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The influence of toxic pollutants on the absolute value and on the kinetics of the degradation of organic substances quantified as BOD

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ABSTRACT

This paper presents the toxic effects of some pollutants such as heavy metals (Cu, Zn, Cr, Ni, Cd, Pb, and Fe) and cyanides on the biochemical process of oxygen consumption for the determination of organic load of wastewater quantified as BOD5. The results show absolute values of BOD5 significantly influenced by the existence of tested substances in the wastewater and allow the establishing of a scale for the inhibitive effect of such substances taking into consideration the degree of reduction of the evaluated indicator. The kinetics completes the overall image on the consequences of the pollutants on the evolution in time of the biochemical reaction of oxygen consumption. The quality indicator BOD5 is used for the indirect determination of organic load from wastewater and it is the most employed parameter for characterising wastewater. The investigation of BOD5-related issues is of a paramount importance in order to ensure the requirements of a proper design and optimal functioning of wastewater treatment plants so that the quality of the effluent meets the quality standards regulated by the legislation regarding the preservation of water resources.

Keywords: *degradation, metals, organic substances (BOD5), wastewater.*

1. INTRODUCTION

As a result of intense urbanisation and industrialisation, increasing volumes of wastewater are generated, with a variable composition based on the pollution source. The characterisation of wastewater takes into consideration its physical properties, and chemical (organic and inorganic substances) and biochemical composition. Many of these parameters are interdependent [1,2].

Over the years, various analysis methods were developed for the quantification of the organic content of wastewater. For organic content higher than 1 mg/L, a global evaluation is employed, by means of oxidisability analysis. This consists in determining the consumption of oxidised substance (potassium dichromate) required for the oxidation of organic substances from a given volume of water and is expressed as oxygen equivalent. This determination is known as chemical oxygen demand (COD) [3,4].

The biochemical oxygen demand (BOD) is a parameter frequently used for characterising organic pollution and it represents the quantity of oxygen required for the biochemical decomposition of organic substances in aerobic conditions. The usual incubation period is 5 days, at a temperature of 20^{o}C. The BOD test results are reported as mg/L dissolved oxygen [3].

In establishing a relationship between these two parameters, the nature and sources of wastewater have an important role. The biological treatability of wastewater may be defined as the capacity of organic matter to be degraded, correlated to the capability of biomass to decompose it in a given time allowed for the process to take place. Symons defines the treatability of wastewater by means of the BOD/COD ratio (R). If R = 0.5 – 1.0, wastewater has a good treatability, while for R = 0.1 – 0.2, wastewater is hard to be treated by means of biological processes or contains toxic substances. For R values ranging from 0.2 to 0.5, the biological treatability is medium and the adaptation of bacterial population to the composition and concentration of wastewater is required [5].

The biochemical oxygen demand is an expression of the quantity of oxygen required for the biochemical degradation of organic matter from the wastewater. BOD measurement is used for determining the quantity of biodegradable organic matter present in water.

The BOD analysis is an attempt to simulate by a laboratory test the effect that organic material in a water body will have on the dissolved oxygen in that water body. There are two stages of decomposition involved in biological oxygen demand (BOD): a carbonaceous stage and a nitrogenous stage. The carbonaceous stage, or first stage, represents that portion of oxygen demand involved in the bacterial conversion of organic carbon to carbon dioxide. The nitrogenous stage, or second stage, represents a combined carbonaceous plus nitrogenous demand, when organic nitrogen, ammonia, and nitrite are converted to nitrate by bacteria, a process that also consumes dissolved oxygen [6].

Sometimes it is advantageous to measure just the oxygen demand exerted by organic (carbonaceous) compounds, excluding the oxygen demand exerted by the nitrogenous compounds. To accomplish this, the nitrifying organisms can be inhibited from using oxygen by the addition of a nitrification inhibitor to the samples. The result is termed carbonaceous biochemical oxygen demand (CBOD) [7].

There are two commonly recognized methods for the measurement of BOD: dilution method and manometric method. In order to obtain BOD through the dilution method, dissolved oxygen concentrations in a sample must be measured before and after the incubation period, and appropriately adjusted by the sample corresponding dilution factor [8]. In the manometric method, the sample is kept in a sealed container fitted with a pressure sensor. The main advantages of this method compared to the dilution method are simplicity, direct reading of BOD value and continuous display of BOD value at the current incubation time [9].

Water is an important factor within the ecological equilibrium and its pollution is an issue with various consequences on human population. The effects of water pollution are various and complex, based on the nature and the content of the contaminants. The issues related to water pollution are addressed through water treatment [10-13].

The BOD test is used to measure the potential of wastewater and other waters to deplete the oxygen level of receiving waters. The test is also used to examine influents and effluents from wastewater treatment facilities to compute the efficiency of operation of the treatment units [14,15,16].

This paper presents the toxic inhibitive effect of metal ions (Cu, Zn, Cr, Ni, Cd, Pb, and Fe) and of cyanide ions from wastewaters on the process of biochemical consumption of oxygen, which reflects in the absolute value and in the kinetics of the degradation of organic substances quantified as BOD_5.

2. EXPERIMENTAL SECTION

The wastewater used within the research study was sampled from the Bucharest sewer system. The wastewater has a great variability as the city of Bucharest has an increased population and diverse industrial and economical activities are conducted within the city. Wastewater samples were taken from the inffluent of the municipal wastewater treatment plant (untreated wastewater) as well as from the effluent resulting from the secondary treatment step (biologically treated wastewater), so that the content of specific toxic pollutants is negligible. The experiments were conducted using a BOD_5 analyser composed of 6 respirometry units, which records the BOD_5 manometrically (Figure 1). The values of BOD_5 were recorded every 2 h for 5 days. The wastewater samples had different organic loads and 1 mg/L heavy metal and cyanide were added separately to each sample. A blank sample consisting of raw municipal wastewater was used. The determination of wastewater quality indicators was accomplished using standardized methods of analysis using conventional techniques and instrumental analysis methods [17-20].

3. RESULTS SECTION

The experimental results were processed in order to establish the effects of the presence of toxic pollutants on the absolute value of BOD_5. The graphic representation of the evolution in time of BOD_5 shows the influence of the toxic substances from water sample on the BOD_5 value. The value of BOD_5 was lower than the value of the blank sample, except for iron ions (see Table 1 and Table 2), where the value remained the same.

The reduction of the value of BOD_5 (expressed as percentage) compared to the blank sample ranged as follows (see Table 1): Cu = 42 – 50%; Ni = 37 – 48%; Cd = 26 – 41%; CN = 22%; Cr = 16 – 20%; Zn = 0 - 6%; Pb = 0 – 4%; Fe = 0%. As it may be seen from Table 2, the reduction of the value of BOD_5 (expressed as percentage) that highlights the toxicity of the tested ions, is higher for wastewaters with low organic loads (biologically treated) compared to raw wastewaters.

Starting from this data analysis, the toxicity of the tested ions varies as follows:

Cu > Ni > Cd > CN > Cr > Zn > Pb > Fe

Another important observation refers to different adaptation time required for the biochemical oxygen demand processes to start, higher values being noticed in cases where heavy metal ions identified as toxic were used (see Table 3). For example, in the case of copper, significant higher values were recorded ranging from 16 to 53 hours, compared to the pollutant iron, in this case 2-4 hours being required for the degradation of organic substances to start.

For establishing the rates of the biochemical oxygen consumption, a computing method for autocatalytic reactions reported in the literature was used [21]. According to it, the rate of the oxygen consumption in the reaction of BOD_5 may be described by equation (1):

$$\frac{dy}{dt} = k\,(y-b)\,(L-y) \quad (1)$$

where:

L = the total biochemical oxygen demand (BOD_5) determined experimentally;

y = the biochemical oxygen demand (BOD_5) determined experimentally at time moment t;

b = the size of the bacterial population;

k = the rate constant for the biochemical oxygen demand.

After integration and linearization, the equation (1) may be written as equation (2) and its graphical representation leads to a linear curve described by a slope equal to $(-k\,L\log e)$.

$$\log\frac{(L-y)}{(L\,y)} = f(t) \quad (2)$$

The values of the reaction rates for different organic loads and the presence of inhibitive substances are shown in Table 3.

As we know, the biochemical reaction of oxygen consumption takes place in two phases: I. the degradation of the readily assimilable substances; II. the conversion of nitrogen compounds, respectively their oxidation to nitrites and nitrates. From the analysis of the experimental results obtained for two types of wastewater, it may be concluded that in the first phase, the degradation rates are not significantly different when toxic ions are added. After a longer adaptation time, corresponding to a stronger inhibitive effect, the values of the rates for the second phase are higher; however the absolute value of BOD_5 in the presence of toxic substances does not attain the value of the blank sample, except the case of pollutant iron.

Table 1. Values of BOD_5 obtained in the presence of toxic pollutants and their percentage reduction compared to the blank sample - raw wastewater .

Benchmark	M.U.	Cu	Ni	Cd	CN	Cr	Zn	Pb	Fe
100 mg O_2/L	mg/L	50	52	59	-	-	-	92	-
reduction (%)		50%	48%	41%	-	-	-	8%	-
110 mg O_2/L	mg/L	56	-	71	86	92	107	110	110
reduction (%)		49%	-	35%	22%	16%	6%	0%	0%
320 mg O_2/L	mg/L	184	200	235	-	255	320	309	320
reduction (%)		42%	37%	26%	-	20%	0%	4%	0%

Table 2. Values of BOD_5 obtained in the presence of toxic pollutants and their percentage reduction compared to the blank sampl - biologically treated wastewater.

Benchmark	M.U.	Cu	Ni	Cd	CN	Cr	Zn	Pb	Fe
31 mg O_2/L	mg/L	12	15	16	17	28	28	30	31
reduction (%)		60%	52%	47%	45%	9%	9%	3%	0%

Table 3. Values of rate constants for oxygen consumption for wastewater with different organic loads in the presence of toxic substances.

	Raw wastewater						Biologically treated wastewater	
	L = 100 mg O_2/L		L = 110 mg O_2/L		L = 320 mg O_2/L		L = 31 mg O_2/L	
	0		1		2		3	
Benchmark	I	0.0016	I	0.0014	I	0.0013	I	0.0057
	II	0.0005	II	0.0004	II	0.0003	II	0.0014
Cu	I	0.0021	I	0.0049	I	0.0011	I	0.0084
	II	0.0103	II	0.0100	II	0.0003	II	0.0126
adaptation		34 h		18 h		16 h		53 h
Ni	I	0.0016	I	-	I	0.0014	I	0.0049
	II	0.0035	II	-	II	0.0003	II	0.0067
adaptation		20 h		-		20 h		16 h
Cd	I	0.0027	I	0.0037	I	0.0016	I	0.0058
	II	0.0021	II	0.0006	II	0.0002	II	0.0008
adaptation		26 h		38 h		20 h		18 h
CN	I	-	I	0.0023	I	-	I	0.0055
	II	-	II	0.0007	II	-	II	0.0028
adaptation		-		6 h		-		32 h
Cr	I	-	I	0.0018	I	0.0009	I	0.0043
	II	-	II	0.0009	II	0.0003	II	0.0018
adaptation		-		24 h		8 h		16 h
Zn	I	-	I	0.0016	I	0.0002	I	0.0029
	II	-	II	0.0005	II	0.0003	II	0.0017
adaptation		-		10 h		4 h		10 h
	0		1		2		3	
Pb	I	0.0017	I	0.0023	I	0.0007	I	0.0073
	II	0.0007	II	0.0005	II	0.0002	II	0.0012
adaptation		6 h		6 h		8 h		10 h
Fe	I	-	I	0.0014	I	0.0013	I	0.0061
	II	-	II	0.0005	II	0.0003	II	0.0013
adaptation		-		4 h		2h		2 h

4. CONCLUSIONS

With proper analysis and environmental control, almost all wastewaters can be treated biologically. Since the biochemical oxygen demand (BOD_5) is the main parameter used for characterizing the organic load of wastewater, it is crucial that the environmental engineer understands the importance of the accuracy of the analysis of BOD_5 when designing the wastewater treatment plants.

The presence of toxic ions such as heavy metals (Cu, Zn, Cr, Ni, Cd, Pb, and Fe) and cyanide in wastewater has an increased inhibitive effect on the biochemical reaction of oxygen consumption. The absolute value of BOD_5 is closer to its real value as the tested ion has a lower toxicity, a toxicity scale based on the reduction of the value of BOD_5 being established. In order to determine an accurate value of BOD_5, the degree of reduction induced by the presence of toxic ions in the wastewater should be taken into consideration.

Generally, the process starts after a variable adaptation time and the first phase of the degradation of organic substances has a higher rate, followed by a second phase where the reaction rate decreases. An exception is recorded in cases where the tested ions have a strong toxic effect, for example the oxidation of organic compounds in the presence of copper and nickel ions.

Regarding the issues related to the evaluation of the quality indicators of wastewater, the results reported in this paper provide useful information required for designing and optimal operation (in respect to efficiency, economical aspects, and adaptation to pollution sources) of a wastewater treatment plant.

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