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APOLINARY KOWAL, ANDRZEJ LISOWSKI, WŁADYSŁAW ADAMSKI*

BIOCHEMICAL OXIDATION OF POLLUTANTS IN WASTEWATERS FROM WET DEDUSTING OF COPPER-MILL WASTE GASES

Biological treatability of the wastewater from wet dedusting of metallurgic gases has been examined. The mixture of the wastewater, non-adapted activated sludge and municipal wastewaters has been aerated in respirometers. The nature and sequence of the biodegradation processes, and their kinetics have been determined on the basis of the observed results.

1. INTRODUCTION

Biological treatment with activated sludge was applied to the industrial wastewaters coming from wet dedusting of waste gases in copper mills. These wastewaters were characterized by a high content of organic and mineral pollutants. Spectrophotometric analysis (I.R.) of the ether and chloroform extracts has shown that monocyclic aromatic hydrocarbons, mainly phenols, amines and amides were the prevailing organics. Aromatic and aromatic-aliphatic ketones, aliphatic hydrocarbons and mixed ethers appeared in smaller quantities. The basic inorganic pollutants were chlorides, sulphates, sulphides, sulphites, thiocyanates, and ammonium compounds. Cyanides, phosphates and salts of zinc, lead and copper appeared in much smaller quantities.

Among chemical compounds listed in table 1 there are also some toxic substances and inhibitors of biochemical processes, namely: thiocyanates, cyanides, sulphides, sulphites, heavy metals and some hydrocarbons. The presence of these compounds did not exclude the possibility of wastewater treatment. There are in the literature many examples of the application of biological methods to the treatment of industrial wastewaters more contaminated and containing much higher quantities of toxic compounds [1]. This is possible since microorganisms can be adapted even to such compounds, however, within a definite range of concentrations. As the adaptation process to the destruction of toxic or bioresis-

* Institute of Environment Protection Engineering, Wrocław Technical University, Wrocław, Poland.

Table 1

Chemical composition of the wastewater from wet dedusting of copper waste gases

Pollutant	Unit	Concentration	Pollutant	Unit	Concentration
pH	pH	4.7	Ammonium nitrogen	mg/dm^3N	203
COD	mg/dm^3O_2	8050	Nitrate nitrogen	mg/dm^3N	0
Permanganate value	mg/dm^3O_2	4625	Nitrite nitrogen	mg/dm^3N	0
BOD_5	mg/dm^3O_2	4100	Organic nitrogen	mg/dm^3N	118
Volatile Phenols	mg/dm^3	464	Calcium	mg/dm^3Ca	500
Chlorides	mg/dm^3Cl^-	2430	Magnesium	mg/dm^3Mg	200
Sulphates	$mg/dm^3SO_4^{-2}$	1951	Iron	mg/dm^3Fe	109
Sulphites	$mg/dm^3SO_3^{-2}$	282	Copper	mg/dm^3Cu	1.7
Sulphides	mg/dm^3S^{-2}	92.1	Zink	mg/dm^3Zn	6.8
Tiocyanides	mg/dm^3SCN^-	380	Lead	mg/dm^3Pb	1.2
Cyanides	mg/dm^3CN^-	3.7	Total solids	mg/dm^3	14280
Phosphates	$mg/dm^3PO_4^{-3}$	15.6	Mineral solids	mg/dm^3	7920

tant compounds may be inhibited due to the competition of the substrates more biodegradable, the biological treatment of some industrial wastewaters is conducted in multistage system — each step being optimized for removal of a selected pollutant.

It is obvious that biochemical processes in wastewaters from wet dedusting will not be so effective as in sewage or other wastewaters containing only easily biodegradable organics. In order to assure optimal conditions of the process it may appear that the wastewaters from wet dedusting should be diluted with municipal wastewaters, as well as some exceptionally acute toxic compounds should be removed from the wastewaters prior to biological treatment. This refers chiefly to heavy metals, which even in small quantities may exert an inhibitory effect on biological process. In general, this phenomenon is manifested after a certain period of time, i.e. after a threshold quantity of the heavy metals ions cumulated in cells is exceeded. Basic factor govering the applicability of the biological methods to the industrial wastewater treatment is the biodegrability of the majority of its components. If the wastewater contains large quantities of refractory compounds, then other treatment methods have to be employed.

For these reasons biological treatment of the wastewaters from wet dedusting must be a complex process comprising of biochemical degradation reactions of various chemical compounds characterized by different action with respect to microorganisms. For the recognition of some processes and their kinetics the reported respirometric investigations have been carried out.

2. METHODS

The investigations have been performed by using a respirometer described in fig. 1 [2]. The design of respirometer allowed simultaneous measurement of oxygen demand and of carbon dioxide produced, as well as sampling of wastewater for chemical analyses. Biolo-

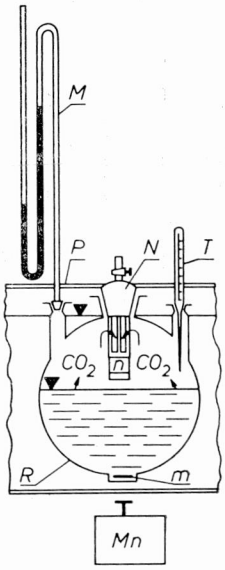

Fig. 1. Respirometer
R — reactor (respirometric flash), *P* — water tank, *M* — manometer, *T* — thermometer, *N* — valve, *n* — vessel with KOH solution, *m*, *Mn* — magnetic stirrer

Rys. 1. Respirometer
R — reaktor (kolba respirometryczna), *P* — zbiornik z wodą, *M* — manometr, *T* — termometr, *N* — nasadka z zaworem, *n* — naczynie z roztworem KOH, *m* — mieszalnik magnetyczny, *Mn* — mieszadło magnetyczne

gical treatment of wastewaters was preceded by removal of heavy metal ions. The wastewater were alkalized with a concentrated NaOH solution up to pH 9 and filtered in order to separate the deposits of heavy metals hydroxides. Although the filtrate contained the ions of heavy metals (Fe, Cu, Zn, Pb) nevertheless their total concentration did not exceed 1 mg/dm^3. The alkalized wastewaters were mixed together with municipal wastes in the voluminous ratios 1:9, 1:3, 1:1 and 9:1 and with 0.763 g/dm^3 of non-adapted activated sludge. Both 1 dm^3 samples of the mixtures and a control sample were introduced into the respirameters.

3. DISCUSSION

Changes occurring in the chemical composition of the biologically treated wastewater samples, and total oxygen consumption resulting from chemical and biological processes, are presented in figs 2–5.

In all the samples investigated biodegradation of pollutants was a multistage process, selective with respect to the given chemical compounds. At first adaptation of activated sludge was observed. This step was characterized by a slight COD removal and small

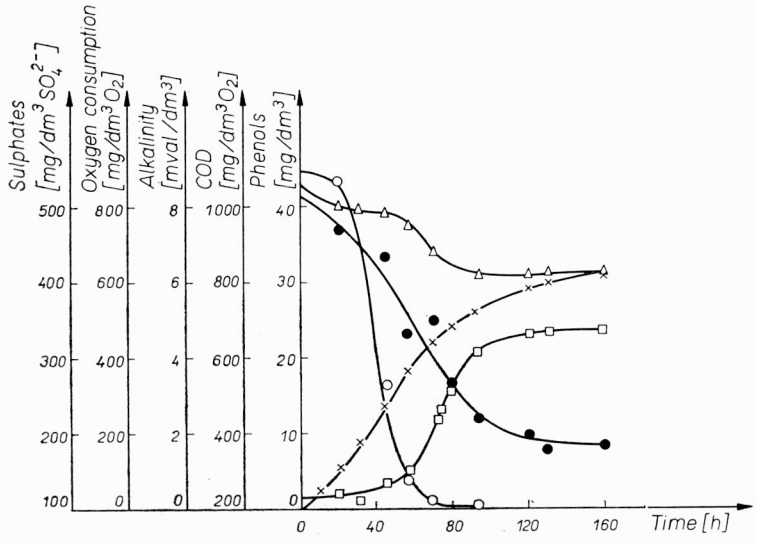

Fig. 2. Biological treatment of wastewater from wet dedusting. Dilution with municipal wastes 1:9
△ – alkalinity, x – oxygen consumption, ● – COD, □ – sulphates

Rys. 2. Biologiczne oczyszczanie ścieków z mokrego odpylania. Rozcieńczenie ściekami miejskimi 1:9
△ – zasadowość, x – ZT, ● – CHZT, □ – siarczany

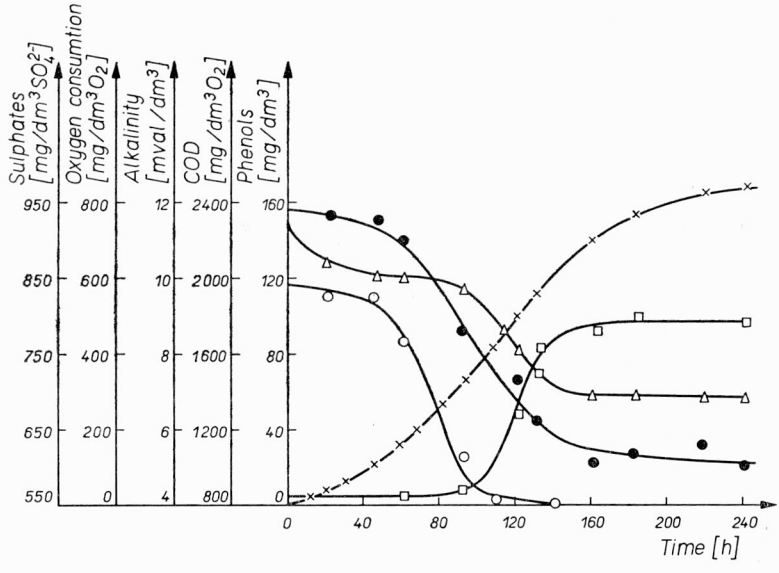

Fig. 3. Biological treatment of wastewater from wet dedusting. Dilution with municipal wastewater 1:3
△ – alkalinity, x – oxygen consumption, ● – COD, □ – sulphates, o – phenoles

Rys. 3. Biologiczne oczyszczanie ścieków z mokrego odpylania. Rozcieńczenie ściekami miejskimi 1:3
△ – zasadowość, x – ZT, ● – CHZT, □ – siarczany, o – fenole

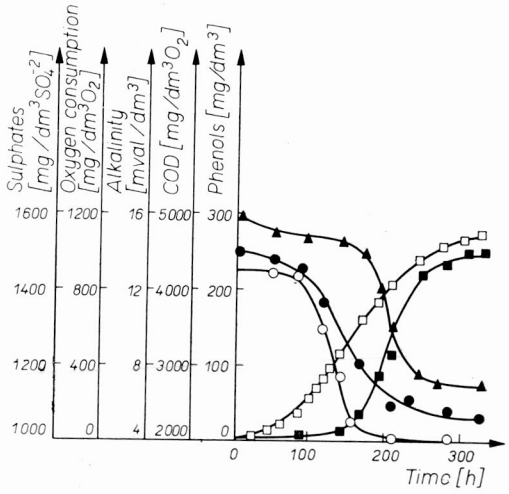

Fig. 4. Biological treatment of wastewater from wet dedusting. Dilution with municipal wastewater 1:1

▲ – alkalinity, □ – oxygen consumption, ■ – sulphates, o – phenoles, ● – COD

Rys. 4. Biologiczne oczyszczanie ścieków z mokrego odpylania. Rozcieńczenie ściekami miejskimi 1:1

▲ – zasadowość, □ – ZT, ■ – siarczany, o – fenole, ● – CHZT

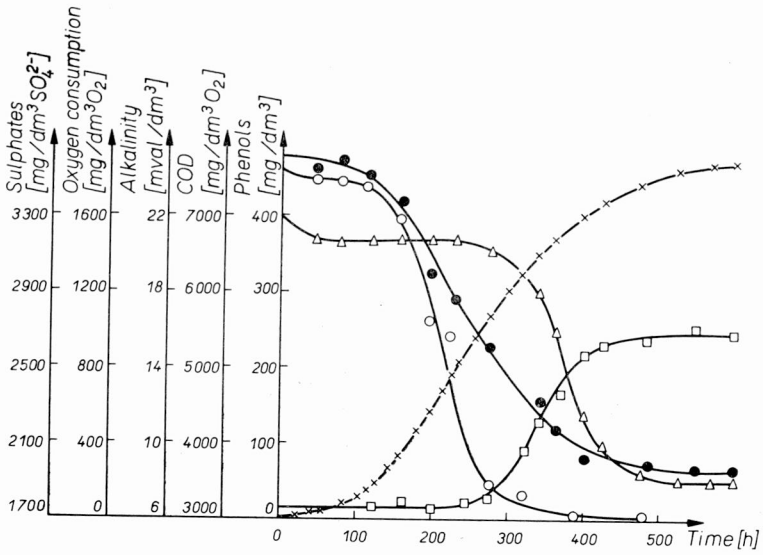

Fig. 5. Biological treatment of wastewater from wet dedusting. Dilution with municipal wastewater 9:1

△ – alkalinity, x – oxygen consumption, □ – sulphates, o – phenols, ● – COD

Rys. 5. Biologiczne oczyszczanie ścieków z mokrego odpylania. Rozcieńczanie ściekami miejskimi 9:1

△ – zasadowość, x – ZT, □ – siarczany, o – fenole, ● – CHZT

oxygen consumption resulting from the biodegradation of substances easily assimilated by microorganisms. The adaptation of activated sludge gave rise to the acceleration of wastewater treatment manifested by the increase in COD removal and oxygen consumption rates as well as by the initiation of phenols degradation.

The next stage of the process, occurring after most of the phenols were degraded, was characterized by reactions of inorganic sulphur compounds yielding sulphuric acid. Due to its presence in treated wastewater the concentration of sulphate ions raised up and the alkalinity decreased. The increment of sulphates was approximately equivalent to the decrement of sulphides (table 2).

Table 2

Effect of the biological treatment process on the concentration of the supernatant inorganic sulphuric compounds

Percent of wastewater in sample %	Removal of sulphides		Removal of sulphates		Removal of tiocyanides		Increase of sulphates	
	mg/dm³ SO_4^{-2}	%	mg/dm³ SO_4^{-2}	%	mg/dm³ SO_4^{-2}	%	mg/dm³ SO_4^{-2}	%
10	25	100	38	100	53	100	115	51
25	46	100	89	100	104	100	235	42
50	108	100	150	100	204	100	482	47
90	231	100	304	100	358	100	924	52

At the final phase of the biodegradation the rate of oxygen consumption, and that of COD removal decreased. High total BOD_5 removal indicates almost complete degradation of the organic pollutants susceptible to biodegradation. In biologically treated wastewaters there remained, however, some substances resistant to biodegradation. As it follows from the table 3 their contents, denoted by COD, were as high as 40 to 50 %

Table 3

The effect of the biological wastewater treatment process on BOD_5 and COD of the supernatant

Percent of industrial wastewater in sample %	Time h	COD		BOD_5	
		mg/dm³ O_2	% removal	mg/dm³ O_2	% removal
10	0	1030	—	750	—
	160	370	64	24	97
25	0	4500	—	2120	—
	240	1068	55	69	94
50	0	4500	—	2120	—
	320	2224	51	84	96
90	0	7820	—	4038	—
	600	3645	53	98	95

The rate of biochemical processes was not identical in all the samples. From the comparison of the oxygen consumption values at the initial phase it follows that biodegradation of organic compounds easily assimilated by microorganisms was undisturbed not only in sewage (control sample) but also in the mixture containing 10% of the wastewater from wet dedusting (fig. 6, curves *0* and *1*). In both cases no differences in the rate of

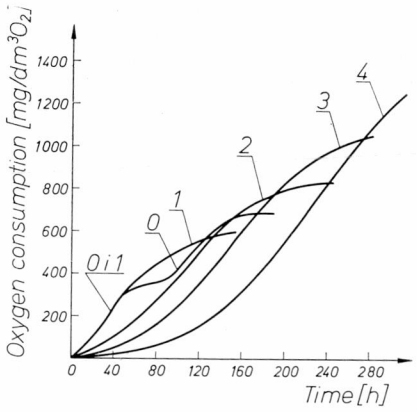

Fig. 6. Oxygen consumption in biological treatment of municipal wastewater (curve *0*) and wastewater from wet dedusting mixed with municipal wastewater in voluminous ratio 1:9 (curve *1*), 1:4 (curve *2*), 1:1 (curve *3*) and 9:1 (curve *4*)

Rys. 6. Zużycie tlenu w procesie biologicznego oczyszczania ścieków miejskich (krzywa *0*) oraz ścieków z mokrego odpylania zmieszanych ze ściekami miejskimi w stosunkach objętościowych 1:9 (krzywa *1*), 1:4 (krzywa *2*), 1:1 (krzywa *3*), 9:1 (krzywa *4*)

oxygen consumption have been stated. These differences were found in the remaining samples in which the percent of wastewaters from wet dedusting was higher. Lower oxygen consumptions in the samples were due to the toxicity of industrial wastewater pollutants for non-adapted microorganisms. The toxic effect enhanced by the increasing percentage of industrial wastewater in the mixture treated, was reflected in smaller amounts of the oxygen consumed.

The impurities of wastewater from wet dedusting inhibited the adaptation of microorganisms to degradation of phenols and other components more resistant to biodegradation. The lower the dilution degree of the wastewater with municipal sewage the slower was the adaptation. From the data presented in figs. 2–5 it follows that in the samples containing 10, 25, 50, and 90% of phenols by volume of wastewater from wet dedusting their removal was initiated after 20, 44, 88 and 115 h, respectively.

Phenols and their derivatives have retarded completely the degradation of thiocyanates and oxydation of sulphites. The raise in sulphate ions concentration and the drop in wastewater alkalinity, which resulted from these reactions started as late as the majority of phenols had undergone biodegradation.

Contrary to the processes mentioned above chemical oxidation of sulphides to sulphites was undisturbed in presence of phenols and other organics. This was demonstrated by the experiment in which alkalized wastewaters from wet dedusting were aerated for a long time without activated sludge [3]. Aeration resulted in oxidation of sulphides to sulphates via sulphites, the latter being oxidized to sulphates very slowly. For this reason the decrease in sulphite ions concentration in wastewater was approximately equivalent to the increase in concentration of sulphides. No thiocyanates and phenols removal was stated in the process.

The components of the wastewaters from wet dedusting had a toxic effect on nitrifying bacteria. Biochemical oxidation of ammonium salts to nitrites and nitrates occurred solely in the control sample (municipal sewage), the removal of ammonium nitrogen being equal to 25 mg/dm^3 or to 75 %, approximately. In result of nitrification the rate of oxygen consumption (fig. 6, curve *0*) increased again, the total yield of nitrites and nitrates amounted to 22.4 mg/dm^3. This, in turn, contributed to the decrease in pH value from 8.6 to 5.8. The same trend was also stated in the remaning samples containing wastewaters from wet dedusting. It was, however, due to the acidic action of H_2SO_4 — the product of sulphites oxidation and thiocyanates biodegradation.

5. CONCLUSIONS

1. During aeration of the mixture of wastewater from wet dedusting and non-adapted activated sludge, the following processes occur succesively:

— biodegradation of organics available to microorganisms and adaptation of the biomass to less susceptible substrates,

— biodegradation of phenols and the other more resistant organic substances,

— oxidation of sulphites and biodegradation of thiocyanates.

In the final phase of the treatment, biochemical processes are retarded due to biodegradation of most substrates available to microorganisms.

2. Some components of the wastewater from wet dedusting hinder the biodegradation of organic substances easily available to microorganisms. This effect has not been observed only at the dilution rate with municipal sewage 1:10.

3. The adaptation of activated sludge to biodegradation of phenols and other more resistant organics is slower–the higher the per cent ratio of wastewaters from wet dedusting in the treated mixture.

4. Both phenols and their derivatives hinder the oxidation of sulphites and biodegradation of thiocyanates. These reactions are initiated as late as after the degradation of the majority of the phenolic compounds. In the contrary to the processes mentioned the oxidation of sulphides to sulphites in the presence of phenols and other organics is undisturbed.

5. Components of the wastewater from wet dedusting have a toxic effect on nitrifying bacteria and prevent the oxidation of ammonium salts to nitrites and nitrates.

6. Wastewater from wet dedusting include 40 to 50 % of nonbiodegradable (refractory) organics. In this case other treatment methods should be employed to get a better quality effluent.

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SUKCESYWNOŚĆ BIOCHEMICZNYCH PROCESÓW UTLENIANIA ZANIECZYSZCZEŃ ŚCIEKÓW Z MOKREGO ODPYLANIA GAZÓW HUTNICZYCH

Zbadano podatność ścieków z mokrego odpylania gazów hutniczych na biologiczne oczyszczanie. Ścieki wraz z niezaadoptowanym osadem czynnym i ściekami miejskimi napowietrzano w respirometrach i obserwowano zachodzące w nich zmiany. Określono biochemiczne procesy rozkładu, ich kolejność oraz kinetykę.

DIE REIHENFOLGE DES BIOCHEMISCHEN ABBAUES IM ABWASSER AUS DER NASSENTSTAUBUNG VON HÜTTE-ABGASEN

Untersucht wurde die Abbaubarkeit von Abwässern aus der Naßentstaubung von Hütteabgasen durch biologische Verfahren. Diese Abwässer wurden gemeinsam mit nicht adaptiertem Belebtschlamm und mit kommunalem Abwasser vermischt und in Respirometern belüftet. Beobachtet wurden die mit der Zeit ablaufenden Wechselvorgänge. Bestimmt wurden die biochemischen Abbauprozeße, sowie die Reihenfolge und Kinetik des Abbaues.

ПОСЛЕДОВАТЕЛЬНОСТЬ БИОХИМИЧЕСКИХ ПРОЦЕССОВ ОКИСЛЕНИЯ ЗАГРЯЗНЕНИЙ СТОЧНЫХ ВОД ОТ МОКРОГО ОБЕСПЫЛИВАНИЯ ПЕЧНЫХ РАЗОВ

Исследована восприимчивость сточных вод от мокрого обеспыливания печных газов на биологическую очистку. Сточные воды с неприспособленным активным осадком и городскими сточными водами подвергались аэрации в респирометрах. Одновременно велись наблюдения за изменениями в них с течением времени. Определены биохимические процессы разложения, их последовательность и кинетика.