HgSO_4$)	COD (mg $O_2 \cdot L^{-1}$) (without $HgSO_4$)
L1	148 ± 4	1420 ± 22	1437 ± 22
L2	294± 5	8749 ± 60	8740 ± 57
L3	252 ± 5	2499 ± 40	2507 ± 42
L5	132 ± 6	611 ± 15	604 ± 16

Table 4 *Determination of the COD value with and without $HgSO_4$ addition*

The results show there were no significant differences between the COD value with and without $HgSO_4$ addition in samples with a chloride content below 300 $mg \cdot L^{-1}$.

As the chloride content in the analysed samples was not very high, chloride additions were made to sample L3 with a view to designing a robust method. The results obtained are detailed in Table 5.

Cl^- addition ($mg \cdot L^{-1}$)	Cl^- concentration in the sample ($mg \cdot L^{-1}$)	COD (mg $O_2 \cdot L^{-1}$) (with $HgSO_4$)	COD (mg $O_2 \cdot L^{-1}$) (without $HgSO_4$)
0	252 ± 5	2499 ± 40	2507 ± 42
50	302 ± 5	2489 ± 38	2408 ± 40
150	402 ± 5	2502 ± 35	2500 ± 35
300	552 ± 5	2488 ± 42	2468 ± 37
500	752 ± 5	2510 ± 45	2490 ± 37

Table 5 *Determination of the COD value with and without $HgSO_4$ addition with different chloride additions*

The results indicate that concentrations up to 750 mg $Cl^- \cdot L^{-1}$ did not interfere in the COD determination in the type of samples selected for this study, unlike reports in the literature [9-11]. The addition of mercury sulphate was therefore unnecessary in determining the COD in the test ceramic industry wastewater and sludge and could therefore be eliminated from the analysis process.

Study of the need to use Ag_2SO_4

The results of the COD in different sludges, on performing the test with and without the addition of silver sulphate, are set out in Table 6.

Sample	COD (mg $O_2 \cdot L^{-1}$) (with Ag_2SO_4)	COD (mg $O_2 \cdot L^{-1}$) (without Ag_2SO_4)
L2	8749 ± 60	8795 ± 60
L3	2499 ± 40	2479 ± 38
L5	611 ± 15	615 ± 16

Table 6 *Determination of the COD value with and without Ag_2SO_4 addition in three selected test sludges*

No significant differences were observed in the results obtained with and without silver sulphate addition in the analysed samples. The use of this catalyst may therefore be unnecessary, owing to the nature of organic compounds present is this type of samples.

4. CONCLUSIONS

In this study, a linear relationship was found between the COD value and organic matter content, so that COD measurement can be used as quality control method for determining organic matter content in industrial wastewater and sludge reused in spray dryers.

COD digestion time was reduced to 30 min, making it suitable for use as a control method before the tank truck is unloaded, to reduce the risk of defects appearing and to increase productivity and improve end-product quality.

The methodology developed is more environmentally respectful because it suppresses the use of hazardous reagents such as mercury sulphate and silver sulphate, as they are unnecessary for determining COD in ceramic industry wastewater and sludge samples. This eliminates the use of 6.4 g $HgSO_4$ and 2.4 g Ag_2SO_4 per day, assuming 8 tank trucks are controlled per day, entailing quite a considerable reduction in toxic waste.

The proposed method is appropriate for accepting or rejecting ceramic industry wastewater and/or sludge for use in spray dryers.

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