XXV. CERTAIN FACTORS THAT INFLUENCE THE RATE OF ACTIVATED SLUDGE AND SEWAGE OXIDATIONS.

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WE have shown in previous papers [Wooldridge and Standfast, 1936, 1, 2] that oxygen absorption by sewage, by sludge or by sewage-sludge mixtures may be conveniently studied by means of Barcroft differential manometers and that small but significant differences may be investigated by replicated experiments [Corbet and Wooldridge, 1936]. The present paper describes the results of experiments on the effects of various conditions on the rates of oxidation.

Effect of temperature on the oxidation of sewage.

As sewage oxidation normally takes place somewhat below atmospheric temperature it is possible, if the oxidation is due to the presence of highly specialised flora or fauna, that its rate might be greater or less at higher temperatures such as 30° or 37° than at, say, 18°. Samples of many different sewages and effluents have been studied at 18°, 22°, and 30° or 37°, and all, with the exception of a few effluents, have shown increased rate of absorption of oxygen with rise in temperature. No direct comparison, however, was made on any one sample of its rates of oxidation at 30° and 37°. The results in Table I illustrate the relative

Table I. *Effect of temperature on the oxidation of sewage.*

2 ml. of crude sewage and 1 ml. of phosphate buffer, p_H 7.4, were placed in the right-hand cup of each Barcroft manometer, with buffer and water in the left-hand cups. Carbon dioxide was absorbed by placing 10% potash in the inner tubes sealed into the bottom of the cups. The results given are the mean in every case of six experiments simultaneously made, the manometers being shaken in a bath of water kept at the stated temperature. The figures heading the columns represent the number of hours after the experiment began and those in the body of the table give the corresponding oxygen uptake (expressed in μ l. at N.T.P.) by 1 ml. of sewage.

Sewage	Temp. °C.	Hours									
		3	7	24	27	31	48	51	67½	104	120
I	18	15	52	159	170	184	228	232	258	296	328
	22	19	73	179	190	205	257	265	297	363	388
	37	56	128	231	248	265	312	320	350	405	423
II	18	10	31	86	92	99	126	130	148	170	177
	22	12	38	89	95	104	133	137	159	191	202
	37	24	61	116	125	133	166	169	190	230	245
III	18	2	3.3	5.5	6	7	8.6	8.7	11	18	21
	22	2	3.8	7.1	7.8	8.1	10.4	10.9	12.9	20.3	24.3
	37	3	4.6	8.3	8.6	9.2	11.4	11.5	16.4	27.3	33

rates at 18°, 22° and 37° of three sewage liquors of different strength; sewage III was a treated effluent. With all three samples similar results were obtained. We have on occasion, however, found that with a satisfactory sewage effluent the

rate of oxidation at 37° or 30° may be slightly lower than that at 22°. The explanation of this has not been found but it may be associated with the nitrate content of the effluent. Although it has been shown that sewage oxidation will generally proceed more rapidly at 30° or 37° we have carried out most of our work at 22° or 24° as we wished to study the problem at temperatures nearer to those generally maintained in sewage purification plants.

Effect of hydrogen ion concentration on sewage oxidation.

Samples of sewage were adjusted to various p_H values between 4.0 and 10.0 by the addition of small amounts of acid or alkali and their rates of oxidation followed in a Barcroft apparatus. Results so obtained seemed to suggest that the oxidation took place readily between p_H 6.0 and 9.0, with perhaps an optimum between 7.0 and 8.0, but unfortunately the p_H values did not remain constant and no definite conclusion from these experiments is warranted. Table II gives

Table II. *Effect of p_H on oxygen absorption by crude sewage.*

The figures in the table represent the oxygen absorption in μ l. at N.T.P. by 1 ml. of crude sewage over a period of 9 hours when shaken with excess air in a Barcroft apparatus at varying p_H values, the latter being kept constant by the addition of buffer of the required p_H . The CO_2 evolved was absorbed by KOH papers. The final p_H values were examined and found to be identical with the original. Each right-hand cup contained 2 ml. of sewage and 1 ml. of the buffer and each left-hand cup 2 ml. of water and 1 ml. of buffer. Temperature 22°.

Buffer	p_H	Hours						
		1	2	3	4	5	6	9
Phthalate	4.5	0	0	0	0	0	0	1.6
	5.2	0	0	0	0	0.2	1.3	2.0
	6.0	2.7	5.5	8.1	14.0	20.2	41.2	61.0
Phosphate	6.1	4.3	8.2	12.0	22.6	35.0	53.7	102.0
	6.6	6.0	11.9	20.0	32.3	49.0	71.0	131.0
	7.3	10.1	20.0	34.0	54.0	77.0	93.3	133.0
	8.0	9.9	19.3	31.3	46.5	66.4	85.3	126.0
Borate	8.0	4.5	7.9	12.1	15.9	19.8	25.9	55.0
	8.4	1.6	9.7	10.3	14.7	19.3	25.0	57.3
	9.0	4.5	8.4	11.9	15.4	18.8	24.1	52.3
	9.6	4.4	7.5	9.7	11.2	12.9	14.2	23.0

results obtained with samples of a crude sewage buffered at various p_H levels. It will be seen that practically no oxidation occurs below p_H 5.0 and that it begins to fall off again above 9.0. Between p_H 6.6 and 9.0 there is fairly rapid oxidation with perhaps a maximum rate at about 7.3. The presence of phthalate or of borate buffer appears to inhibit somewhat the oxidation (*cf.* the values obtained at p_H 6.0 and at 8.0 in the presence of phosphate and phthalate or borate buffers).

When a similar experiment is carried out with a suspension of washed activated sludge the oxidation of the sludge is found to be fairly vigorous over a wider range, *viz.* between p_H 6.0 and 10.0, whilst its inhibition at p_H 5.0 is only slight. Little oxidation usually occurs at p_H 4.0 or at values above 12.0. Illustrative results are given in Table III. It will be noticed that the phthalate and borate inhibitions are less marked with the oxidation of sludge than with that of sewage. Allowing for the borate inhibition there would appear to be no significant optimum p_H for the oxidation of sludge between 6.0 and 9.0.

The rate of oxidation of a sewage at various concentrations of hydrogen ions in the presence of sludge, however, resembles that for sewage alone, for the

Table III. *Effect of p_H on the oxidation of sludge.*

The figures in the table represent the oxygen absorption in $\mu\text{l.}$ at N.T.P. of 1 ml. of sludge over a period of 5 hours when shaken with excess air in a Barcroft apparatus at different p_H values, the latter being kept constant by the addition of buffers. The CO_2 evolved was absorbed by KOH. The sludge was prepared by washing several times with water a sample obtained from the activated sludge tank and filtering the final suspension through muslin. The last cup had 1 ml. $N/10$ NaOH added instead of buffer. The p_H was determined again at the end of the experiment and found to be unchanged (no test was made on the $N/30$ NaOH). Each right-hand cup contained 1 ml. of sludge suspension, 1 ml. of the required buffer and 1 ml. water, the left-hand cups containing only the buffer and water. Temperature 22° .

Buffer	p_H	Hours				
		1	2	3	4	5
Phthalate	5.0	22.5	46.2	65.4	83.0	101.0
"	6.0	44.7	74.7	97.5	118.5	134.5
Phosphate	6.0	47.3	78.2	100.3	121.3	138.2
"	7.0	32.0	60.3	83.6	103.9	122.4
"	8.0	36.0	68.3	92.8	115.0	135.9
Borate	8.0	29.5	58.0	80.0	100.5	118.0
"	9.0	31.7	63.4	85.0	106.0	124.0
"	10.0	30.4	60.0	84.0	95.0	108.6
$N/30$ NaOH between	12.0-13.0	5.1	7.2	11.7	14.4	16.2

Table IV. *Effect of p_H on the oxidation of crude sewage in the presence of washed sludge.*

The figures in this table represent the difference between the oxygen absorbed by a sludge-sewage mixture and that absorbed by the sludge alone at different p_H values. Results are given in $\mu\text{l.}$ of O_2 at N.T.P. The experiments were made at 24° . Each right-hand cup contained 0.5 ml. of a washed sludge suspension previously adjusted to the required p_H , 0.5 ml. of the requisite buffer and 2 ml. of a Seitz-filtered crude sewage, also adjusted to the necessary p_H . In the left-hand cup the sewage was replaced by water. The final p_H values were determined and found not to differ from the initial values. CO_2 was absorbed by KOH.

Buffer	p_H	Hours				
		1	2	3	4	5
Phthalate	4.0	0	0	0	0	0
	5.0	0.8	2.4	2.4	2.4	2.4
	6.0	4.5	17.0	33.0	55.0	81.0
Phosphate	6.0	7.9	30.0	51.5	73.0	90.8
	7.0	30.0	56.0	73.5	90.0	102.0
	8.0	26.0	49.6	64.0	83.4	92.7
Borate	8.0	15.0	24.9	35.4	49.5	66.3
	9.0	15.0	25.3	32.8	49.8	65.3
	10.0	1.2	2.7	3.9	5.7	5.7

optimum again returns to the region of p_H 7.0 (*v.* Table IV) and little or no oxidation takes place at p_H 5.0 or 10.0. The rate of oxidation is approximately constant between p_H 6.0 and 9.0 if allowance is made for the effect of borate buffer. It is perhaps worthy of notice that although the sludge itself may be undergoing oxidation to some extent at p_H 5.0 and 10.0 (see Table III) this does not appear to enable it to oxidise the sewage at these p_H values, a result which indicates that some of the substrates of washed sludge are different from those of sewage. We may conclude therefore that for the oxidation of sewage by the activated sludge process it is preferable to work at p_H values between 7.0 and 8.0, but little loss in efficiency will take place if the p_H should drop to 6.0 or rise to 9.0. Outside these values considerable loss in efficiency may be expected.

Evolution of carbon dioxide in sewage oxidations.

It is to be expected that with the oxidation of the carbonaceous constituents of sewage some carbon dioxide would be produced and in order to avoid error due to the production of this gas it is usual in work with a Barcroft differential manometer to remove the carbon dioxide from the atmosphere in the cups by placing 0.3 ml. of 10% KOH (as liquid or impregnated filter-paper) in the small inner tubes fused to the bottom of the cups. All the experiments so far reported have been carried out with KOH present, but usually without paper as there appears to be no significant difference under our experimental conditions between the two techniques for carbon dioxide absorption [Corbet and Wooldridge, 1936]. By carrying out simultaneously two sets of similar experiments, identical except that the potash is present in one set and absent from the other, a difference will be noted in the volumes of the right-hand cups of the two series, the difference being due to the presence of carbon dioxide in those cups containing no KOH. In this way, and employing the appropriate manometer factor, the actual amount of carbon dioxide produced can be calculated from the readings of the two sets of experiments. Different constants are necessary for the same manometer in the presence or absence of KOH because of the different solubilities of the gaseous contents of the cup when it contains either oxygen and nitrogen alone or oxygen, nitrogen and carbon dioxide [*v.* Dixon, 1934]. Tables V and VI give typical results obtained when crude sewage or a sewage-sludge

Table V. *Oxygen absorption and carbon dioxide evolution by a crude sewage at p_H 7.0.*

The results given are the mean of six different experiments run concurrently. Each left-hand cup contained 1 ml. of phosphate buffer p_H 7.0, and 2 ml. of water; each right-hand cup contained 2 ml. of crude sewage in place of the water. The O_2 absorption figures were obtained from manometers containing 10% KOH in the cups and the CO_2 figures by deducting the change in volume of right-hand cup contents when no KOH was present from the change in volume when the CO_2 was absorbed by KOH, the appropriate factors being used for estimating these volume changes. The latter are expressed in μ l. at N.T.P.

	Hours									
	1	2	3	4	5	6	9	20	21	
O ₂ absorbed	20.2	33.2	44.9	59.8	78.2	100.1	147.0	218.0	220.0	
CO ₂ evolved	4.5	8.9	15.0	23.7	38.0	52.3	79.7	122.0	123.0	
Ratio CO ₂ /O ₂	0.22	0.27	0.34	0.40	0.49	0.52	0.54	0.56	0.56	

mixture is allowed to oxidise in this way. The results given in Table V show the quantity of oxygen absorbed and the amount of carbon dioxide evolved over a period of 21 hours by a crude sewage. From an examination of these results it will be seen that the ratio of the carbon dioxide produced to the oxygen utilised is much less than unity although as the oxidation proceeds the ratio appears to increase. A similar result is obtained when a sewage-sludge mixture is allowed to oxidise at varying p_H , *e.g.* at p_H 6.4, 7.0 or 8.0 (Table VI). These results may be due to the retention of carbon dioxide by the colloidal mixtures but a preferable explanation is that in the early stages the oxidation of the carbonaceous sewage constituents is less complete than at a later stage or that a greater proportion of the oxygen is utilised in oxidising nitrogenous or other non-carbon materials in the earlier part of the oxidation. The fact that the ratio would appear to be somewhat higher in an acid medium might be explained on the basis of a greater inhibition of non-carbonaceous oxidation, *e.g.* ammonia, at this p_H .

Table VI. *Oxygen absorption and carbon dioxide evolution by a sewage-sludge mixture at different p_H values.*

Each left-hand cup contained 1.5 ml. water and 1.5 ml. of the requisite phosphate buffer. In the right-hand cups the water was replaced by 1.5 ml. of a sewage-sludge mixture. The oxygen absorption values were obtained directly from the manometric readings of experiments in which the CO_2 evolved was absorbed by 10% KOH. The CO_2 evolved was obtained by deducting from the above readings those obtained from manometers in which no KOH was present. The appropriate factors for converting the readings into $\mu\text{l.}$ gas at 0° and 760 mm. pressure were used.

		Hours				
p_H		1	2	3	4	5
6.4	O_2 absorbed	78	108	133	159	179
	CO_2 evolved	37	68	100	124	145
	Ratio CO_2/O_2	0.47	0.63	0.75	0.78	0.81
7.0	O_2 absorbed	95	143	178	212	238
	CO_2 evolved	35	72	102	133	151
	Ratio CO_2/O_2	0.37	0.50	0.57	0.64	0.63
8.0	O_2 absorbed	80	131	179	227	268
	CO_2 evolved	39	74	103	139	178
	Ratio CO_2/O_2	0.49	0.55	0.58	0.61	0.66

Saturation of activated sludge with sewage.

From experience with activated sludge plants at sewage disposal works it is known that the sludge, if it is "overworked", may become ineffective as a sewage purifying agent. This is mainly due to a supersaturation of the sludge with sewage constituents so that the addition of a further quantity of sewage cannot lead to any further increased activity on the part of the sludge, with the result that the final addition of sewage is not oxidised. In support of this view the following experiments (Table VII) made with a sludge saturated with crude sewage may be examined. Sludge was obtained from the experimental tank, washed with water, subsequently shaken with a large volume of crude sewage (about

Table VII. *Effect of the saturation of a sludge with sewage upon its ability to oxidise added sterile sewage.*

The activated sludge was saturated by shaking twelve times with a large excess of crude sewage. The sewage was sterilised by passing through a Seitz filter. In the table below SL. = 1 ml. saturated sludge. (CS.) = 0.5 ml. sterile sewage placed initially in side arm of cup, B. = 1 ml. buffer of p_H 7.0, W. = water to make a total volume of 3 ml. and (w.) = 0.5 ml. water in side arm.

The sludges used in Exps. A and B were different samples. Carbon dioxide was absorbed by KOH in all cups. The figures heading the columns state the time, in hours, after the beginning of the experiment at which the contents of the side arm were tipped into the cups. The figures in the table represent the oxygen absorption due to the added CS. by the saturated sludge in the first 2 hours after tipping. The volume of oxygen absorbed is expressed in $\mu\text{l.}$ at 0° and 760 mm., the figures of Exp. A having been corrected for the oxygen uptake due to the sludge alone in the same period. In Exp. B the control unsaturated sludge figure gives the rate at which the initial sludge, before treatment with excess of sewage, oxidised sterile sewage.

Exp.	Contents of cups		Hours of shaking before tipping					
	Left	Right	0	1	2	3	4	5
A	B. + W. + (CS.)	SL. + B. + W. + (CS.)	71	74	82	89	114	—
B	SL. + B. + W. + (w.)	SL. + B. + W. + (CS.)	37	44	51	56.5	62	71
	Control unsaturated sludge		75	—	—	—	—	—

ten times its own volume) and allowed to sediment. The supernatant sewage was siphoned off and fresh sewage added. This process was repeated twelve times, after which the sludge was considered to be saturated with sewage; it was then allowed to sediment and suspended in water. 1 ml. of this saturated sludge suspension was used in the cups of the Barcroft manometer. By suspension in water and admixture with water and buffer the saturation of the sludge would be somewhat reversed but the results clearly show the inhibiting effect of the preliminary treatment with excess of sewage upon the oxidising activity of the sludge towards further sewage. In Exp. A of Table VII, 1 ml. of sludge was present in the right-hand cup but none in the left, whilst every cup had 0.5 ml. of a Seitz-filtered crude sewage in its side arm, this sewage being tipped into the main contents of the cup at various times after the beginning of the experiment. The figures given are a measure of the extra oxygen absorption due to the added sterile sewage for the first 2 hours after its addition. In Exp. A the figures represent the differences between the corresponding oxygen absorption values for saturated sludge *plus* sterile sewage and saturated sludge *plus* water. It will be seen from these results that the oxygen consumption or the rate of oxidation of the added sewage by the sludge steadily increases with the length of time the saturated sludge undergoes oxidation before the sewage is added. Exp. B, Table VII, shows similar results obtained with another saturated sludge in a different way. In this experiment several Barcroft manometers were used as before but the saturated sludge was placed in both cups, water being tipped into the left-hand cup and sterile sewage into the right-hand cup at the appropriate times. The manometric readings therefore give a direct measure of the oxygen absorption due to the addition of the sewage. As before the figures show that the sewage is not oxidised as rapidly by the saturated sludge as it is by a saturated sludge that has been previously aerated for some time. In this particular experiment it appears that it was necessary to aerate the saturated sludge for about 5 hours before its activity to oxidise further sewage became approximately equal to that of the washed sludge from which the saturated sample was originally prepared. That these results are due to a supersaturation of the sludge with the sewage can be illustrated by the experimental results given in Table VIII. They

Table VIII. *Rates of autoxidation of three sludges A, B and C (Exp. 1) and the rates at which these same sludges oxidised added sterile sewage (Exp. 2).*

Sludge A, a suspension of washed activated sludge from the experimental tank; Sludge B, the same sludge after saturation with sewage; Sludge C, sludge B washed several times with water. The oxygen absorption values represent the volumes absorbed in 2 hours, expressed in $\mu\text{l.}$ at N.T.P. The experiments were made at 22° . The contents of the Barcroft manometers are given in the table, Sl. representing 1 ml. of the appropriate sludge. CS.=1.5 ml. sterile sewage, B.=buffer, p_H 7.4 (0.5 ml.) and W.=water to make the volume of liquid to 3 ml. CO_2 was absorbed by KOH.

Exp.	Contents of cups		Sludge		
	Left	Right	A	B	C
1	B. + W.	Sl. + B. + W.	34	140	82
2	Sl. + B. + W.	Sl. + B. + CS.	88	30	77

show that sewage had been taken up by the sludge as a result of the preliminary treatment, for the saturated sludge had a much greater rate of autoxidation than either the original sludge or the saturated sludge after several washings with water. Nevertheless, when the rates at which these three sludges oxidise an additional amount of sewage are compared, the saturated sludge is shown to be

much the least efficient. These experiments with saturated sludges appear to emphasise the importance of feeding activated sludge carefully and not with too much sewage and seem clearly to show the value of submitting an activated sludge to periodical aeration in the absence of added sewage, thereby avoiding supersaturation and so allowing the sludge the more effectively to do its work in the future. Especially is this likely to be so in works practice where the sewage-sludge mixture is not submitted to such complete aeration as it is in the experimental manometer cups.

CONCLUSIONS.

1. The rate of oxidation of sewage increases with rise of temperature from 18° to 37° .
2. Sewage undergoes oxidation readily between p_H 6.0 and 9.0 with a possible optimum at about p_H 7.3. Oxidation to a smaller extent takes place at p_H 5.0 and at p_H 10.0 but at p_H 4.0 it is completely inhibited. The oxidation of washed activated sludges takes place vigorously at all p_H values between 5.0 and 10.0, but none occurs at 12.0. The effect of p_H on the oxidation of sewage in the presence of sludge is the same as for sewage alone.
3. Carbon dioxide is evolved in sewage and sludge oxidations but the ratio CO_2/O_2 is much less than unity: it appears to increase as oxidation proceeds.
4. The harmful effect of supersaturating a sludge with sewage upon the ability of a sludge to oxidise further sewage is clearly indicated and the reversal of this effect by preliminary aeration of the saturation sludge or by its thorough washing is demonstrated.
5. For efficient working of an activated sludge plant therefore the p_H of the system should be kept between 5.0 and 10.0, but preferably between 6.0 and 9.0. In feeding the sludge with sewage care must be taken that the sludge does not become "overloaded" or supersaturated with sewage. Occasional aeration of an activated sludge in the absence of added sewage improves its efficiency for subsequent sewage oxidation.

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