

**IMPROVING THE DENITRIFICATION POTENTIAL IN BIOLOGICAL
WASTEWATER TREATMENT
BY DOSING CARBON FROM
SLUDGE HYDROLYSIS**

Medhat A. E. Moustafa

* Sanitary Eng. Department. Faculty of Engineering,
Alexandria University, Egypt

ABSTRACT

Laboratory-scale studies were undertaken to investigate the influence of varying hydrolysis conditions on the composition and amount of the produced hydrolysate, as well as the quality of hydrolysate as carbon source for denitrification. Three parameters were targeted for optimization, namely, temperature, retention time and pH value. The results showed that a soluble COD in the order of 18% in terms of sludge total COD at a temperature of 35°C, initial pH value of 6.4 and a retention time of 6.0 hours was achieved. At an initial pH value of 11, a temperature of 20°C and a retention time of 6.0 hours an increase up to 28% soluble COD was obtained. A significant soluble COD production of about 45% could be obtained at a temperature of 35°C, pH value of 11 and a retention time of 6.0 hours. The use of the produced hydrolysate had succeeded to improve the denitrification rate up to 9.75 mg NO₃-N/g VSS *h. Simultaneous removal of phosphorus up to 1.0 mg P/l was obtained.

KEYWORDS

Internal carbon source; Sludge hydrolysis; Biological hydrolysis; Chemical hydrolysis; Optimization of Sludge hydrolysis process; Conditioning of hydrolyzed sludge, Denitrification; Biological phosphorus removal.

INTRODUCTION

The most important dissolved nutrients in wastewater are: organic carbon, phosphorus and nitrogen. These three pollutants are often regarded as the major nutrients in wastewater, particularly in terms of their impact on receiving waters and crops growth. Although the lack of carbon, nitrogen, phosphorous and minor elements leads to deficiency symptoms in the crops and growth limitation, a surplus in nitrogen supply leads to deterioration in the quality of cultivated plants (El-Gohary, F., 1986).

The presence of trace amounts of phosphorus (even less than one part per million) in the treated wastewater from municipalities and industries are often responsible for eutrophication. This leads to short as well as long-term environmental and aesthetic problems in the receiving bodies (Zaho, D., et al., 1996)

In order to face the recent serious problems of eutrophication and water scarcity, great attention must be focused on the advanced biological wastewater treatment processes which combine the processes of carbon oxidation, nitrification and denitrification. The main aim of these processes is the reduction of the nutrient content to the acceptable limits before its reuse in other purposes without environmental pollution.

Biological nitrogen removal is one of the most economic and effective means of nitrogen reduction. Normally there are no problems to achieve extensive nitrification and denitrification. However some wastewaters with high nitrogen concentration do not contain enough organic carbon to get a complete denitrification (e.g. some industrial wastewaters, landfill leachates). In these cases external sources of organic carbon have to be added to optimize denitrification and minimize nitrogen effluent levels (Werner, M., and Kayser, R., 1991).

Methanol is mainly used as the hydrogen donor for denitrification because of its highly carbon content. For complete denitrification 3 kg Methanol per 1kg $\text{NO}_3\text{-N}$ (1.30 DM per 1 kg N) is necessary (Henze and Bundgaard, 1982), so that it can be a cost-intensive factor for wastewater treatment in the developing countries.

The future of denitrification as a means of removing nitrogen from wastewater depends on the availability of an effective but inexpensive carbon source. The trend in recent years is moving towards the use of internal carbon for the reasons of better economy, less sludge production and more optimal usage of organics within the wastewater.

The thought of using sludge in a positive way was already around in the late 1980s. One attempt in this regard was made in a EUREKA project called "HYPRO" (the hydrolyze project). HYPRO was aimed at hydrolyzing the particulate organic matter to easily biodegradable organic matter, which could then be used as a carbon source in the denitrification process. In HYPRO several hydrolysis methods were tried. Thermal hydrolysis and biological hydrolysis were tested in pilot plants and on a large scale.

These hydrolysis methods produced an excellent carbon source thus improving the denitrification capacity of the sewage plant (Karlsson, 1990).

The success of sludge hydrolysis process to produce a good source of carbon in the Scandinavian EUREKA-project HYPRO (Henze and Harrermoeas, 1990) was the motive for the application of this concept in the developing countries

Hence the objective of this study was to investigate the hydrolysis process with respect to the production of a carbon source from primary sludge, for use in the denitrification process. Two aspects were taken into account. One aspect was the degree of COD solubilization and the other one was the quality of COD produced. The hydrolysate was optimized through variation of several parameters such as temperature, pH, COD, DOC, MLSS, VSS, TKN, and $P_{tot.}$.

Experimental Work

1- MATERIALS AND METHODS

1-a –Characterization of the primary sludge:

Different samples of sludge were withdrawn from the primary sludge well at different periods during the year and analysed to characterise the primary sludge. The primary non-precipitated sludge can be characterized as shown in table (1).

Table (1). Characteristics of the primary sludge

Parameter	Sample (1)	Sample(2)	Sample (3)	Sample (4)	Sample (5)
Supernatent pH	7.2	7.4	6.8	7.6	7.7
Alkalinity as CaCO ₃ mg/l	1700	2510	1500	2450	1440
Volatile acids (acetic), mg/l	314	-	521	370	410
BOD ₅ mg/l	776	720	476	520	1250
COD mg/l	2300	2700	3100	1250	3640
Sludge Total Solids %	1.91	3.23	1.92	1.65	4.12
Volatile Solids, % of TS	70	81	60	67	66
Specific filtration resistance 10 ⁹ s ² /g	8.7	35.2	19.6	9.5	15.6

Experimental unit:

The bench scale experimental apparatus of sludge hydrolysis utilised in this study consisted, as shown in figure (1) of four double wall acrylic glass reactors 1.50 L capacity. A rise in temperature of these reactors between (20 - 40 °C) could be achieved by means of warm water bath.

This water bath is an acrylic glass basin 50 cms in diameter, containing a controllable thermostatic heater to raise the temperature of water up to 40°C and a small delivery pump to pump the warm water around the reactors. Each reactor was fitted with one adjustable stirrer anchored to motor with number of revolutions from 20 - 200 rpm. For filling with sludge, the top part of each reactor was open. For emptying and sampling outlet nozzles with different heights were arranged. Before the beginning of sludge hydrolysis process, one hour was needed to attain the desired degree of temperature. After that the reactors were filled with sludge and the value of pH was measured and adjusted to the required different values by dosing of (NaOH). The time of the experiment was 6.0 hours, at constant temperature.

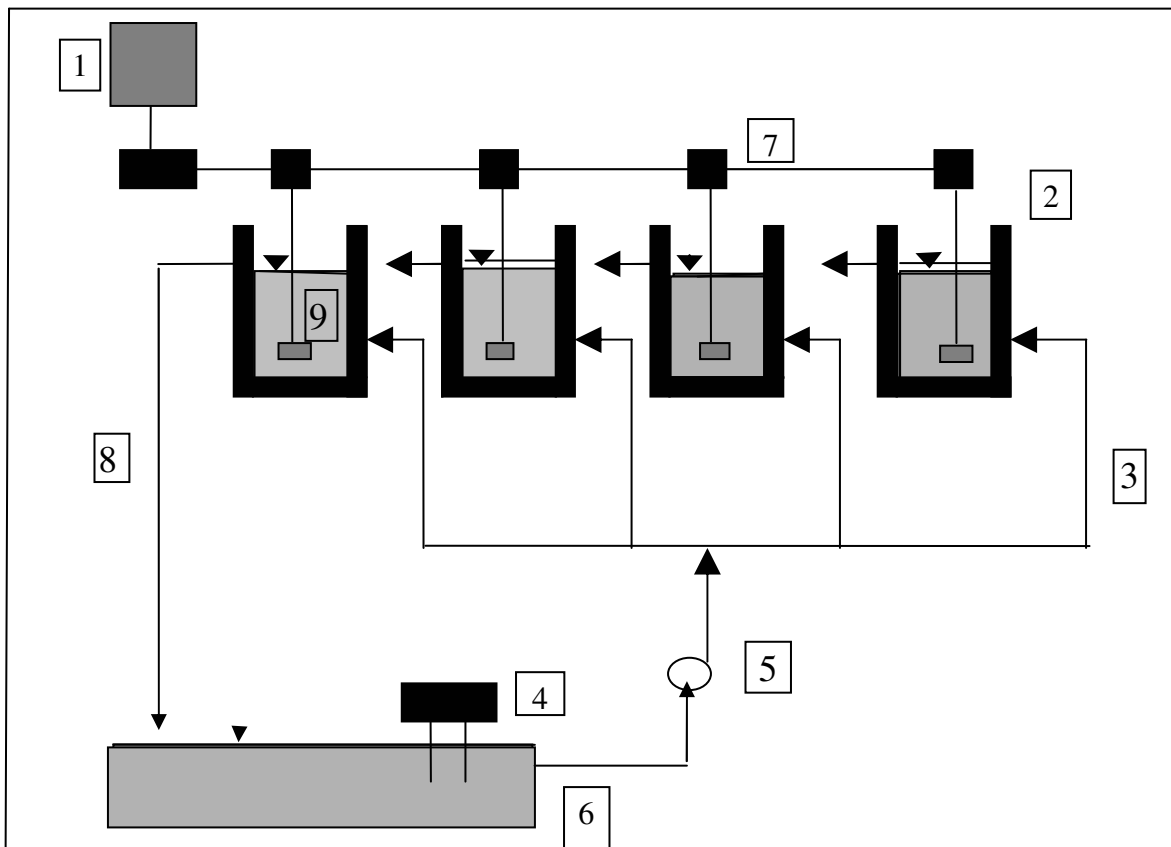


Figure (1). Sludge Hydrolysis Apparatus

- | | |
|--------------------------------------|---------------------|
| 1-Motor. | 6-Water bath. |
| 2- Double wall acrylic glass reactor | 7-Stirrer. |
| 3-Warm water hose. | 8-Returned water. |
| 4-Thermostatic heater. | 9-Hydrolysed sludge |
| 5-Delivery pump. | |

Methods of sludge hydrolysis

Two hydrolysis methods were investigated, namely, biological and chemical hydrolysis. Temperature, retention time and pH value were the main parameters which were targeted for optimization. The biological hydrolysis was carried out under mesophilic conditions 20-35°C at an initial pH value of 6.4 with a retention time of 6.0 hours. The chemical hydrolysis was carried out at a temperature of 20°C for different pH values in the range of 8-11 with a retention time of 6 hours. Sodium hydroxide and calcium hydroxide solutions were used to raise the pH value.

RESULTS

Biological hydrolysis:

An important aspect of the present study was to investigate the effects of the basic operational parameters as temperature, pH adjustment and retention time on the characteristics of hydrolysate. In order to operate a biological hydrolysis reactor with minimum loss of carbon, the retention time was 6.0 hours. Samples were taken at different retention time (1/2, 1, 2, 4 and 6 hours) for different degrees of temperature. These samples were analysed for pH, COD, NH₄-N, DOC, and P_{tot}.

Figure (2) shows that an increase of COD solubilization to the order of 18% was achieved when the temperature was increased from 15°C to 35°C. The rise of temperature increased the degree of COD solubilization when it was accompanied by an increase of retention time.

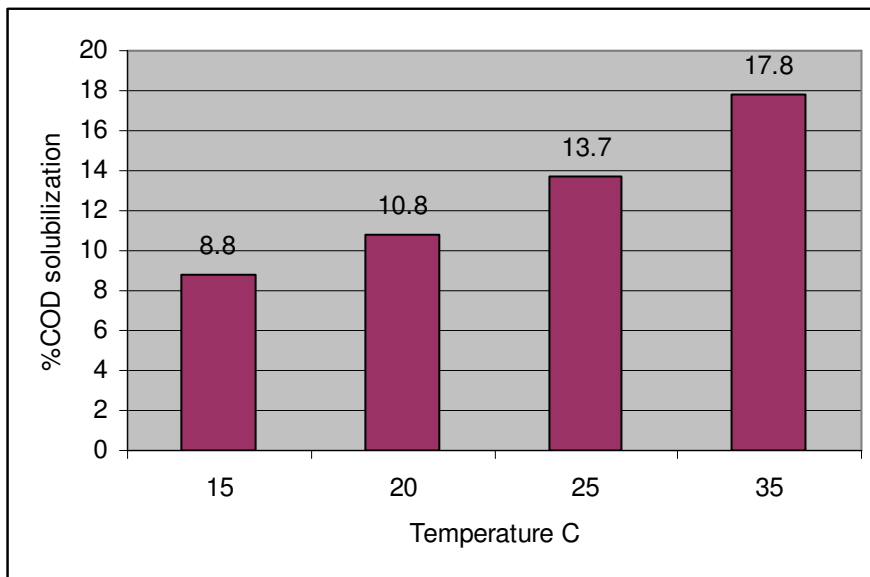


Figure (2). COD solubilization during the biological hydrolysis at different temperatures, initial pH 6.4 and a maximum retention time 6 hours

Spectral Absorption Coefficient (SAC) was measured by a spectrophotometer at a wave length of 254nm. DOC was expressed as mg/l oxalic acid using a calibration curve between DOC and SAC. Figure (3) shows DOC progress during the biological hydrolysis at different temperature, an initial pH value of 6.4 and a maximum retention time of 6.0 hours.

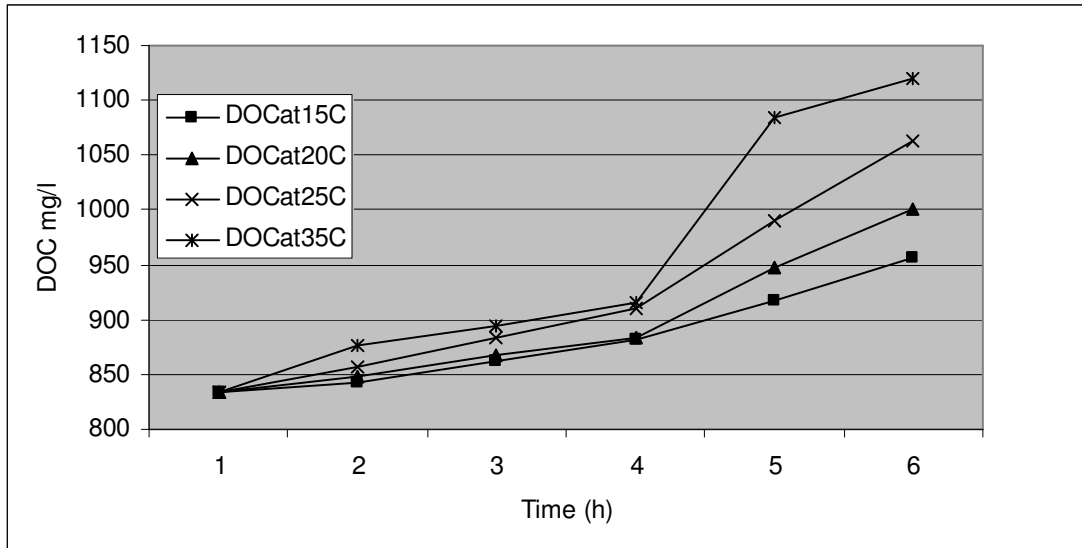


Figure (3). DOC progress during the biological hydrolysis at different temperatures, initial pH 6.4 and retention time 6 hours

As shown in figure (4) the relation between COD and DOC in the biological process is linear. The DOC/COD ratio ranged between 0.4 to 0.43.

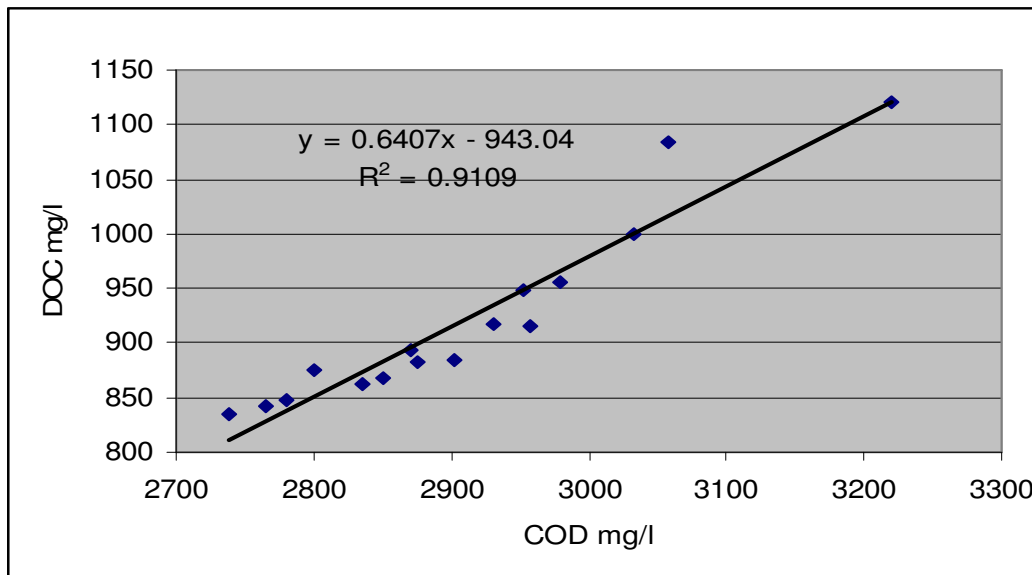


Figure (4). Correlation between COD and DOC during the biological hydrolysis

During the biological hydrolysis the released nutrients were also measured. The increase of NH₄-N was 3.0 mg NH₄-n/gVSS whereas the increase of P_{tot} was less than 1 mg P/g VSS.

Chemical hydrolysis:

The chemical hydrolysis was used to study the kinetics of alkaline hydrolysis and to determine the parameters that control the process. The variables which have been taken into consideration were: concentration of alkali, sludge solid content, retention time and temperature. pH value was the most effective factor in the chemical hydrolysis. Figure (5) shows the COD solubilization at different pH values at constant temperature of 20°C and a maximum retention time of 6 hours. The COD solubilization increased proportionally with the increase of pH value.

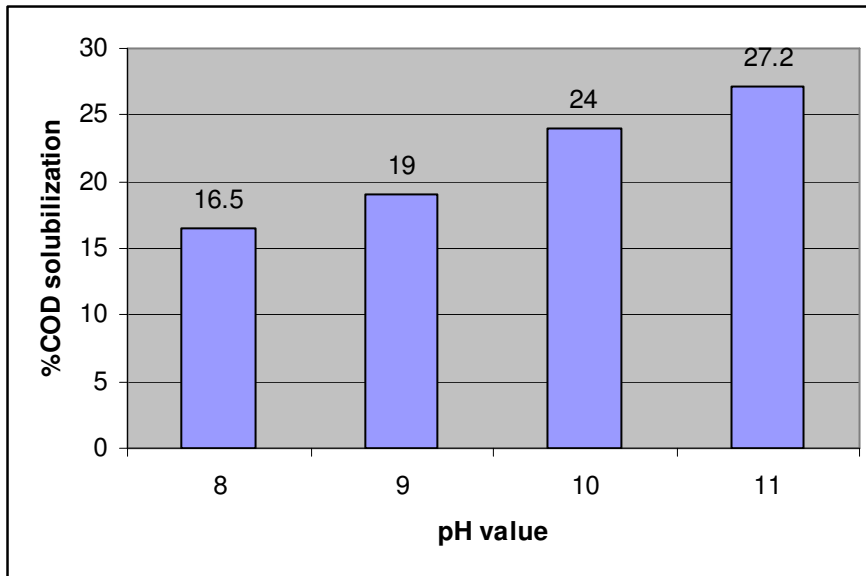


Figure (5). COD solubilization during the chemical hydrolysis at different pH values, a temperature of 20C and a retention time of 6.0 hours

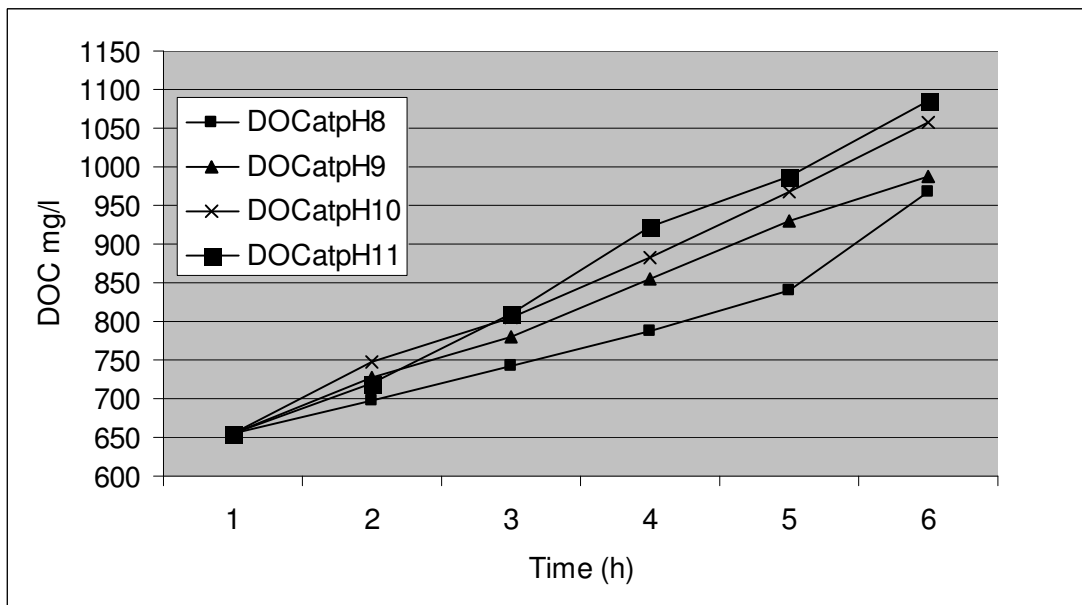


Figure (6). DOC progress during the chemical hydrolysis at different pH values, a temperature of 20C and a retention time of 6.0 hours

Figure (6) shows DOC progress during the chemical hydrolysis at different pH value. The correlation between COD and DOC is shown in figure (7). The DOC/COD ratio during the chemical hydrolysis was 0.38.

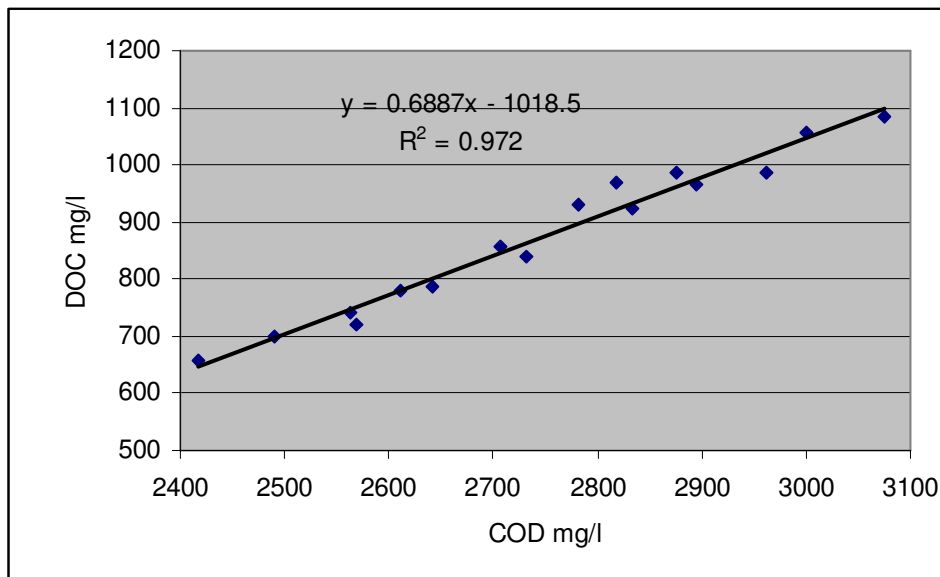


Figure (7). Correlation between COD and DOC in the chemical hydrolysis at different pH values, a temperature of 20C and a retention time of 6.0 hours

Optimization of the operation conditions of the sludge hydrolysis process:

The experiments with primary sludge hydrolysis conducted at a temperature of 35°C, an initial pH value of 6.4 and a retention time of 6 hours showed a degree of COD solubilization up to 18%. The chemical hydrolysis with NaOH increased the amount of COD solubilization to 27% at a temperature of 20°C, pH value of 11 and a retention time of 6 hours. The hydrolysis process was carried out at a temperature of 35°C, pH value of 11 and a retention time of 6 hours. The obtained results showed an increase in COD solubilization up to 44%.

Conditioning of hydrolyzed sludge:

Ferric chloride (FeCl₃) and calcium hydroxide (Ca(OH)₂) were used, as conditioners, to investigate their effect on the quantity and quality of hydrolysate.

Quantity of hydrolysate:

Quantity of hydrolysate, in brief, means the volume of the generated hydrolysate related to the amount of the hydrolysed sludge. Centrifugation, Sedimentation and Flotation were used, as phase separation methods, to recover the hydrolysate. The amount of COD return was calculated and expressed as mg COD/g VSS. To investigate the effect of conditioning on the quantity and quality of the obtained hydrolysate, the hydrolyzed sludge was conditioned. Ferric chloride and calcium hydroxide were used

as conditioners. The dose of conditioners was in the range of (100 - 120) mg/l. Centrifugation was the quickest way to recover the hydrolysate.

The main disadvantage of this method is the high solids content of the obtained hydrolysate. Sedimentation and floatation were investigated as alternative methods to recover the hydrolysate. The volume of hydrolysate, obtained from conditioned hydrolysed sludge, was estimated by means of graduate cylinder. The obtained results are given in table (2).

Table (2). COD return as mg COD/g VSS for different methods of phase separation at a temperature of 20°C, an initial pH value of 6.4 and a retention time of 6.0 hours (VSS = 26.7 g/l)

Conditioner	Method of phase separation		
	Sedimentation	Centrifugation	Flotation
None	32-38 mg COD/g VSS	130-150 mg COD/g VSS	25-30 mg COD/g VSS
Ferric chloride (100-120 mg/l)	40-50 mg COD/g VSS	140-160 mg COD/g VSS	32-45 mg COD/g VSS
Calcium hydroxide (100-120 mg/l)	28-35 mg COD/g VSS	108-120 mg COD/g VSS	22-34 mg COD/g VSS

The highest value of COD return was obtained by centrifugation as compared to the other two methods.

Quality of hydrolysate

The quality of hydrolysate means the chemical as well as the physical properties of the hydrolysate. One of the main physical properties of the hydrolysate is the solids content or more precisely the degree of turbidity. The solid content of hydrolysate, obtained from conditioned hydrolysed sludge, was measured for the different methods of phase separation and expressed as mg/l. The obtained results are given in table (3).

Table (3). Total solids content of the hydrolysate for different methods of phase separation of conditioned hydrolysed sludge at a temperature of 20°C, an initial pH value of 6.4 and a retention time of 6.0 hours

Conditioner	Method of phase separation		
	Sedimentation	Centrifugation	Floatation
None	209 mg/l	412 mg/l	228 mg/l
Ferric chloride 100-120 mg/l	79 mg/l	114 mg/l	88 mg/l
Calcium hydroxide 100-120 mg/l	122 mg/l	195 mg/l	98 mg/l

The most clear COD return was obtained by sedimentation as compared to the other two methods.

Usability of hydrolysate:

Improving the denitrification potential

The quality of the carbon source produced by biological as well as chemical hydrolysis was evaluated by measuring the denitrification rate of activated sludge. Nitrate consumption for different carbon doses was measured and tabulated in table (4) for the biological hydrolysate. All experiments were carried out at an ambient temperature \cong 20°C in a sealed reactor to realise the anoxic conditions. A magnetic stirrer has been used to ensure uniform distribution of hydrolysate and to prevent settling of the suspended solids. Figure (8) shows the nitrate reduction process of the biological hydrolysate at different C/N ratios, temperature of 20°C and a retention time of 2.0 hours

The denitrification velocity has been calculated according to the following equation:

$$V_{\text{deni}} = \frac{(\text{NO}_3 - \text{N}_0) - (\text{NO}_3 - \text{N}_t)}{\text{VSS} * T} \quad \text{mg NO}_3 - \text{N/h} * \text{g VSS}$$

where:

V_{deni} = Denitrification velocity mg NO₃ - N/h* g VSS.

NO₃ - N₀ = Initial nitrate concentration mg/l.

NO₃ - N_t = Nitrate concentration at time t mg/l.

T = Time in hours.

VSS = Volatile suspended solids g/l.

Table (4). Results of the denitrification process (nitrate reduction) by using the biological hydrolysate at temperature of 20°C, different C/N ratios and a retention time of 120 min (VSS = 1.49 g/l)

Parameter	COD/NO ₃ -N ratio			
	1.36	2.46	3.6	7.2
Time (min.)	NO ₃ - N mg/l	NO ₃ - N mg/l	NO ₃ - N mg/l	NO ₃ - N mg/l
0	39	39	39	39
15	36.6	33.5	31.2	30.4
30	35.9	32.8	27.3	23.4
45	35.1	30.8	23.4	17.5
60	33.9	27.3	20.3	15.0
90	31.2	25.3	17.2	11.4
120	28.8	23.4	15.6	9.9

$$V_{\text{deni. max.}} = (39 - 9.9) / 2 * 1.49 = 9.8 \text{ mg NO}_3\text{-N / h} * \text{g VSS.}$$

$$V_{\text{deni. min.}} = (39 - 28.8) / 2 * 1.49 = 3.4 \text{ mg NO}_3\text{-N / h} * \text{g VSS}$$

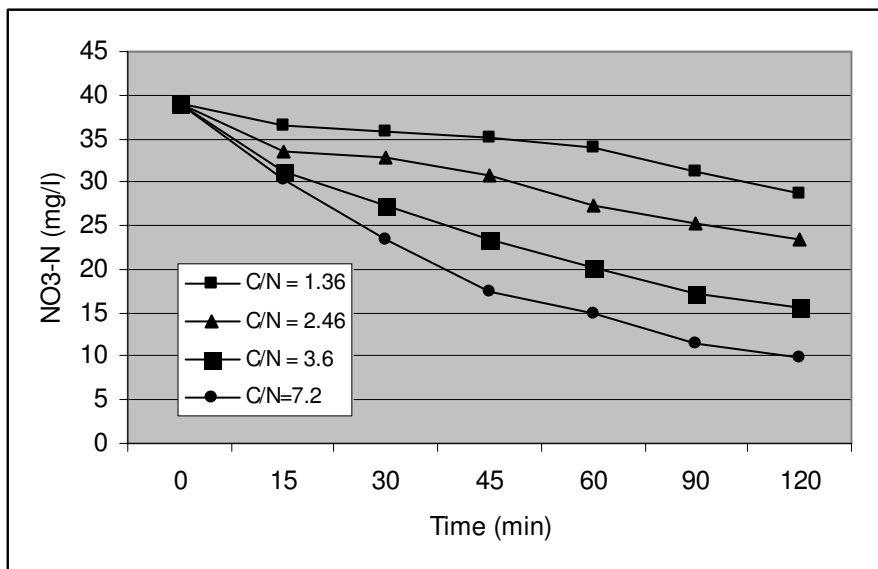


Figure (8). Relation between nitrate reduction and C/N ratio of the biological hydrolysate

Biological phosphorus removal:

To study the effect of hydrolysate upon the biological phosphorus removal, as well as for nitrogen removal, samples were taken every 15 minutes in the first hour and every 30 minute in the second hour. These samples were analysed for phosphorus content. The obtained results are given in table(5).

Table (5). Results of the biological phosphorus elimination at different C/N ratios by using the biological hydrolysate

Parameter	COD/NO ₃ -N	
	3.6	7.2
time (min)	Ptot. (mg/l)	Ptot. (mg/l)
0	20.1	20.1
15	11.3	10.2
30	9.2	7.4
45	7.6	4.2
60	6.5	3.4
90	5.4	2.4
120	4.5	1.2

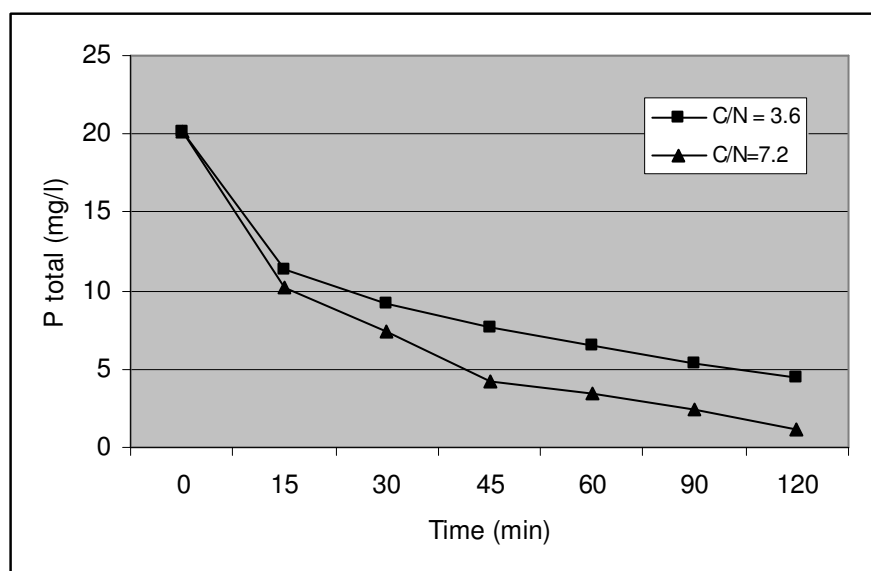


Figure (9) Relation between phosphorus reduction and C/N ratio of the biological hydrolysate

DISCUSSION

Figure (2) shows that, there was an increase in the COD solubilization up to (18%) when the retention time was increased from ½ h to 6.0 hours at a temperature of 35°C and initial pH value of 6.4. An increase of pH value, with NaOH, increased the COD solubilization to the order of (28%), at pH_{initial} of 11, a temperature of 20°C and a retention time of 6.0 hours. This is because; the raising of the initial pH increased the buffer capacity from pH_{initial} to pH_{end} and thus allows more VSS to be produced. The primary sludge was hydrolysed under the optimized conditions of operation of both biological and chemical hydrolysis i.e. pH value of 11, a temperature of 35 °C and a retention time of 6.0 hours. The degree of COD solubilization under the above conditions has been increased to 44%.

The amount of ammonium (NH₄-N) mobilized during the biological hydrolysis was corresponding to 1.0 mg NH₄-N per 10 - 12 mg of solubilized CODreturn. This can be explained by the degradation of proteins and desamination of amino acids. This indicates the success of bacteria in the disintegration of proteins. On the other hand, it is well known that the NH₃/NH₄ ratio heavily depends on the pH value as well as on the temperature of sludge: the higher pH value and temperature, the higher the NH₃ content. The (NH₃) was released during the chemical hydrolysis by the strong effect of high pH value and temperature. Release efficiency was close to 40% at pH value of 11 and a temperature of 35°C.

The phosphorus content of the biological hydrolysate has increased to some extent from 21.75 mg/l to 26.82 mg/l at a temperature of 20 °C and from 24.95 mg/l to 32.34 mg/l at a temperature of 35 °C at the same pH value and retention time. This increase is attributed to the use of non-precipitated sludge in this research. The use of calcium hydroxide to rise the pH value reduced the phosphorus concentration to the range of 9.17 - 7.63 mg/l.

The quality of the carbon source produced either by the biological hydrolysis or by the chemical-biological hydrolysis was evaluated by measuring the denitrification rate of activated sludge from a biological denitrification plant. The course of nitrate consumption for different carbon doses was tabulated in table (4) for the biological hydrolysate.

Based on NO₃-N, denitrification rates were calculated. As shown in figure (8) the denitrification rates were found to be (3.4 - 9.8) mg NO₃-N /g VSS*h for the biological and (2.50 - 5.60) mg NO₃-N /g VSS*h for the chemical hydrolysate for COD/NO₃ -N ratio of 7.20.

It is clear that the biological hydrolysate was the best source of carbon. This can be explained by the high content of fatty acids resulted during the acid production stage in the fermentation process (Henze, M. and Harremoes P., 1990). The COD consumption of around (5-7) mg COD per 1 mg N denitrified was found for both types of

hydrolysate in the experiments. Thus hydrolysis products appear to be excellent carbon sources for denitrification.

Examination of table (5) reveals that, the use of chemical hydrolysate (low phosphorus content) resulted in better efficiency for phosphorus removal than the biological hydrolysate. Removal of the initial phosphorus content up to 1.0 mg/l was achieved at C/N ratio of 7.2 at a temperature of 20 °C and a retention time of two hours. The behaviour of phosphorus removal by the use of biological as well as chemical hydrolysate was depicted in figure (9).

CONCLUSIONS

From the present laboratory scale investigations on the hydrolysis of non precipitated primary sludge, the following conclusions can be drawn:

- 1- COD solubilization increases with retention time but the economic aspect should be taken into consideration.
- 2- Optimum temperature of biological hydrolysis seems to be between 20 - 35 °C.
- 3- The hydrolysate is an easy-to-handle product with no hazardous effects. It reacts quickly and no adaptation periods are needed.
- 4- The hydrolysis products from biological hydrolysis provided an excellent carbon source for denitrification. Furthermore, since pH adjustment of biological hydrolyzed sludge increases the dissolved COD, there seems to be a possibility for combining a high hydrolysis yield with a little decrease in the denitrification potential.

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