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BIODEGRADATION OF PRE-OZONATED INDUSTRIAL WASTEWATERS

Effect of pre-ozonation on the biochemical treatment of scrubbing waters was investigated. Pre-ozonation increased the susceptibility of these wastewaters to biodegradation, decreased oxygen demand per unit of the permanganate value removed and permitted higher activated sludge loading.

1. INTRODUCTION

Biochemical treatment of highly concentrated industrial wastewaters is often faced with difficulties caused by high concentrations of refractory and toxic substances. For the biological treatment of those wastewaters either high dilution ratio with municipal sewage or physical-chemical pretreatment are required. If the industrial wastewaters contain a variety of chemical compounds (both organic and inorganic), ozonation is the most effective treatment method. The basic parameters of the ozonation of organic compounds have been described by RAWSON [14] EINSENHAUER [4], GORBENKO [5], HEVES [8], GOULD [6] and BERNATEK [1].

The unsaturated organic compounds were efficiently decomposed, whereas the degradation of saturated compounds was slow. In general, carbon dioxide and short chain of saturated organic acids were the major products of ozonolysis.

So far ozone has been used for the treatment of phenols, petroleum and dye contained in wastewaters, as well as for the wastewaters generated during coal gasification and photograph processing [2, 3, 10-12, 15].

The applications of the ozonation process are strongly limited by economical factors.

If ozonation is applied prior to biochemical treatment, the removals of pollutants will be higher, whereas the ozone doses required and the operational costs will be decreased as compared with the application of ozonation alone.

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2. EXPERIMENTAL METHODS

The investigations were carried out on scrubbing water samples collected in a copper smelter. Scrubbing waters are highly polluted. Most of the organic pollutants belong to aromatic compounds such as phenols, amines and amides. Aromatic ketones, aromatic-aliphatic esters and aromatic hydrocarbons occur in lower concentrations. The main inorganic pollutants contained in scrubbing waters are chlorides, sulphates, sulphides, sulphites, ammonia salts and heavy metals.

The chemical composition of the scrubbing waters tested is shown in table 1.

Table 1

Chemical composition of scrubbing waters from a copper smelter
Skład chemiczny wód z płuczek gazowych z huty miedzi

Parameters	Units	Concentration
Extinction	—	0.70
pH	—	4.6
Alkalinity	g $CaCO_3/m^3$	750
Permanganate value	g O_2/m^3	13200
BOD_5	g O_2/m^3	16000
COD	g O_2/m^3	29400
Chlorides	g Cl/m^3	8240
Sulphides	g S/m^3	80
Sulphites	g SO_3^{-2}/m^3	2200
Sulphates	g SO_4^{-2}/m^3	2140
Organic nitrogen	g N/m^3	2200
Ammonia	g N/m^3	1000
Nitrite	g N/m^3	0
Nitrate	g N/m^3	0
Phosphate	g PO_4^{-3}/m^3	0
Phenols	g/m^3	325
Total solids	g/m^3	76520
Mineral dissolved solids	g/m^3	45640
Volatile solids	g/m^3	4300

In order to precipitate heavy metals, the scrubbing waters were alkalized to a pH of 9.8.

The wastewaters were ozonated first with doses varying from 765 to 12 321 g O_3/m^3, and then biologically treated. The biological tests were carried out in a Warburg respirometer.

Raw or pre-ozonated scrubbing waters were inoculated with activated sludge, which was adapted earlier, and placed in the vessels of the respirometer.

Oxygen consumption was measured according to standard techniques [13]. The process had been conducted for 50-60 hours, until oxygen consumption by activated sludge became almost unnoticeable. The mixture was next filtered and permanganate value (PV) was determined [7].

3. OZONATION OF SCRUBBING WATERS

The effectiveness of the ozonation process is shown in fig. 1. During ozonation pH continuously decreased to achieve the value of 3.6 with a dose of 7 020 g O_3/m^3. With doses ranging within 7 020-10 958 g O_3/m^3 the pH decrease was less evident. Higher ozone doses resulted in a further rapid decrease of pH.

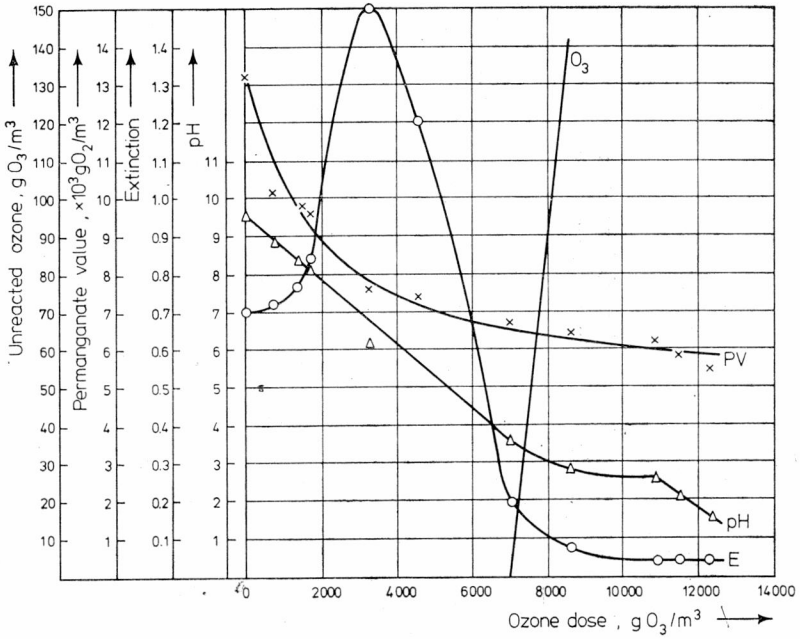

Fig. 1. Effectiveness of scrubbing waters ozonation

Rys. 1. Efektywność ozonowania z płuczek gazowych wód

The value of extinction for scrubbing water (measured in the maximum of absorption $\lambda = 700$ nm) was the highest when the applied dose amounted to 3 276 g O_3/m^3, and rapidly decreased with the increasing doses. The highest effectiveness of the oxidation process was achieved with low ozone doses. With the dose of 3 276 g O_3/m^3, PV was removed in 42%. Then the dose was increased to 12 321 g O_3/m^3, PV removal increased only by about 17%. Unreacted ozone appeared when the dose of 7 020 g O_3/m^3 was used, and its quantity rapidly increased as the dose increased.

4. BIOLOGICAL TREATMENT OF OZONATED SCRUBBING WATERS

Raw and ozonated scrubbing waters were mixed with activated sludge in the ratios that would ensure a constant PV sludge loading of 0.8 O_2/g MLVSS. d. Under the circumstances only 10% of PV of raw scrubbing waters was removed. The oxygen consumption per

Table 2

Effectiveness of biodegradation of ozonated scrubbing waters
Efektywność biodegradacji ozonowanych z płuczek gazowych wód

Parameters	Units	Ozone dose (g O_3/m^3)							
		0	765	1458	3276	7020	8635	10958	12321
Sludge loading	$g \frac{PV}{MLVSS}$	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Initial PV	g O_2/m^3	13200	10200	9800	7600	6700	6400	6200	5400
Final PV	g O_2/m^3	11880	7650	8000	5770	4500	3750	3200	2700
PV removal	%	10	25	23	24	33	41	48	50
Oxygen consumption	g O_2	3.20	3.43	3.83	4.60	4.15	4.55	4.48	3.69
Oxygen consumption ratio	g O_2/PV	2.43	1.35	2.13	2.52	1.89	1.72	1.49	1.37

unit of PV removed was 2.43 g O_2/g (table 2). Biodegradation preceded by ozonation with doses from 765 to 3 276 g O_3/m^3 decreased PV by about 25%. Higher ozone doses increased the efficiency of that process up to or above 50% (fig. 2). Ozonation combined with biological treatment yielded total PV removals from 42 to 79% depending on the ozone dose used.

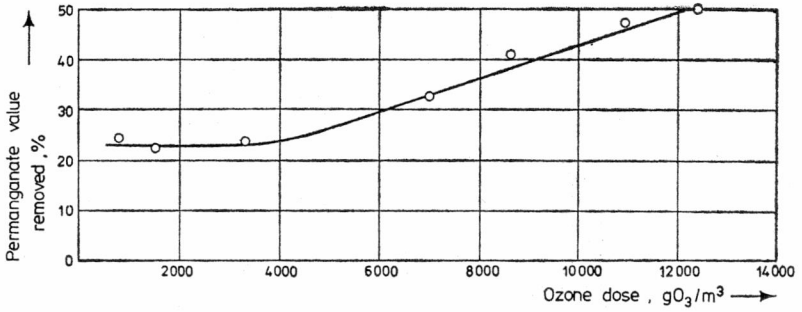

Fig. 2. Effectiveness of PV removal in biochemical reactions
Rys. 2. Efektywność usuwania utlenialności w reakcjach biochemicznych

Oxygen consumption for biochemical oxidation was dependent on the ozone dose employed in the ozonation process. In the range of low doses (to 3 276 g O_3/m^3) oxygen consumption increased. Higher doses of ozone (fig. 3) resulted in a slight decrease of oxygen consumption with a simultaneous decrease in PV.

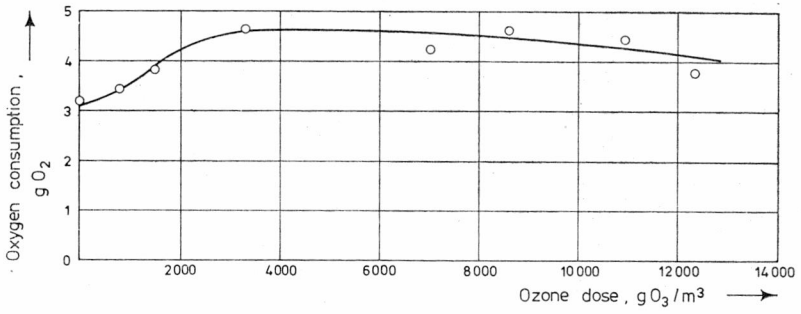

Fig. 3. Oxygen consumption in biochemical reaction
Rys. 3. Zużycie tlenu w reakcji biochemicznej

Maximum oxygen consumption per unit of the PV removed was obtained with dose of 3 276 g O_3/m^3. A further increase of the ozone dose caused a considerable decrease of oxygen consumption (fig. 4). Biodegradation of pre-ozonated scrubbing waters depends on sludge loading. In this part of the experiment scrubbing waters were pre-ozonated with a dose of 7 680 g O_3/m^3. A 50% removal of PV was achieved at a sludge loading of 0.3-0.5 g PV/g MLVSS (table 3). Higher sludge loading only slightly decreased the PV removal.

Table 3

Biodegradation of raw and ozonated scrubbing waters
Biodegradacja surowych i ozonowanych z płuczek gazowych wód

Parameters	Units	Raw sewage	Ozonated sewage	Biodegradation of raw sewage				Biodegradation of ozonated sewage				
Sludge loading	$g \frac{PV}{MLVSS}$	—	—	0.3	0.5	1.0	2.0	3.0	0.3	0.5	1.0	3.0
PV	$g\ O_2/m^3$	13200	6600	9400	9740	11250	11380	11500	3170	2800	3550	4080
PV removal	%	—	50	29	26	15	14	13	52	58	46	38
Oxygen consumption	$g\ O_2$	—	—	4.29	4.89	4.93	1.43	1.14	3.52	4.28	5.08	4.06
Oxygen consumption ratio	$g\ O_2/g$ PV	—	—	1.13	1.42	2.53	0.50	0.67	1.03	1.13	1.66	1.62

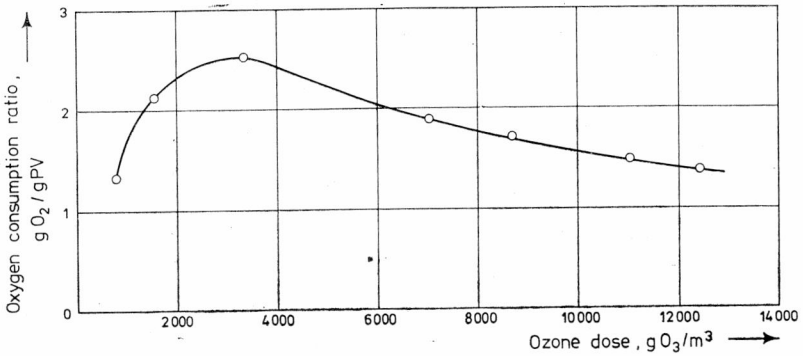

Fig. 4. Oxygen consumption per unit PV removed versus ozone dose
Rys. 4. Zużycie tlenu na jednostkę utlenialności usuniętej przez dawkę ozonu

Biodegradation of raw scrubbing waters at low sludge loading yielded PV removal as low as 30% or even less (15%) when higher loadings were applied (fig. 5).

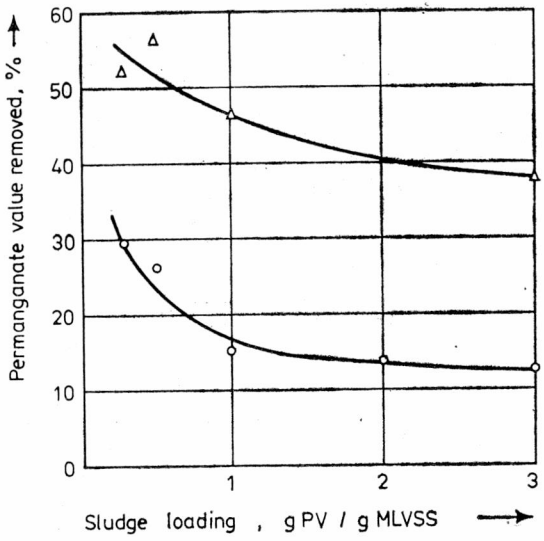

Fig. 5. PV removed from raw (o —— o) and ozonated wastes (△——△)
Rys. 5. Usunięcie utlenialności z surowych (o —— o) i ozonowanych (△——△) ścieków

The highest oxygen consumption was achieved both in raw and ozonated scrubbing waters at sludge loading of about 1 g PV/g MLVSS (fig. 6).

The oxygen consumption per unit of the PV removed for raw scrubbing waters had its maximum at the same point as oxygen consumption and after having achieved this maximum rapidly decreased.

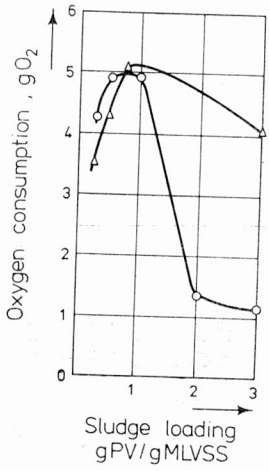

Fig. 6. Oxygen consumption in biochemical reactions in raw (o ——o) and ozonated wastes (△——△)
Rys. 6. Zużycie tlenu w reakcjach biochemicznych w surowych (o ——o) i ozonowanych (△——△) ściekach

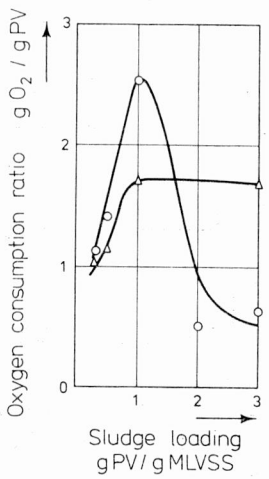

Fig. 7. Oxygen consumption per unit of removed PV in raw (o ——o) and ozonated wastes (△——△)
Rys. 7. Zużycie tlenu na jednostkę usuniętej utlenialności w surowych (o ——o) i ozonowanych (△——△) ściekach

On the contrary, in ozonated scrubbing waters oxygen consumption per unit of the PV removed increased with sludge loading to 1.0 g PV/g MLVSS and subsequently remained on the same level despite the rapid decrease of PV.

5. CONCLUSIONS

The ozonation of scrubbing waters removed about 50% of PV. The low effectiveness of ozonation, the high amount of unreacted ozone, and pH decreasing with the increase of ozone dose indicate that during ozonation sulphides and sulphites are oxidized, and unsaturated organic compounds reacted to straight organic acids and aldehydes.

A sludge loading of about 1.0 g PV/g MLVSS applied in raw scrubbing water almost completely stops biochemical reactions.

In ozonated scrubbing waters the process is inhibited to a certain degree; this inhibition takes place only when sludge loading of 3.0 g PV/g MLVSS is applied.

Ozonation with doses to 327 g O_3/m^3 only slightly increases the biodegrability of scrubbing waters. Higher ozone doses bring about a higher efficiency of biochemical reactions. The increase of oxygen consumption per unit of PV removed with high doses of ozone is probably caused by organic compounds which contain oxygen in their molecules (e.g. organic acids, aldehydes etc.).

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BIODEGRADACJA I WSTĘPNE OZONOWANIE ŚCIEKÓW PRZEMYSŁOWYCH

W artykule omówiono wpływ wstępnego ozonowania na biochemiczne oczyszczanie przemywanych wód. Wstępne ozonowanie zwiększa podatność tych wód na biodegradację, zmniejsza zapotrzebowanie tlenu na jednostkę usuwanej utlenialności i pozwala na wyższe obciążenia osadu czynnego.

VORBEHANDLUNG VON INDUSTRIELLEN ABWASSERN MIT OZON

Besprochen wird der Einfluss einer Vorbehandlung mit Ozone auf die darauf folgende biologische Reinigung von Industrie-Abwassern. Eine Vorozonierung macht die Abwasser dem biologischen Prozess mehr zugänglich, vermindert den Sauerstoffbedarf (berechnet als Permanganatverbrauch) und ermöglicht eine höhere Belastung des Belebtschlamms.

БИОДЕГРАДАЦИЯ И ПРЕДВАРИТЕЛЬНОЕ ОЗОНИРОВАНИЕ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД

В статье обсуждено влияние предварительного озонирования на биохимическую очистку промывных вод. Предварительное ознирование увеличивает податливость этих вод на биодеградацию, уменьшает потребность в кислороде на единицу удаляемой окисляемости и позволяет повысить нагрузку активного ила.