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BIODEGRADATION OF o-NITROPHENOL UNDER AEROBIC CONDITIONS

o-nitrophenol comes from a variety of man-made sources, specifically from chemical synthesis. As o-nitrophenol enters the environment in a combination with other constituents of wastewater discharges, it has become necessary to determine its environmental impact. Biodegradation of o-nitrophenol involved three types of samples: municipal sewage, artificial wastewater, and mineral wastewater. The experiments were run under static and dynamic conditions. After adaptation, activated sludge was able to degrade o-nitrophenol at concentrations up to 400 g/m^3.

1. INTRODUCTION

o-nitrophenol is widely applied to the manufacture of explosives, chemicals, medicaments, rubber, and leather. Wastewater discharges containing o-nitrophenol have a disadvantageous effect on the colour, smell, and taste of the receiving stream. o-nitrophenol concentrations harmful to aquatic organisms amount to 0.9 g/m^3 [1].

The investigations on the biodegradability of o-nitrophenol reported in the literature generally involved isolated microorganisms. Thus, GERMANIER and WUHRMANN [2] showed that *Pseudomonas* sp. is able to degrade o-nitrophenol by denitrification; the metabolism takes the following course: o-nitrophenol→pyrocatechol→oxyhydroquinone→β-ketone adipic acid.

2. EXPERIMENTAL METHODS

The experiments were run in respirometers (static conditions) and in an ejector system (dynamic conditions, through-flow reactors) [3]. Biodegradation involved three types of samples: municipal sewage, artificial wastewater, and mineral wastewater. Analyses comprised o-nitrophenol concentrations [4], permanganate COD, dichromate COD, ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, and

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pH. BOD_5 was determined in through-flow reactors. Twice or three times a week the sludge volume index was measured by the Mohlman method. Activated sludge was subject to microscopic examinations.

3. RESULTS

3.1. RESPIROMETER SYSTEM

Preliminary investigations have shown that the oxidation of o-nitrophenol averages 95.7% of theoretical oxygen demand under conditions of dichromate COD determination and 78.5% under conditions of permanganate COD determination. Experiments concerning municipal sewage samples led to the following findings: o-nitrophenol underwent sorption and desorption; thereafter, its concentration was unchangeable before the degradation process was completed (fig.1). The adaptation process took from 110 to 194 h at initial o-nitrophenol concentration ranging between 50 and 300 g/m^3. At these concentrations, there occurred an inhibiting effect on the biodegradation of other pollutants present in the municipal sewage. This effect was indicated by the decreasing calculated values of L_0 (final oxygen demand) and of the K_{1N} to K_{1K} ratio (the ratio of the rate constant of first-order reaction for samples containing o-nitrophenol to the rate constant of first-order reaction for control samples). The data of interest are listed in tab. 1. The calculations involved equations of a monomolecular reaction which is the best to describe the biodegradation of o-nitrophenol. The oxygen uptake curves run below the control curve (fig. 1). In the course of biodegradation nitrite nitrogen concentration increased, whereas permanganate COD and colour decreased rapidly.

Biodegradation by non-adapted sludge (tab. 1, fig. 2) took a course similar to that in the municipal sewage. The time of adaptation at identical initial concentrations of o-nitrophenol was more prolonged, ranging from 19 to 272 h for o-nitrophenol concentrations of 10 to 300 g/m^3. Thereafter, the degree of degradation increased rapidly. The shorter time of adaptation for the microorganisms present in municipal sewage should be attributed to the availability of easy degradable substances occurring in this medium. In mineral medium o-nitrophenol was the sole carbon and energy source for non-adapted sludge. At concentration varying between 10 and 300 g/m^3, o-nitrophenol accounted for the inhibition of biochemical processes (oxygen uptake, fig. 2; L_o – values, tab. 1). No inhibition of biochemical processes or nitrification was found to occur at o-nitrophenol concentration of 5 g/m^3.

3.2. EJECTOR SYSTEM

Table 2 gives the treatment parameters for wastewater containing o-nitrophenol. An almost complete removal was achieved on the eighth day of the treatment process.

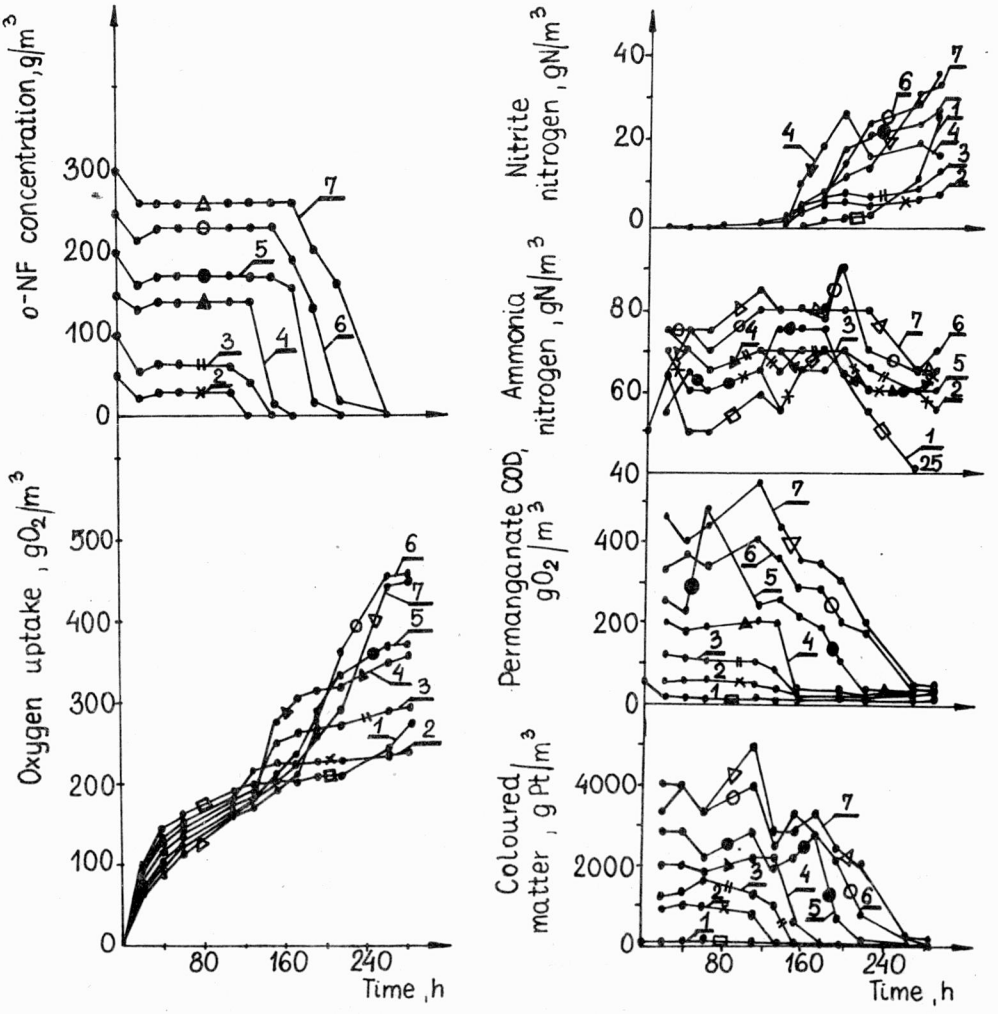


Fig. 1. Variations in the concentration of o-nitrophenol, oxygen uptake, nitrite nitrogen, ammonia nitrogen, permanganate COD, and coloured matter in municipal sewage

1 – lack of o-nitrophenol, 2 – 50 g/m³, 3 – 100 g/m³, 4 – 150 g/m³, 5 – 200 g/m³, 6 – 250 g/m³, 7 – 300 g/m³

The removal efficiencies for municipal sewage were as follows: o-nitrophenol, approximately 100%; dichromate COD, 90%; BOD_5, 96%; and permanganate COD, 93% (fig. 3). Some disturbances of the treatment process may be attributed to the increased BOD_5 loadings of the sludge and the tank. As a result, the removal efficiency for o-nitrophenol, permanganate COD and BOD_5 dropped to the level of about 30%, 50% and 68%, respectively. The concentration of adapted sludge fell between 5000 to 6000 g MLSS/m³. The prevalent population was that of rotifers.

Table 1

Parameters of equation for a monomolecular reaction determined by respirometric experiments

Medium	o-nitrophenol concentration g/m³	$y = L_0[1-e^{-K_1(t-t_{op})}]$ L_0 g O_2/m³	K_1 d⁻¹	t_{in} d	K_{1N}/K_{1K}
Municipal sewage	0	200.96	0.75754	–	–
	50	183.57	0.77374	–	1.0214
	100	179.72	0.76538	–	1.0103
	150	177.54	0.64525	–	0.8517
	200	178.05	0.50922	–	0.6722
	250	179.72	0.515	–	0.6798
	300	167.26	0.49413	–	0.6523
Non-adapted activated sludge with mineral broth	0	426.71	0.29227	0.08	–
	5	427.45	0.29623	0.08	1.0135
	10	326.0	0.353	0.13	1.2077
	20	269.67	0.38476	0.09	1.3164
	50	240.0	0.3183	–	1.0890
	75	184.23	0.297	–	1,0161
	150	112.31	0.3383	–	1.1574
	200	118.24	0.2659	–	0.9097
	300	124.46	0.3106	–	1.0627

Notations:
y – oxygen uptake to moment t, g O_2/m³,
L_0 – final oxygen demand, g O_2/m³,
K_1 – rate constant for first-order reaction, d⁻¹,
t – duration of reaction, d,
t_{in} – duration of inhibition, d,
K_{1N} – K_1 for samples containing o-nitrophenol, d⁻¹,
K_{1K} – K_1 for control samples, d⁻¹.

The decreasing effluent levels of pH, alkalinity, and ammonia nitrogen and the increased effluent concentrations of nitrite nitrogen and nitrate nitrogen indicate that there was a nitrification of the first and second phases in the municipal sewage (fig. 3).

The efficiency of removal for atrificial wastewater was the following: o-nitrophenol, approximately 100%; BOD_5, 98% to 99%, permanganate COD, 95 to 98%; and dichromate COD, 83 to 93%. There was a wide spectrum of genera and species, which was an indication of a good efficiency.

Prior to the experimental series with mineral wastewater, the activated sludge was adapted to 5 g/m³ concentration of o-nitrophenol in artificial wastewater, whereas nutrient medium and peptone were eliminated step by step. This stage covered a period of 52 days. The experimental series with mineral wastewater

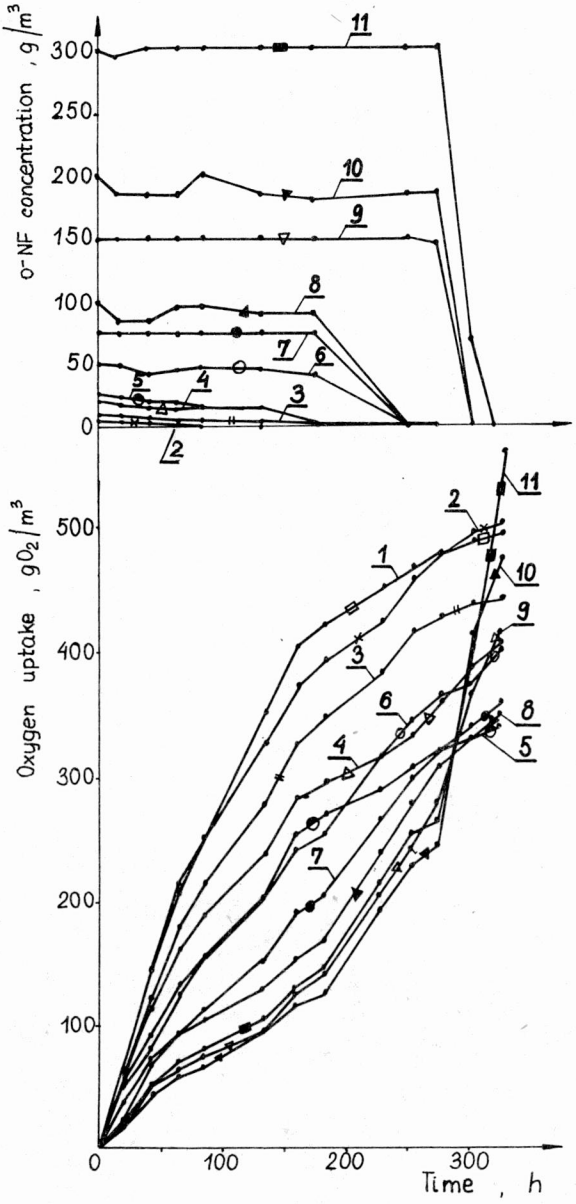


Fig. 2. Variations in the concentration of o-nitrophenol and oxygen uptake in the mineral medium due to the action of non-adapted activated sludge

1 – o-nitrophenol, *2* – 5 g/m³, *3* – 10 g/m³, *4* – 20 g/m³, *5* – 25 g/m³, *6* – 50 g/m³, *7* – 75 g/m³, *8* – 100 g/m³, *9* – 150 g/m³, *10* – 200 g/m³, *11* – 300 g/m³

Table 2

Parameters of the activated-sludge process

Sample	o-nitro-phenol dosage g/m^3	Number of days d	Flow rate dm^3/h	Aeration time h	Hydraulic loading of the tank m^3/m^3 d	BOD_5 loading of the tank g O_2/m^3 d	BOD_5 loading of the biomass g $O_2/g \cdot d$	Sludge content kg MLSS/m^3	Sludge volume index cm^3/g
municipal sewage	5–400	94	0.1	13	1.85	190–1240	0.01–0.29	3.5–9.0	54–88
artificial wastewater	50–400	68	0.1	10.8	2.2	440–1144	0.1–0.3	3.0–6.7	74–195
mineral wastewater	28–450	148	0.096	13	1.85	192–1379*	0.22–1.08*	0.7–4.7	35–95

* Dichromate COD loading.

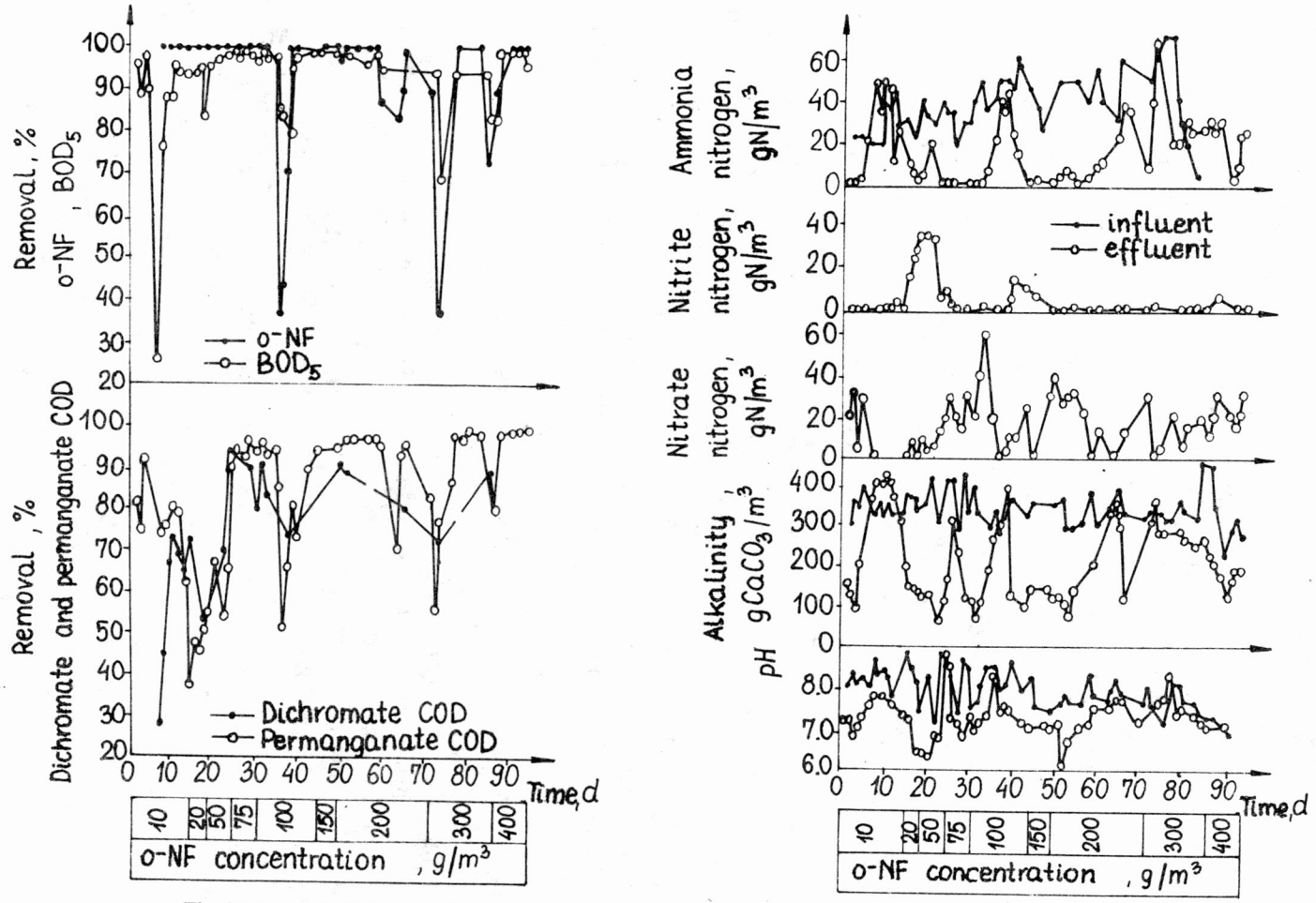
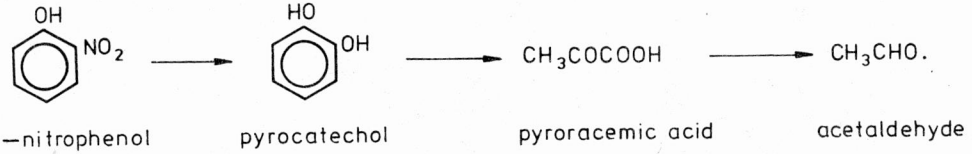


Fig. 3. Removal efficiency and variations in the concentrations of nitrogen compounds, pH and alkalinity in municipal sewage containing o-nitrophenol

involving o-nitrophenol concentrations ranging from 28 to 450 g/m^3 took 150 days. The extended adaptation procedure yielded an almost 100% removal of the nitro compound, and a reduction of permanganate COD and dichromate COD amounting to 98% and 92%, respectively. Some rapid variations in o-nitrophenol content accounted for the temporary disturbance of the nitrification process. Despite a por spectrum of microorganisms, the activated sludge showed a good ability to degrade o-nitrophenol. The intermediate products of biochemical degradation in the mineral medium were identified by thin-layer chromatography. They are as follows:



There is only partial agreement between these results and the findings reported by GERMANIER and WUHRMANN [2]. Apart from pyrocatechol, the identification procedure revealed the occurrence of pyroracemic acid and acetaldehyde. The GERMANIER report [2] includes β-ketone adipic acid.

The data for municipal sewage containing o-nitrophenol were used for calculating the rate constant of the treatment process in terms of the Eckenfelder formula [5]. The calculated value 0.9165×10^{-3} m^3/g MLSS h reaches the lower limit of the interval ($1 \times 10^{-3} - 2 \times 10^{-3}$ m^3/g MLSS h). The values of the rate constant falling in this range indicate that o-nitrophenol may be regarded as biodegradable.

4. CONCLUSIONS

1. o-nitrophenol is modestly susceptible to chemical degradation.
2. o-nitrophenol concentration of 5 g/m^3 in raw wastes has no inhibiting effect on non-adapted activated sludge.
3. After adaptation, activated sludge is able to degrade o-nitrophenol at concentrations up to 400 g/m^3 under BOD_5 loading amounting to 0.3 g O_2/g MLSS day and aeration of 13 h.
4. Intermediate products of biochemical degradation are pyrocatechol, pyroracemic acid and acetaldehyd.

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BIODEGRADACJA o-NITROFENOLU W WARUNKACH TLENOWYCH

o-nitrofenol w ściekach jest produkowany przede wszystkim przez przemysł chemiczny. Ponieważ o-nitrofenol przedostaje się do środowiska w połączeniu z innymi składnikami ściekowymi, konieczne jest określenie jego podatności na rozkład biochemiczny lub biologiczny. W procesie biodegradacji fenolu wykorzystano trzy rodzaje ścieków: miejskie, sztuczne i mineralne. Badania przeprowadzono w warunkach statycznych i dynamicznych. W procesie osadu czynnego, po okresie adaptacji, możliwy jest rozkład fenolu o stężeniu do 400 g/m^3.

БИОДЕГРАДАЦИЯ О-НИТРОФЕНОЛА В КИСЛОРОДНЫХ УСЛОВИЯХ

О-нитрофенол, находящийся в сточных водах, происходит прежде всего из химической промышленности. Из-за того, что о-нитрофенол переходит в среду в соединении с другими элементами сточных вод, необходимо определение его податливости к биохимическому или биологическому разложению. В процессе биодеградации фенола использованы три вида сточных вод: городские, искусственные и минеральные. Исследования были проведены в статических и динамических условиях. В процессе активного оседания, после срока приспособления возможно разложение фенола концентрации до 400 г/м^3.