Organic Load Monitoring

in the Biological Denitrification Process as done in a Plastic Fiber Chemical Plant.

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Introduction

To evaluate the pollution level in industrial waste water it is important to know the exact content of organic substances.

The evaluation of organic substances is traditionally made by analytical methods based on oxygen consumption in a chemical oxidation reaction (mg/L of O_2 as COD) or in a biochemical oxidation reaction (mg/L of O_2 BOD) of such organic substances.

Instruments which carry out the direct measurement of pollutant charge by means of Total Organic Carbon (TOC) content are becoming more and more widespread.

These analyzers are able to use different technology, particularly in the oxidation stage. The one chosen by the plastic fiber chemical plant is based on the low temperature oxidation of the organic material promoted by UV light.

This technique was preferred because it does not allow corrosion or poisoning of the catalyst in the same way that the high temperature combustion technique does.

Determination of Organic Material

It is well known that COD measurement does not represent the exact organic load in industrial waste water, since the dichromate oxidation is not able to thoroughly oxidize certain organic substances such as aromatic hydrocarbon, pyridine etc.

On the contrary TOC measurement offers the following advantages:

- very speedy analysis and response time.
- on site installation
- high precision and accuracy
- low costs per analysis compared to laboratory COD or on line COD analysis.
- no introduction of dangerous materials such as silver, mercury-chrome and iron into laboratory waste waters (these metals are actually present in the residual solution of COD method).

Working principle of a TOC analyzer

TOC determination is based on chemical oxidation by persulphate and oxygen at low temperatures, catalyzed by UV radiation.

CO_2 deriving from the oxidation of the organic carbon in the sample is measured by an appropriate ND-IR analyzer, which handles the linearization, autocalibration and autocleaning functions.

The waste water sample is introduced to the analyzer by a peristaltic pump which allows a quick and "on-time" analysis of the water which is present in the waste at a specific time.

The system allows the operator to introduce a sample manually, via a three way valve, allowing for the batch analysis of a grab sample or a standard solution.

The instrument measures the total organic carbon (TOC) after acidification with H_3PO_4 , and scrubbing with CO_2 free compressed air .

If the acidification stage is bypassed, total carbon (TC= TOC+TIC) can be measured.

Different measuring ranges can be chosen before installation of the analyzer, or during its operation if required. This is done with a new configuration of the tubing and pumps, and new calibration.

Only a few hours are required to change the measurement ranges.

On line analysis

The plant effluent analyzed was a mixture of substances deriving from the polymerization processes which took place during chemical fiber production (i.e. PA-6, PES and ACN) as well as organic intermediates (i.e. MA and MAS).

The effluent, after pH adjustment, was treated in the course of the biologic denitrification process because of its high concentration of nitrates.

The biologic denitrification process is based on the following reaction in which NO3- is reduced to N_2.

1)	$2\,NO_3 + 4e$	⇨	$2\,NO_2$
2)	$2\,NO_2 + 6e$	⇨	N_2
3)	$2\,NO_3 + 10e$	⇨	N_2

Electrons used for the reduction of nitric-nitrogen to nitrogen are supplied by the oxidation reactions of organic matter effected by denitrifying bacteria which belong to species: Pseudomonas, Micrococcus, Bacillus.

In order to guarantee that these microorganisms are properly fed, an organic substrate (i.e. methanol) is added to the effluent, thus avoiding an incomplete denitrification stage.

The entire redox reaction is

$$6\,N0_3^- + 5CH_3OH \Rightarrow 3N_2 + 5CO_2 + 7\,H_2O + 6OH^-$$

From a stechiometric point of view, 5/6 of the methanol moles are used to reduce one nitrate mole; so the exceeding methanol is added because some are oxidized by dissolved oxygen and some are used by the bacteria.

In order to assure good bacterial growth there must be a correct mixture of nutrients containing :

carbon / nitrogen / phosphor
in the ratio of
C : N : P = 100 : 5 : 1

The efficiency of the denitrification reaction not only depends on the organics vs nitrates ratio, but also on pH , on water temperature and the retention time in the activated sludge treatment plant.

For good monitoring of the plant's operation, analysis must be performed on various different samples , at different points of the plant .

Those points are :

1) Inlet waste water flowing into the treatment plant (S12). In this stage the waste water pH is lowered to 4 and passes through a clarification stage.
2) Mixing (Balancing) tank (S22): At this point the methanol and the phosphoric acid are added to the waste water in a measured amount which is related to organic load and the initial nitric load. The addition of chemicals can be completely automated with the use of the output signal given by the on line analyzer.
3) Denitrification tank (S23). The waste water undergoes, in this stage, biologic denitrification. In this tank denitrifying bacteria metabolize organic substances and reduce the nitrates to elementary nitrogen.
4) Outlet (S36): water coming from the denitrification tank and flowing into the biologic oxidation tank where the bacteria metabolize the residual organics and where oxygen is added from the aeration turbines.

The aerated water mixture left the oxidation tank and flowed into the settling tank where the particles were collected on the bottom and the clarified water flows away.

Grab samples were taken by automatic sampling unit and analyzed in the laboratory in order to determine the COD values and to calculate the correlation factor between the COD and TOC analysis for each sampling point.

The sampling point reliability as well as the efficiency of analyzer oxidation was tested.

Results

In the final table, the COD and TOC values are shown along with the related correlation factors of four samples identified by S12, S22, S23, S36.

Keeping in mind that the analytical correlation factor of COD/TOC results from the theoretical ratio between the value expressed as O_2 / C : 2,66, we looked at the experimental results:

We observed that:

- The correlation factor between COD and TOC of waste water is specific to the water being tested and its characteristic value depends on the type of organic compound present in the water itself as well as the ratio existing between Organic material vs other material (such as N or S compounds which can be oxidized by the COD analysis).
- Correlation factors of samples S12, S23, S36 have given values very similar to the theoretic ratio O_2/C. This is due to the lowered oxidability of dichromate for specific organic matter which is present in the waste water (acrylonitrile, methyl acrylate etc.).
- Sample S22 , in which the organic load is enriched with methanol , has shown a higher correlation factor (3.5) and corresponds to the theoretic COD/TOC ratio (and the experimental one) we found for methanol (i.e. 4).
- The Organic load of industrial waste water may easily be monitored on line with the help of a TOC analyzer, and since it is possible to convert the recorded TOC value to COD using the right correlation factor, we can compare them to all historical date relative to the plant.

A solution was analyzed several times at different moments , and the values obtained are as follows :

82.5	82,2	83,2	82.6	83.2	83.4
83.6	83.1	82.3	82.7	82.6	82.5
82.8	83.4	83,3	83.5	83.1	84.0
82.9	82.3	84.1	83.5	82.5	82.9

The average of the different measurements is 83 mg/L TOC with a deviation of 0,58

In the previous table the tests done to evaluate the analyzer's reproducibility and reliability (s) are shown.

They were calculated on the basis of a sample mean value of 83 mg/l of C and corresponds to 0.58.

In order to evaluate the oxidation efficiency of the TOC method, several tests on standard solutions of organic and inorganic matter, suitably prepared, were performed.

All obtained values are shown in the final table.

From these results it is evident to see the efficiency and thoroughness of the TOC analysis made with low temperature UV persulfate oxidation technology.

Conclusions

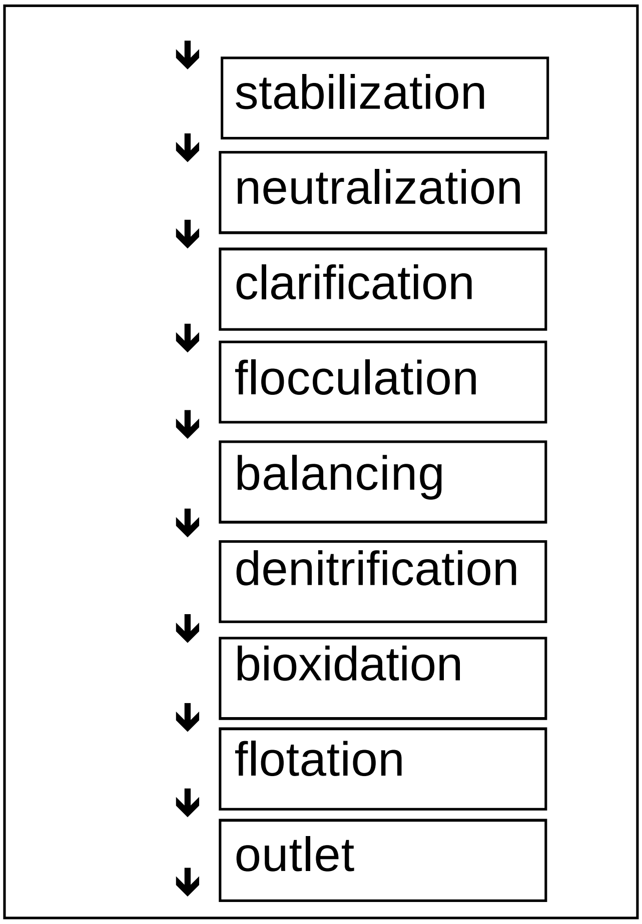
It can be concluded that TOC measurements are comparable to the more common laboratory COD measurements for the better evaluation of the true organic load present in the plant waste water and consequently its pollution state.

The next step would be to evaluate the possibility of complete automation of the Waste water treatment plant using all data received from the different analyzers, flowmeters and then optimize the process.

It has been estimated that at the end of this project, running costs of the w.w.t.p. would be reduced.

(Data obtained from research done by Mr. Bombardieri and Mr. Catucci)

chemicals	*theoretical mg/L concentration*	*measured value mg/L*	*oxidation efficiency %*
sodium carbonate (as TC)	1000	1003	100.3
sodium carbonate (as TC)	500	499	99.3
potassium phtalate	500	498	99.6
caprolactam	647	637	98.5
sodium carbonate (as TOC)	500	3	-
sodium sulfate (as TOC)	500	2	-
methanol	1000	988	98.8
pyridine	1000	991	99.1
ethanol	1000	500	100.0



Tank		S12			S22			S23			S36	
Date	COD	TOC	f	COD	TOC	f	COD	TOC	f	COD	TOC	f
14/jan	278	107	2.60	500	151	3.31	65	24	2.71	56	20	2.80
15	258	88	2.90	385	113	3.41	62	23	2.70	50	22	2.30
16	108	39	2.80	524	152	3.45	36	14	2.57	34	13	2.61
17	122	49	2.49	584	154	3.79	42	16	2.63	38	15	2.53
18	154	54	2.85	588	165	3.56	40	14	2.86	38	14	2.71
19	142	53	2.68	416	119	3.50	42	15	2.80	30	11	2.73
20	112	39	2.87	466	122	3.82	42	14	3.00	30	11	2.73
21	127	53	2.40	410	122	3.36	38	13	2.92	30	12	2.50
22	133	54	2.46	613	174	3.52	36	13	2.77	26	12	2.17
23	270	95	2.84	536	160	3.35	50	18	2.78	38	13	2.92
24	205	76	2.70	398	117	3.40	84	21	2.75	50	17	2.90
25	270	101	2.68	536	153	3.50	50	19	2.60	38	14	2.71
26	216	81	2.65	532	153	3.47	52	19	2.80	40	14	2.76
27	182	67	2.71	708	197	3.60	50	18	2.78	50	17	2.94
28	180	65	2.77	780	101	3.71	40	13	3.08	36	14	2.57
29	235	85	2.76	1085	297	3.65	131	46	2.80	79	30	2.60
30	260	91	2.86	557	165	3.38	187	63	2.97	127	50	2.56
31	163	60	2.70	465	120	3.88	60	22	2.73	34	13	2.61
1/feb	134	50	2.70	345	90	3.83	36	12	3.00	38	13	2.92
2	187	66	2.83	566	162	3.49	56	20	2.80	32	12	2.67
3	200	71	2.80	824	121	3.50	96	36	2.67	34	13	2.61
4	168	61	2.75	619	160	3.87	44	16	2.75	24	9	2.67
5	125	50	2.50	322	87	3.70	38	13	2.77	30	11	2.73
6	297	112	2.65	642	170	3.78	170	60	2.83	83	32	2.60
7	267	93	2.87	872	229	3.80	84	30	2.80	38	14	2.71
8	234	85	2.75	496	150	3.31	48	18	2.67	34	12	2.83
9	500	185	2.70	784	210	3.73	166	58	2.86	132	46	2.90
10	167	62	2.69	809	220	3.68	79	28	2.82	67	24	2.79
11	174	63	2.76	484	145	3.34	56	19	2.95	46	16	2.88
12	169	60	2.82	892	232	3.84	243	93	2.61	145	54	2.69
average	201	74	2.72	577	161	3.58	74	26	2.85	51	19	2.69
1/mar	202	74	2.73	420	120	3.50	49	17	2.88	48	18	2.66
2	174	63	2.76	524	145	3.61	47	17	2.76	38	15	2.53
3	216	79	2.73	465	137	3.39	44	17	2.58	42	16	2.62
4	200	71	2.80	439	124	3.35	50	18	2.78	44	17	2.60
5	238	92	2.59	481	134	3.60	33	12	2.73	32	12	2.58
6	202	71	2.84	926	262	3.53	34	13	2.63	26	9	2.88
7	470	188	2.49	806	233	3.45	49	18	2.72	33	12	2.75
8	239	85	2.81	568	154	3.68	42	17	2.47	34	13	2.61
9	233	90	2.58	520	143	3.63	62	22	2.81	50	21	2.38
10/mar	269	97	2.76	573	153	3.74	65	24	2.70	36	13	2.77
		av	**2.71**		**av**	**3.57**	**avera.**	**2.71**		**aver.**	**2.64**	
1/oct	451	167	2.70	539	150	3.60	114	43	2.65	48	19	2.52
2	270	102	2.65	568	167	3.40	80	22	2.70	44	17	2.58
3	321	121	2.65	528	151	3.50	40	16	2.50	30	12	2.50
4	290	112	2.60	512	148	3.45	46	17	2.70	38	14	2.70
5	606	224	2.70	841	246	3.42	68	25	2.73	38	14	2.71
6	263	104	2.53	628	180	3.49	72	27	2.68	46	19	2.42
7	268	96	2.80	859	148	3.57	76	29	2.60	48	19	2.52
8	380	146	2.60	677	184	3.68	42	16	2.62	34	12	2.83
9	224	86	2.61	752	220	3.41	66	25	2.65	40	16	2.50
10/oct	304	116	2.62	684	191	3.57	62	25	2.48	36	14	2.57
		av	**2.65**		**av**	**3.51**			**2.63**			**2.59**