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BIODEGRADATION OF FORMALDEHYDE: KINETICS OF THE REACTION

Laboratory tests were run to investigate the biochemical degradation of formaldehyde by activated sludge in a complete-mix reactor. Parameters describing the kinetics and stoichiometry of the reaction were determined. It has been found that in the course of the process pH drops to an acidic level. This acidification should be attributed to the presence of formic acid (an intermediate product of oxidation) as well as to the nitrification and assimilation of ammonia nitrogen. This undesirable phenomenon can be eliminated when nitrates are used as a nitrogen source.

Analytical formulae were derived to enable upgrading of the process (e.g., design of a full-scale system for formaldehyde removal from industrial gases).

1. INTRODUCTION

The widespread use and production of formaldehyde and its derivatives, which has become a necessity at the present stage of technological development, causes penetration of toxic substances to the ambient environment. In the past few years the attention of environmental scientists and engineers has been directed to formaldehyde emissions [1], [2]. The admissible concentrations of air-borne formaldehyde are very low, because this compound is very toxic [3]. The establishment of low admissible levels for air pollutants does not mean that the environment is efficiently protected. It just indicates that the release of those pollutants into the atmosphere calls for appropriate control measures. One of these is biodegradation. In the course of the biodegradation formaldehyde is oxidized to carbon dioxide and water; this process is accompanied by partial assimilation of carbon and formation of formic acid which is an intermediate product [4].

Taking into account the usefulness of biological methods when applied to the treatment of industrial gases [5]–[8] attempts have been made to use biological processes for the treatment of formaldehyde-laden air [9], [10].

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One of the systems in which industrial gases are treated is a biological scrubber involving activated sludge as the sorbing medium. In an absorber the gas stream is treated by direct contact with activated sludge. Suspension saturated with polluting substances is passed to the aeration tank, wherein the pollutants undergo biodegradation which brings about self-regeneration of the sorbent thus becoming fit for reuse. The biological scrubber makes a unit system with an adequately selected small activated sludge treatment plant. The design of a biological scrubber for formaldehyde removal requires information on the kinetics of biodegradation of this compound.

The available literature reports [4], [11]–[13] contain descriptions of the biodegradation process in question, but they do not allow generalizations which are required for our particular case. Keeping this in mind, the authors of this paper attempted to investigate and describe the phenomenon in a quantitative manner. The investigations were conducted under laboratory conditions in a complete-mix activated sludge reactor at almost constant loading. The experiments involved artificial wastewater samples containing formaldehyde (with no methanol addition) and mineral salts.

2. APPARATUS

The experiments were run in a glass apparatus (fig. 1). The system consisted of the following major parts: activated sludge tank, settling tank and aerating nozzle. The

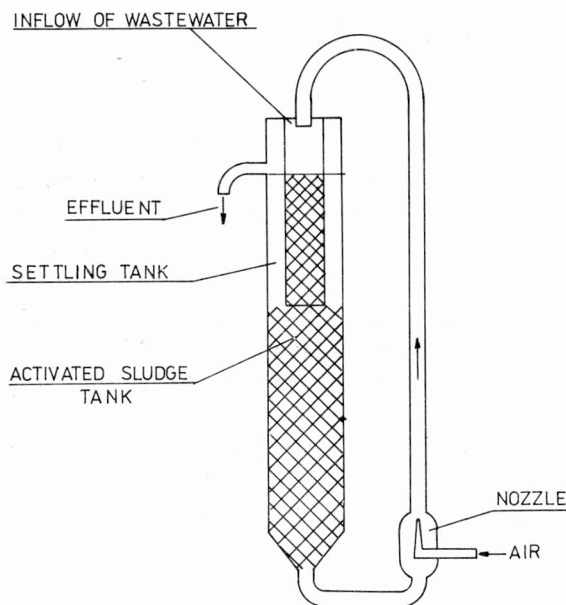


Fig. 1. Experimental system

total effective volume V_{total} amounted to 2.450 dm³, of which the volume of the settling tank V_0 and the volume of the activated sludge tank together with nozzle and pipes V_k accounted for 0.755 dm³ and 1.695 dm³, respectively. The activated sludge tank was fed continuously through a peristaltic pump. Sludge concentration was kept almost constant by manual removal of excess biomass growth in the course of the experiments. An almost ideal mix in the activated sludge reactor was checked experimentally.

3. MATHEMATICAL MODEL OF THE REACTOR

Figure 2 gives the schematic diagram of the activated reactor for the biodegradation of organic compounds under through-flow conditions with complete mix.

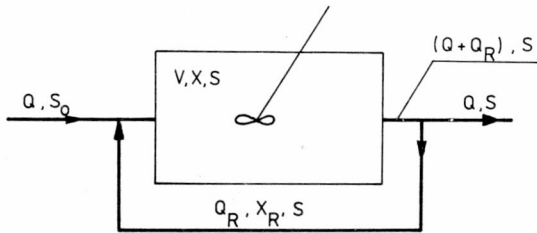


Fig. 2. Schematic diagram of a complete mix reactor
(index R refers to the recirculation stream)

Thus, the substrate balance takes the form

$$Q(S_0 - S) - V \cdot \mu \cdot x \cdot \frac{1}{Y_t} = 0 \quad (1)$$

where:

- μ — specific growth rate (1/d),
- Y_t — growth yield coefficient (g SS*/g),
- x — biomass concentration (g SS*/m³),
- S_0 — influent substrate concentration (g/m³),
- S — effluent substrate concentration (g/m³),
- Q — flow rate (m³/d),
- V — volume of activated sludge tank (reactor), (m³).

The μ/Y_t quotient indicates the biodegradation rate for the substrate.

From equation (1) it is obvious that

$$k = \frac{\mu}{Y_t} = \frac{(S_0 - S)Q}{V \cdot x} \quad (2)$$

SS* — suspended solids.

Assuming the Monod model [14] for the μ versus S (k versus S) relation, equation may be rewritten as

$$k = \frac{\mu_m}{Y_t} \cdot \frac{S}{K_s + S} = \frac{(S_0 - S) Q}{V \cdot x} \quad (3)$$

where:

μ_m – maximum growth rate (1/d),

K_s – Michaelis constant (g/m³),

$\mu_m/Y_t = k_m$ – maximum value of biodegradation rate for substrate.

When investigating the biodegradation of the given organics, the problem can be reduced to the evaluation of the k versus S relation (eq. (3)) or, more exactly, to the estimation of the coefficients of microbiological kinetics, i.e., K_s and $k_m = \mu_m/Y_t$. The growth yield coefficient $Y_t = V \cdot \Delta x / Q \Delta S$ can be calculated from biomass increment and substrate decrement. The theoretical plot of the k versus S relation, as well as the meaning of the constants k_m and K_s are shown in fig. 3.

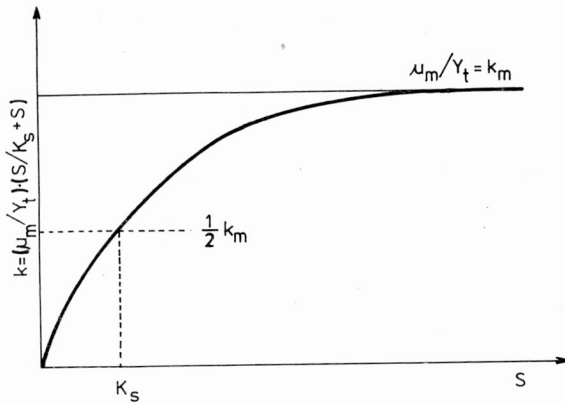


Fig. 3. Graphical representation of the Monod model (3)

To evaluate k_m and K_s we can use eq. (3) or take into account the various linearized transformations [15] of eq. (3). Hence, we write

$$\left(\frac{1}{k}\right) = \frac{Y_t}{\mu_m} + \frac{Y_t}{\mu_m} K_s \left(\frac{1}{S}\right), \quad (4)$$

$$\left(\frac{S}{k}\right) = \frac{Y_t}{\mu_m} K_s + \frac{Y_t}{\mu_m} (S), \quad (5)$$

$$(k) = \frac{\mu_m}{Y_t} - K_s \left(\frac{k}{S}\right). \quad (6)$$

4. ANALYTICAL AND MEASURING PROCEDURES

The control of the biodegradation process involved the determinations of influent formaldehyde concentration by colorimetry (chromotropic acid) [16], effluent formaldehyde concentration by colorimetry (para-fuchsin) [17], influent and effluent COD [18], SS of the biomass by gravimetry, pH. Concentrations of NO_3^- , NO_2^- and NH_4^+ in influent and effluent were measured incidentally.

5. EXPERIMENTAL PROCEDURES

The biomass grew on the synthetic wastewater (broth, 200 g/m³; peptone, 310 g/m³; NH_4Cl , 60 g/m³; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 2 g/m³; KH_2PO_4 , 20 g/m³; K_2HPO_4 , 50 g/m³; and NaCl , 70 g/m³). Inoculation involved raw sludge from a municipal sewage treatment plant. In the course of the adaptation process, the retention of the biomass in the tank raised serious problems. The white, opalizing colour of the effluent indicated that sludge in colloidal form was washed out. This is likely to be due to the low pH value in the reactor (pH < 6). To abate the undesirable phenomenon, two methods were attempted. Retention time in the aeration tank was extended to about 24 h (at the same time the loading of the settling tank was reduced), and the concentrations of nutrients, especially phosphates, were increased to achieve a rise in the buffer capacity of the solution. Higher concentrations of NH_4Cl , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KH_2PO_4 and NaCl amounted to 120, 10, 160, 400, and 100 g/m³, respectively.

After having reduced the effect of acid reaction, it was possible to run the experiments according to the assumed model. In each experiment (which took 7 days) the influent concentration of formaldehyde was kept constant, and so was the concentration of the biomass by removal of excess sludge. Even though decreased, the acidic effect brought about some limitations to the experimental conditions. Thus, experiments with increased sludge loading were successfully conducted only at low sludge concentration. For example, each attempt to ensure approximately steady state conditions at sludge concentration and sludge loading greater than 2500 g/m³ and 0.2 g COD/g SS day, respectively, failed to be successful because of a rapid drop in pH and rapid washing out the biomass in colloidal form. Our attempts to run the process at low loading values were also a failure. Low biomass concentrations required low influent concentrations of formaldehyde, and these changed significantly in the raw wastewater tank, probably as a result of bacterial infection. It was within several hours (e.g., during night) that formaldehyde concentration and pH dropped rapidly, the drop in dichromate COD being less distinct. The results from this experimental series are listed in tab. 1.

The disadvantageous phenomena observed in the course of the experiments made the authors attempt a partial qualitative interpretation. The effect of the

Table 1

Biodegradation of formaldehyde in the presence of ammonium chloride as nitrogen source

$\left[\frac{\text{g CH}_2\text{O}}{\text{m}^3} \right]$	S_0 $\left[\frac{\text{g COD}}{\text{m}^3} \right]$	X $\left[\frac{\text{g SS}}{\text{m}^3} \right]$	pH in tank	S $\left[\frac{\text{g COD}}{\text{m}^3} \right]$	k $\left[\frac{\text{g COD}}{\text{g SS d}} \right]$	ΔX $\left[\frac{\text{g SS}}{\text{d}} \right]$	ΔS $\left[\frac{\text{g COD}}{\text{d}} \right]$	Y_t $\left[\frac{\text{g SS}}{\text{g COD}} \right]$	COD removal [%]
424	547	2050	6.08	14	0.263	0.099	0.942	0.105	97
390	565	2480	5.86	17	0.224	0.149	0.973	0.153	97
279	457	2410	5.83	19	0.185	0.029	0.792	0.037	96
167	200	920	7.16	27	0.184	0.024	0.097	0.249	87
391	484	1790	6.92	35	0.242	0.116	0.793	0.147	93
580	659	1960	6.71	37	0.312	0.068	1.102	0.062	94
599	668	2040	6.83	38	0.303	0.069	1.113	0.062	95
746	782	1960	6.04	40	0.370	0.168	1.300	0.130	95
734	732	1890	6.82	44	0.355	0.240	1.213	0.198	94
704	772	1590	6.02	47	0.437	0.060	1.310	0.046	94
525	584	1190	6.17	50	0.447	0.032	0.980	0.033	91
703	810	1696	6.08	55	0.434	0.100	1.345	0.074	93
384	513	1276	6.01	56	0.363	0.063	0.887	0.071	89
737	802	1760	6.20	58	0.412	0.078	1.329	0.059	93
710	785	1450	6.65	66	0.483	0.037	1.300	0.028	92
646	708	1260	6.80	67	0.492	0.016	1.164	0.013	90
657	757	1490	6.07	71	0.453	—	1.265	—	90
756	792	1530	6.79	85	0.489	—	1.320	—	89
701	772	1360	6.78	85	0.454	—	1.270	—	89

Table 2

Biodegradation of formaldehyde in the presence of potassium nitrate as nitrogen source

S_0		X	pH	S		k		ΔX	ΔS		Y_l		Removal of	
$\left[\frac{\text{g CH}_2\text{O}}{\text{m}^3}\right]$	$\left[\frac{\text{g COD}}{\text{m}^3}\right]$	$\left[\frac{\text{g SS}}{\text{m}^3}\right]$	in tank	$\left[\frac{\text{g CH}_2\text{O}}{\text{m}^3}\right]$	$\left[\frac{\text{g COD}}{\text{m}^3}\right]$	$\left[\frac{\text{g CH}_2\text{O}}{\text{g SS d}}\right]$	$\left[\frac{\text{g COD}}{\text{g SS d}}\right]$	$\left[\frac{\text{g SS}}{\text{d}}\right]$	$\left[\frac{\text{g CH}_2\text{O}}{\text{d}}\right]$	$\left[\frac{\text{g COD}}{\text{d}}\right]$	$\left[\frac{\text{g SS}}{\text{g CH}_2\text{O}}\right]$	$\left[\frac{\text{g SS}}{\text{g COD}}\right]$	CH ₂ O %	COD %
—	673	4210	7.30	—	16	—	0.166	0.083	—	1.186	—	0.070	—	96.3
380	412	3390	7.30	0.10	19	0.122	0.127	0.014	0.701	0.726	0.020	0.019	99.97	95.4
765	813	3760	7.38	0.17	19	0.239	0.248	0.102	1.523	1.585	0.067	0.065	99.98	97.7
248	267	3860	7.26	0.08	20	0.070	0.070	0.079	0.457	0.456	0.173	0.173	99.97	92.7
709	778	4230	7.40	—	20	—	0.197	0.140	—	1.435	—	0.097	—	97.4
576	621	3740	7.30	0.17	20	0.169	0.177	0.095	1.071	1.119	0.089	0.085	99.97	96.8
370	400	4030	7.25	0.13	23	0.097	0.099	0.059	0.663	0.676	0.089	0.088	99.96	94.4
—	645	4420	7.25	—	24	—	0.151	0.081	—	1.300	—	0.071	—	96.3
1087	1097	2580	7.49	0.24	26	0.461	0.454	0.145	2.016	1.984	0.072	0.073	99.98	97.6
985	1070	3760	7.40	0.22	33	0.281	0.295	0.141	1.791	1.899	0.079	0.074	99.98	96.9
1284	1286	2850	7.45	0.25	33	0.496	0.484	0.321	2.396	2.337	0.134	0.137	99.98	97.4
1447	1547	3120	7.45	0.29	35	0.501	0.524	0.173	2.649	2.784	0.065	0.062	99.98	97.7
1142	1293	3410	7.43	0.39	36	0.362	0.399	0.192	2.092	2.304	0.092	0.083	99.97	97.2
1658	1814	3120	7.53	0.32	40	0.588	0.629	0.255	3.110	3.325	0.082	0.077	99.98	97.8
1451	1601	3570	7.57	0.33	43	0.439	0.471	0.201	2.656	2.850	0.076	0.071	99.98	97.3
2153	2350	3460	7.50	0.38	47	0.681	0.729	0.387	3.994	4.272	0.097	0.091	99.98	98.0
1885	2064	3340	7.65	0.35	49	0.613	0.655	0.372	3.470	3.723	0.107	0.100	99.98	97.6
—	2081	3030	7.79	0.40	68	—	0.749	0.480	4.278	3.842	0.112	0.125	99.98	96.7

system acidifying may be attributed to the formation of formic acid as the intermediate product [4], [11]. Occasional analyses of inorganic nitrogen compounds have revealed the presence of nitrate ion in the effluent. Nitrate ion is likely to have formed from ammonium ion via nitrification. Such an oxidation of ammonium ion (which comes in the form of ammonium chloride in the influent stream) yields nitric acid and hydrochloric acid. But it is also the assimilation of ammonia by the growing cells that accounts for the release of hydrochloric acid. Hence, these are three contributing factors which should be regarded responsible for the significant decrease of pH in the course of the experiment. This allowed us to believe that if ammonium chloride were replaced by nitrates (e.g., in the form of potassium nitrate) as the nitrogen source for growing cells, the process conditions for the biodegradation of formaldehyde would change substantially. As before, formic acid would be the intermediate product. The additional acidifying effect due to nitrification might be eliminated, and assimilation of nitrogen might increase the alkalinity of the system. Keeping this in mind, we decided to run a new experimental series involving potassium nitrate as nitrogen source. The mineral nutrients applied were the following: KNO_3 , 250 g/m³; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 10 g/m³; KH_2PO_4 , 160 g/m³; K_2HPO_4 , 400 g/m³; and NaCl , 100 g/m³. The results are gathered in tab. 2.

As shown by these data, no acidifying effect is found to occur. On the contrary, there is a slight increase of pH. A new distinct effect was an intensive "flocculation" at increased sludge loading.

6. DISCUSSION OF RESULTS

Making use of the experimental data sets included in tabs. 1 and 2, the coefficients of microbial kinetics, $k_m = \mu_m/Y_t$ and K_s , were estimated. The estimation procedure involved the k versus S relation in a linearized form described by eqs. (4)–(6). As an alternative, the non-linear least-square method was used for the direct approximation by eq. (3) [19]. The estimation results are given in tabs. 3 and 4 for the systems with ammonium chloride and potassium nitrate, respectively.

As shown by these data, each transformation of eq. (3) yields a different estimate of the parameters for the microbiological kinetics. In the case of NO_3^- , the values obtained had no physical meaning. There were also significant differences in the correlation coefficient (R) values, which should be attributed to the considerable scattering of the experimental results in the vicinity of the values calculated when using model (3). When the difference between experimental values and those predicted by model (3) is smaller, the parameter values estimated by different methods are similar. Hence, when there is a considerable scattering of results, approximation by the linearized formulae (4)–(6) should be avoided. Instead, the direct approximation by formula (3) using the non-linear least-square method is recommended. In this way, we shall be able to eliminate such situations, when the parameter values obtained by approximation fail to have any physical sense.

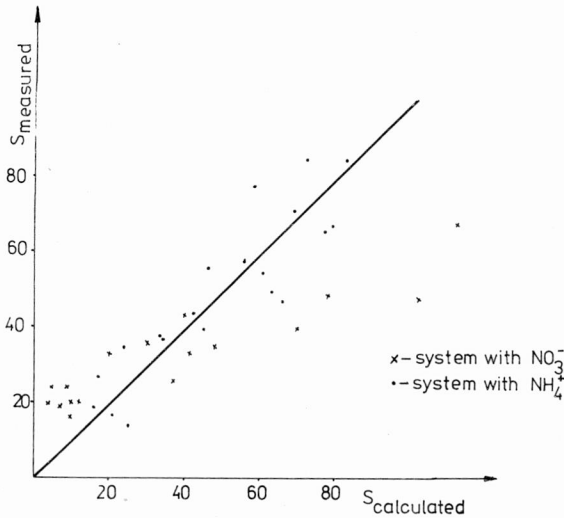


Fig. 4. Comparison of measured (by experiments) and calculated (in terms of eq. (8)) values of S

Transforming eq. (3), we obtain the expression for the necessary activated sludge reactor volume V versus the required COD in the effluent S

$$V = \frac{Q(S_0 - S)(K_s + S)}{k_m \cdot x \cdot S} \quad (7)$$

Equation (3) may also be solved with respect to S . We then obtain the relation describing the effluent COD value as a function of the parameters Q , V , x , S_0 and of the determined coefficients of microbiological kinetics k_m , K_s :

$$S = 0.5 \left[S_0 - K_s - \frac{V}{Q} k_m x + \sqrt{\left(S_0 - K_s - \frac{V}{Q} k_m x \right)^2 + 4S_0 K_s} \right] \quad (8)$$

For comparison, fig. 4 gives measured (tabs. 1 and 2) and calculated (eq. (8)) values of S .

As shown by these plots, the agreement is satisfactory (specifically for the system involving NH_4^+ as nitrogen source). Hence, the data obtained justified the utility of eq. (8) when applied to the design of the treatment process on a larger scale.

The agreement for the system with NO_3^- is much worse than that for the NH_4^+ system, which should be attributed to a weaker approximation of the k versus S relation by model (3). Hence, the design of the treatment process by making use of eq. (8) will be characterized by a greater error than in the case of the NH_4^+ system.

Let us now return to the data sets included in tabs. 1 and 2. It is easily seen that Y_t values are low and distinctly scattered. Hence we thought it would be advisable to take the arithmetic mean which approached 0.09 g SS/g COD both for the NH_4^+ and for the NO_3^- system. We may, therefore, expect that the biomass growth will amount to 10% of the COD load removed.

Table 3

 $k_m = \mu_m/Y_t$ and K_S for the system with ammonium chloride

Parameter	According to formula			Direct approximation by (3)
	(4)	(5)	(6)	
$k_m = \mu_m/Y_t$ [g COD/g SS d]	0.596	0.825	0.489	0.817
K_S [g COD/m ³]	30	58	15	55
Correlation coefficient R	0.766	0.807	0.432	0.889

Table 4

 $k_m = \mu_m/Y_t$ and K_S for the system with potassium nitrate

Parameter	According to formula			Direct approximation by (3)
	(4)	(5)	(6)	
$k_m = \mu_m/Y_t$ [g COD/g SS d]	-0.484	-0.551	-0.104	1.06
K_S [g COD/m ³]	-85	-92	-43	50
Correlation coefficient R	0.696	0.414	0.765	0.771

7. CONCLUSIONS

Biodegradation of formaldehyde in the activated sludge process may be equally efficient when using NH_4^+ or NO_3^- ions as the nitrogen source. The decrease in alkalinity, due to formic acid formation, assimilation, and nitrification of ammonia, brings about a pH drop in the aeration tank. This phenomenon is likely to be one of the major factors affecting the settleability of activated sludge. The result is the wash out of the biomass from the treatment system, which takes place at a sludge loading greater than 0.54 g COD/g SS day. The application of NO_3^- as nitrogen source eliminates the undesirable acidifying effect, thus making the biodegradation run effectively up to the sludge loading value of 0.77 g COD/g SS day. Once this value has been exceeded, the biomass loses its settleability and leaves the system.

The model proposed (eq. (8)) may be successfully applied to the design of the treatment process on a larger scale. The coefficients of kinetics included in the model may be determined by experiments similar to those described in this paper. To estimate these coefficients in terms of eq. (3) it is advisable to make use of the non-linear least-squares method.

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BIOCHEMICZNY ROZKŁAD ALDEHYDU: KINETYKA REAKCJI

Przedstawiono wyniki prac laboratoryjnych nad biochemicznym rozkładem formaldehydu osadem czynnym w reaktorze o pełnym wymieszaniu. Określono parametry kinetyki i stechiometrii przemian. Stwierdzono, że w procesie ma miejsce zakwaszenie środowiska. Wywołane jest to powstawaniem kwasu mrówkowego (produkt pośredni utleniania formaldehydu) oraz nityfikacją i asymilacją azotu amonowego. Zastosowanie azotanów jako źródła azotu wyeliminowało to niekorzystne zjawisko. Podano formuły analityczne, które mogą być wykorzystane do projektowania procesu w większej skali (np. instalacji do usuwania formaldehydu z gazów odlotowych).

БИОХИМИЧЕСКОЕ РАЗЛОЖЕНИЕ АЛЬДЕГИДА: КИНЕТИКА РЕАКЦИИ

Представлены результаты лабораторных работ над биохимическим разложением формальдегида активным илом в реакторе полного перемешивания. Определены параметры кинетики и стехиометрии превращений. Было установлено, что в этом процессе имеет место ацидификация среды. Она вызвана образованием муравьиной кислоты (будущей промежуточным продуктом окисления формальдегида), а также нитрификацией и ассимиляцией аммиачного азота. Применение нитратов в качестве источника азота исключило это отрицательное явление. Даны аналитические формулы, которые можно использовать для проектирования процесса в большем масштабе (напр. установки для удаления формальдегида из отходящих газов).