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Biological degradation of EDTA in pulping effluents at higher pH - a laboratory study

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Sammanfattning/Summary

The biological degradation of EDTA at different pH, sludge load and sludge age has been investigated in laboratory experiments. The experiments showed that relatively fast degradation of EDTA in the form found in this waste water (from production of TMP) took place at least at pH around 8,5 with moderate COD load and high sludge age.

In continuous reactors the degradation of EDTA in a pulp and paper waste water was 2-3 mg EDTA/g SS*day at both pH 7 and 8,5, and at sludge ages from 5 to 21 days. The degradation was dependent on sludge load, and no degradation was seen above
1 g COD/g SS*day.

In kinetic experiments with half strength waste water the same degradation rate (1,5-2 mg EDTA/g SS*day) was found at pH 7 and at pH 8,5 with sludge of low age (9 and 5 days SRT). Much faster degradation was found at pH 8,5 with sludge of high age (21 days in the continuous experiment). The mean degradation rate was over 10 mg EDTA/g SS*day from 20 to 5 mg EDTA/l. v_{max} was determined to be 35 mg EDTA/g SS*day and K_M to 31 mg EDTA/l.

COD removal was at least as good at pH 8,5 as at pH 7. Sludge properties were best at pH 8,5 and long sludge retention time (giving low sludge load). Both sludge volume index and residual suspended solids after sedimentation were lower than under normal conditions at pH 7.

The direct cost for caustic lime would be about 15 SEK per ton of TMP, with a water like the one investigated here. This can vary a lot dependent on starting pH and buffering capacity. Costs for addition of nitrogen source could probably be omitted, but this is normally not more than 1-2 SEK per ton of TMP. The extra need for oxygen in the treatment would not be more than some percent, but may be important if oxygen is limited.

A substantial extra cost would be if the aeration volume has to be increased. According to the best results from the kinetic study, this would not be needed in an extended aeration activated plant with 2 days HRT and sludge concentrations of 2-3 g/l. At lower HRT an increase could be necessary, unless the sludge concentration can be increased. To some extent this can be possible, since the sludge properties may be improved at higher pH.

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Contents

Preface

This study has been jointly sponsored by the Swedish Forest Industries Water and Air Pollution Research Foundation (SSVL) and the Swedish Environmental Protection Agency. The work has been conducted at the Swedish Environmental Research Institute (IVL) in Stockholm.

The access to internal material from Akzo Nobel Chemicals and test water and data from Hallsta Paper Mill, Holmens Bruk AB, is gratefully acknowledged.

Summary

The biological degradation of EDTA at different pH, sludge load and sludge age has been investigated in laboratory experiments. The experiments showed that relatively fast degradation of EDTA in the form found in this waste water (from production of TMP) took place at least at pH around 8,5 with moderate COD load and high sludge age.

In continuous reactors the degradation of EDTA in a pulp and paper waste water was 2-3 mg EDTA/g SS*day at both pH 7 and 8,5, and at sludge ages from 5 to 21 days. The degradation was dependent on sludge load, and no degradation was seen above 1 g COD/g SS*day.

In kinetic experiments with half strength waste water the same degradation rate (1,5-2 mg EDTA/g SS*day) was found at pH 7 and at pH 8,5 with sludge of low age (9 and 5 days SRT). Much faster degradation was found at pH 8,5 with sludge of high age (21 days in the continuous experiment). The mean degradation rate was over 10 mg EDTA/g SS*day from 20 to 5 mg EDTA/l. v_{max} was determined to be 35 mg EDTA/g SS*day and K_M to 31 mg EDTA/l.

A possible explanation to the difference in rate between the continuous experiment and the batchwise kinetic experiment can be a toxic effect in the non diluted waste water, but this can not be shown with data from the present investigation.

The slow, but significant, degradation of EDTA at pH 7 is contrary to most literature data. Degradation at higher pH is shown, as in several other investigations. pH 8,5 and low sludge load and long sludge retention time should give fast and complete degradation of EDTA, at least in the complex forms found in this waste water.

COD removal was at least as good at pH 8,5 as at pH 7. Sludge properties were best at pH 8,5 and long sludge retention time (giving low sludge load). Both sludge volume index and residual suspended solids after sedimentation were lower than under normal conditions at pH 7. About 1,5 kg NaOH/m^3 of waste water was needed in this case to keep pH at 8,5.

It is obviously very important to know the extra cost for a biological treatment that not only removes COD, but also EDTA. However, this can not be properly calculated from the data available. They are still too contradictory, and a long term test in pilot scale is needed to give reliable data about retention times (aeration volumes) and sedimentation properties (settling area and residual suspended solids).

The direct cost for caustic lime would be about 15 SEK per ton of TMP, with a water like the one investigated here. This can vary a lot dependent on starting pH and buffering capacity. Costs for addition of nitrogen source could probably be omitted, but

this is normally not more than 1-2 SEK per ton of TMP. The extra need for oxygen in the treatment would not be more than some percent, but may be important if oxygen is limited.

A substantial extra cost would be if the aeration volume has to be increased. According to the best results from the kinetic study, this would not be needed in an extended aeration activated plant with 2 days HRT and sludge concentrations of 2-3 g/l. At lower HRT an increase could be necessary, unless the sludge concentration can be increased. To some extent this can be possible, since the sludge properties may be improved at higher pH.

Sammanfattning

Biologisk nedbrytning av EDTA vid olika pH, slambelastning och slamålder har undersökts i laboratorieskala. Försöken visade att man kan få en relativt snabb nedbrytning av EDTA i form av de aktuella komplexen, åtminstone vid pH kring 8,5, måttlig COD-belastning och hög slamålder.

Nedbrytningen av EDTA i avloppsvatten från tillverkning av termomekanisk massa mättes i kontinuerliga aktivslamanläggningar till 2-3 mg EDTA/g SÄ*dag, både vid pH 7 och pH 8,5, och vid slamåldrar från 5 till 21 dygn. Nedbrytningen var beroende av slambelastningen, och ingen nedbrytning noterades vid belastning över 1 g COD/g SÄ*dygn.

I satsvisa försök för bestämning av nedbrytningskinetiken uppmättes i två fall ungefär samma nedbrytningshastighet som i de kontinuerliga försöken. Vattnet var här spätt till halv koncentration för att undvika toxiska effekter vid start. Både vid pH 7 och vid pH 8,5 med låg slamålder (9 och 5 dygn) var hastigheten 1,5-2 mg EDTA/g SÄ*dygn.

Vid pH 8,5 och slam med hög ålder (21 dygn i det kontinuerliga försöket) var hastigheten mycket högre. Medelhastigheten var över 10 mg EDTA/g SÄ*dygn från 20 till 5 mg EDTA/l. v_{max} bestämdes till 35 mg EDTA/g SÄ*dygn och K_M till 31 mg EDTA/l.

En möjlig förklaring till skillnaden i hastighet mellan det kontinuerliga och det satsvisa försöket kan vara en toxisk effekt av det outspädda vattnet. Data från den här undersökningen är emellertid inte tillräckliga för att avgöra om så var fallet.

Den långsamma, men signifikanta, nedbrytningen av EDTA vid pH 7 är tvärt emot de flesta data från litteraturen. Nedbrytningen vid pH 8,5 stämmer med andra undersökningar. pH 8,5, låg slambelastning och hög slamålder skulle ge snabb och fullständig nedbrytning av EDTA, åtminstone av de komplexformer som förekom i det här undersökta vattnet.

Reduktionen av COD var minst lika bra vid pH 8,5 som vid pH 7. Slamegenskaperna var bäst vid pH 8,5 och hög slamålder (låg slambelastning). Både slamvolymindex och resthalten av suspenderat material var lägre än under normala förhållanden vid pH 7. Ungefär 1,5 kg NaOH/m^3 behövdes i det här vattnet för att hålla pH vid 8,5.

Det är givetvis viktigt att veta hur stor extra kostnad det skulle bli för en biologisk behandling som inte bara avlägsnar COD, utan även EDTA. Tyvärr är underlaget för detta ännu för dåligt, och resultaten delvis motsägande. Ett långtidstest i pilotskala

skulle krävas för att ge pålitliga data för uppehållstider (luftningsvolymer) och sedimenteringsegenskaper (sedimenteringsyta och resthalt av suspenderat material).

Den direkta kostnaden för kalk för pH-justering skulle bli ca 15 kr per ton massa, med ett vatten som det här undersökta. Den kostnaden kan variera mycket beroende på vattnets ursprungs-pH och buffertkapacitet. Kostnaden för kvävekälla till biologin kunde kanske sparas in, men den är normalt inte mer än 1-2 kr ptm. Det extra syrebehovet i luftningen skulle inte vara mer än någon procent, men kan ha betydelse om syret är begränsat.

En stor extra kostnad skulle tillkomma om luftningsvolymen måste ökas. Enligt den snabbaste omsättningen i de kinetiska försöken skulle det inte behövas i en långtidsluftad aktivslamanläggning med 2 dygns uppehållstid och 2-3 g slam/l. Vid kortare uppehållstider skulle en ökning av volymen kunna bli nödvändig, om man inte kan höja slamkoncentrationen. I många fall kan det säkert vara möjligt, eftersom slamegenskaperna tycks förbättras vid högre pH.

1. Background

Pulp bleaching processes without chlorine chemicals use complexing agents as metal scavengers. Most commonly used are EDTA (ethylene diamine tetraacetic acid) and DTPA (diethylene triamine pentaacetic acid), which are also detected in effluents. No biodegradation of these compounds has been observed in normal biological treatment of pulp and paper effluents or under receiving water conditions.

Both DTPA and Fe(III)-EDTA have been shown to be photodegradable, but not other possible metal complexes of EDTA, e.g. Mn, Mg, Ca and Zn (1). Although no toxic effects of these complexing agents have been observed, a development of a treatment procedure for reduction or elimination of the substances in effluents may be motivated.

Biological degradation of EDTA in sewage water has recently been reported (2). By increasing the pH to about 8,5, an almost complete removal of EDTA was achieved. It has also been shown that EDTA in both bleaching effluent and total effluent from pulp and paper mills can be at least partially degraded under the same conditions (3, 4). DTPA was not degraded in the same way.

Different levels of residual EDTA has been found in the experiments carried out. Is this because one metal complex is biostable under these conditions? Is it sludge age or sludge load that determines the degradation?

2. Objective

The aim of the project was to verify the earlier results for another waste water, and also to try to understand the process better in order to be able to give data for design and cost estimation of treatment in full scale.

3. Materials and methods

3.1 Waste water

Waste water from Hallsta Pappersbruk, Holmens Bruk AB, in Hallstavik, Sweden was used in the experiments. The TMP process water after microflotation, but before nutrient addition and the first activated sludge treatment, was collected in a 1 m^3 polyethylene container on February 9, 1998. The container was sent to IVL in

Stockholm, where it was stored dark at 4°C. pH was 5,2 and COD (chemical oxygen demand) 4 200 mg/l.

Activated sludge from Hallsta was used as inoculum. The sludge contained a lot of extracellular slime and the filament forming *Nosticoida limicola* type III. It was very difficult to filtrate. The initial inoculation was made to about 2,4 g SS/l (suspended solids/l).

Ca-EDTA was purchased from Aldrich. The Mn-EDTA complex was prepared by mixing Na_2-EDTA and a slight stochiometric excess of $MnCl_2$ and adjust pH to 7 by adding sodiumhydoxide. The solution was left over night in darkness and filtered through a glass fibre filter (Whatman GF/C) before use.

3.2 Continuous reactors

Three glass vessels with 5 l inoculated waste water each were used. The vessels and tubing were protected from light, in order to avoid photolytic degradation of Fe(III)-EDTA. Aeration was performed both with relatively large bubbles to provide mixing and with fine bubbles to give effective oxygen transfer.

Addition of waste water was started after 10 days of acclimatisation. Addition was made with a three channel tube pump from a feed tank in a refrigerator. The pump was running for 15 minutes and stopped for 30 minutes, in order to get a relatively high flow rate in the tubes. 80 mg N/l as NH_4Cl and 16 mg P/l as K_2HPO_4 was added to 10 litre portions, when transferred from the coldroom to the refrigerator. pH in the aeration was 6,9-7,1 without regulation.

When the addition of waste water started, sedimentation and recirculation of sludge was also started. The three channel recirculation tube pump was run over the same timer as the addition pump. All equipment containing waste water was protected from light.

After about one month, the content in all reactors were pooled, mixed and redistributed to the three reactors. pH was now regulated to 8,5 with 1 M NaOH in reactor 2 and 3. pH in reactor 1 was about 7. A fraction of the content in reactors 2 and 3 was withdrawn every day to give a low sludge age (SRT = sludge retention time in the system) in reactor 2, and a high sludge age in reactor 3.

During 50 days pH was monitored and dissolved oxygen and COD in the effluent was measured about twice a week. In order to calculate the load and SRT, the influent flow and suspended solids in aeration and effluent were determined at least once a week. During the last two weeks extra addition of Ca-EDTA and Mn-EDTA respectively was made with the nutrients to the waste water.

3.3 Kinetic study

The same reactors as in the continuous experiment were used, but without any addition or recirculation of sludge (batch-wise experiments). Waste water (diluted to half strength to avoid possible toxic effects) was inoculated to about 1 g SS/l with sludge from the three different continuous reactors.

Reactor 1 was adjusted to pH 7, and reactors 2 and 3 to 8,5. Samples were taken at least once a day during at least 7 days.

3.4 Analyses

Samples from the continuous experiment were collected in dark beakers for determination of flow rate and SS in the effluent. A portion was transferred to refrigerator for settling about 30 min. COD was determined in the supernatant, and about 50 ml of supernatant was frozen for later analyses of EDTA.

COD (mg/l) was determined with the Dr Lange ampoule method.

SS (mg/l) was determined according to SS 02 81 12.

SVI (sludge volume index, ml/g) was determined as sludge volume in Imhoff cone divided by SS.

SSVI (stirred sludge volume index, ml/g) was determined as stirred sludge volume (Settling apparatus from Triton Electronics Ltd.) divided by SS.

Microscopic studies were performed with an Olympus BX50 microscope with phase contrast.

3.4.1 Determination of EDTA in water and sludge

The liquid sample pH was adjusted to 2.5-3 with formic acid, and surrogate standards PDTA (diamine propane tetraacetic acid), CDTA (diamine cyklohexane tetraacetic acid) and HDTA (diamine hexane tetraacetic acid), all purchased from Aldrich, were added. Particulate material was removed by centrifugation and dissolved organic matter by passing the sample through a C18 column. The pre-cleaned sample (0.25 ml) was evaporated to dryness after an addition of HCl (6M, 50 µl) and thereafter derivatized with the reagent propanol / HCl as described below.

The determination of photolabile EDTA-complexes (e.g. Fe(III)-EDTA(1, 5)) was carried out according to Langi et al. (6). The test was performed in open beaker using natural day light as a light source. The samples were incubated during 22 hours (4 PM April 14 to 2 PM April 15). The samples were weighted immediately before and after

the exposure time in order to determinate the loss of evaporation. A positive control was included, containing Fe(III)-EDTA dissolved in Milli-Q water at a concentration of 46 mg/l. The concentration of EDTA was analysed before and after the exposure to daylight.

Sludge and water from the different continuous reactors were centrifuged and the obtained pellets, mainly consisting of micro-organisms, were used for analysis of particulate bound EDTA. The concentration of EDTA in the supernatants was determined separately.

The occurrence of natural surfactants in the sludge sample, produced by the micro-organisms in the sludge, caused substantial analytical problems by emulsifying the extracts. However, it was possible to overcome this by heat treatment of the sample, carried out by drying the sample to dryness at 105°C. This treatment diminished the emulsifying properties of the sample to an acceptable level.

The dried sample was extracted three times, after addition of surrogate standards, with a phosphate buffer (0.05 M, pH 3) at 95°C. The combined extract was further acidified (pH < 1) with HCl and concentrated on a GCB-column (graphitized carbon black column)(7). The analytes were eluted by injecting formic acid onto the column. The formic acid was evaporated by means of a gentle steam of nitrogen and the dry residue was derivatized as described below.

The dry weight of the sludge was determined by drying the pellet at 105°C overnight.

The extracts were derivatized into their n-propyl esters by treatment with the reagent solution 1-propanol / HCl (10%), at 95°C for 45 min. The reagent was neutralised and removed by adding a solution of $NaHCO_3$ (0.6 M) and the esters was extracted with hexane (3 ml). The hexane extract was dried over Na_2SO_4 and reduced to a appropriate volume by means of a gentle stream of N_2. Immediately before injected onto the analytical GC-column, internal standard (biphenyl from Aldrich) was added to the sample.

3.4.2 Instrument for EDTA determination

The analyses were carried out with a HP 5890 II gas chromatograph equipped with a Model HP 7376 auto sampler. The flame ionisation detector (FID) was held at 300°C.

The following temperature programme was used: 1 min isothermal at 45°C followed by an increase of 13°C/ min to 295°C and held for 10 min.

A fused silica capillary column DB-5 (10 m), with an ID of 0.25 mm and a film thickness of 0.1 µm was used (J & W, Scientific Inc., Rancho Cordova, CA). A methyl

deactivated retention gap (Chrompack) was used to prevent deterioration of the analytical column.

The detector signal from the gas chromatograph was acquired and integrated with a personal computer with the chromatography data program Turbochrom™.

4. Results

4.1 Analyses of EDTA in waste water and sludge

The waste water from Hallsta contained about 46 mg EDTA/l on arrival to IVL. The concentration didn't change during storage in the coldroom or in the refrigerator during 70 days. Four analyses at different times gave 45-48 mg/l.

The precision of the method used for analysing EDTA in water samples was determined by analysing an authentic sample on different occasions. The reproducibility was ±2,3% in the range 5-45 mg/l. The recovery was mainly between 82-92% with an average of 86% (sd 6,8).

The analytical recovery for the method used for EDTA analysis in sludge was between 65-75%. The precision of the method was not evaluated.

The results from the photodegradation experiment are summarised in table 1.

Table 1. Determination of the content of Fe(III)-EDTA.

Sample	Start	After photolysis	Reduction
	mg/l	mg/l	%
Effluent, Hallsta	43	44	0
Reactor 1 pH 7	16	15	2.5
Reactor 2 pH 8.5	35	35	0
Reactor 2 pH 8.5	15	15	0
Control Fe(III)-EDTA	47	0.2	99.6

The results show that nearly no photolabile EDTA was detected in the examined water samples from reactors 1-3. The light conditions allowed nearly complete degraded of the Fe(III)-EDTA in the control. Thus, light was not a limiting factor for photolysis of occurring Fe(III)-EDTA in the samples.

The concentration of sludge-bound EDTA was determined in the continuous reactors and in reactor 3 in the kinetic study. The EDTA concentrations in the particulate phase

were calculated by subtracting dissolved EDTA from the total EDTA in the sample. The amount of water (containing the dissolved EDTA) in the sludge was determined as loss of drying. The concentration of EDTA in the water phase (supernatant after centrifugation of the sludge) was determined separately.

Bound EDTA was not detected in the sludge from the continuous reactors.

At the end of the kinetic study, sludge from reactor 3 was examined for particulate bound EDTA. Quite low concentration of EDTA, 1.4 mg/kg on a dry weight basis (dw 3,9-6,1% of fresh weight), was detected. Therefore, it was concluded that the observed decrease of the EDTA in the continuous and kinetic experiments was caused by microbial degradation rather than adsorption to particulate material.

Metabolites from degradation of EDTA were not detected in any of the experiments. This was as expected, since the degradation products from EDTA are considered to be readily degradable (8).

4.2. Continuous reactors

4.2.1 pH regulation

pH in reactor 1 was very stable at 7,0-7,2 during the 50 days test, without any regulation. Regulation with 1 M NaOH in reactors 2 and 3 gave a stable pH of 8,5-8,6. Addition of NaOH gave about 4% dilution of the waste water, COD and EDTA removal values are corrected for this. In reactor 2, with low SRT and thus low sludge concentration, 1,6 kg NaOH was needed per m^3 of waste water to keep pH at 8,5. In reactor 3, with high SRT and high sludge concentration, 1,4 kg NaOH/m^3 was needed.

4.2.2 COD removal

COD removal was dependent on the load, as can be seen in figure 1. The added lines indicate that there is a maximum removal of COD in the system, corresponding to about 87% reduction (3650 mg/l in figure 1). The symbols for reactors 2 and 3, with pH 8,5, are well gathered around the lines, and no difference can be seen between the different sludge ages. However, since all the data from SRT 21 days are collected at low loads, they really don’t give a clear correlation.

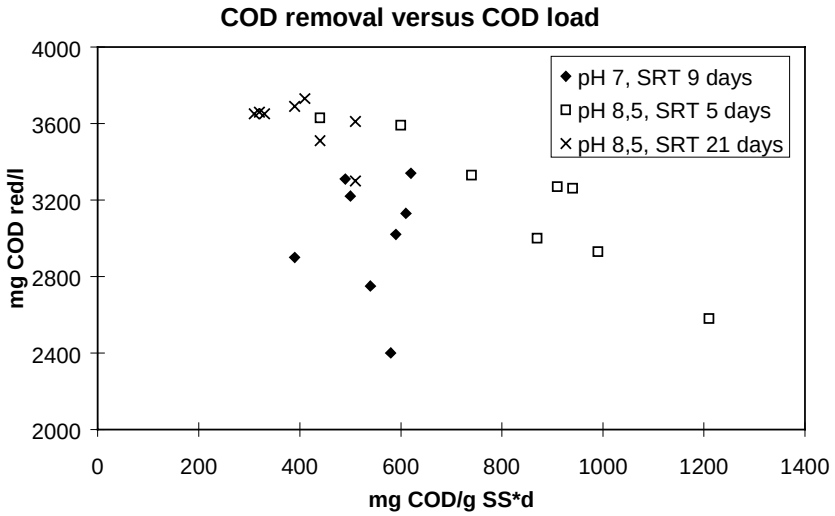

Figure 1. COD removal in the continuous test.

All data from pH 7 are below the correlation line for pH 8,5. This indicates that COD reduction is slower at pH 7 than at pH 8,5. However, part of the difference can be explained by the COD in particles. COD analyses were performed with the supernatant after 30 minutes of settling, and the supernatant from reactor 1 contained more suspended solids than those from reactors 2 and 3.

4.2.3 EDTA removal

The corresponding data for EDTA are shown in figure 2.

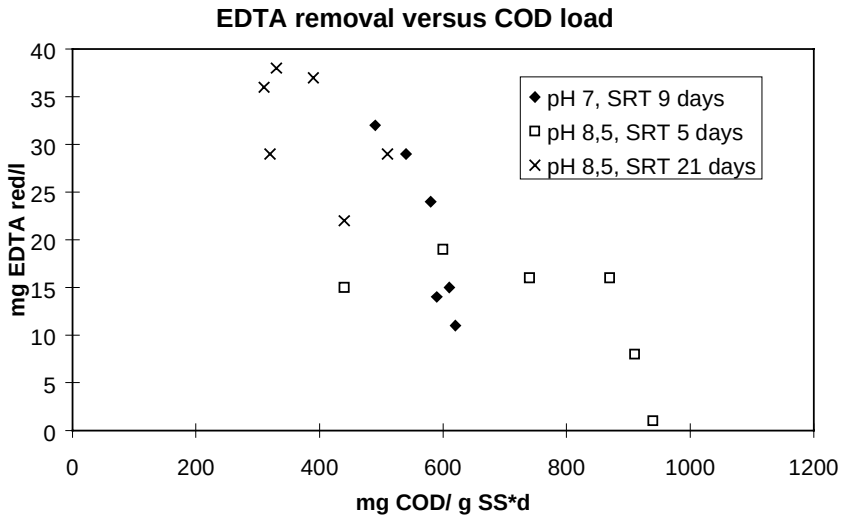

Figure 2. Removal of EDTA in the continuous test.

Again there seem to be a correlation between removal and load. Data from all reactors are relatively well correlated to the line ($r^2 = 0,67$), irrespective of pH and SRT. On the other hand, the dotted line is a possible correlation to pH 7 data, indicating that a lower load is needed to get EDTA degradation at pH 7.

The rate of EDTA removal in the three reactors under loads giving significant EDTA removal were calculated to:

Reactor 1, pH 7,0 and SRT 9 days	2,8 ± 0,9 mg EDTA/g SS*d
Reactor 2, pH 8,5 and SRT 5 days	2,4 ± 0,8 mg EDTA/g SS*d
Reactor 3, pH 8,5 and SRT 21 days	2,9 ± 0,6 mg EDTA/g SS*d

It can be seen that there is no difference in EDTA removal rate in the three reactors, as long as the load is low. In this case, with the same ratio between COD and EDTA in the waste water all the time, it is impossible to distinguish between COD load and EDTA load. and their role in degradation.

Addition of extra Ca-EDTA and Mn-EDTA didn't give any really reliable information, since the load was not low enough to give total degradation of the "natural" EDTA in the waste water. However, the few analyses made indicated that Ca-EDTA behaved like the EDTA present in the waste water. Mn-EDTA seemed to be more readily degraded at pH 8,5, and less degraded at pH 7, compared to the total EDTA in the waste water.

4.2.4 Sludge properties

Before the separation of pH and SRT, the sludge had acceptable properties with SVI 230 ml/g and SSVI 170 ml/g. Flocs were rather compact and contained *Nosticoida limicola* type III and another filament, similar to 021N. Attached ciliates and rotifers were common.

The sludge properties at the end of the experiment are shown in table 2.

Table 2. Sludge properties after 50 days at different conditions.

	SVI ml/g	SSVI ml/g	SS in supern. mg/l	flocs	filaments	ciliates	flagellates
Reactor 1 pH 7, SRT 9 d.	150	130	300	very big, open	abundant	normal	abundant
Reactor 2 pH 8,5, SRT 5 d.	380	290	170	big, open	abundant	normal	abundant
Reactor 3 pH 8,5, SRT 21 d.	250	140	67	normal	normal	normal	normal

Another obvious difference between the sludges was a much higher concentration of spirilles in reactors 1 and 2 compared to 3.

4.3 Kinetic experiments

4.3.1 COD removal

As shown in figure 3, COD removal started much earlier with sludge from reactors 2 and 3 (pH 8,5), than with the pH 7 sludge from reactor 1.

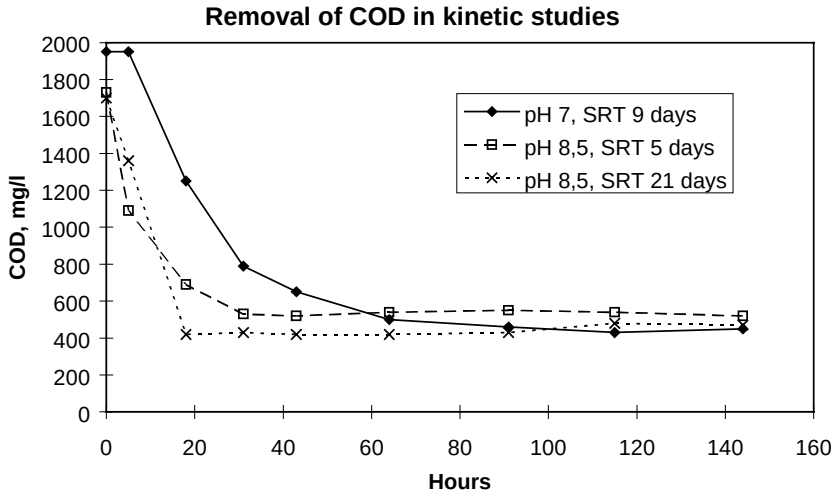

Figure 3. COD removal versus time in batch experiment.

With sludge from reactor 3, pH 8,5 and SRT 21 days, COD removal was fast and "completed" already after 18 hours. The other sludges gave a much slower degradation at low residual concentrations of COD.

4.3.2 EDTA removal

EDTA removal was quite different in the three reactors, figure 4.

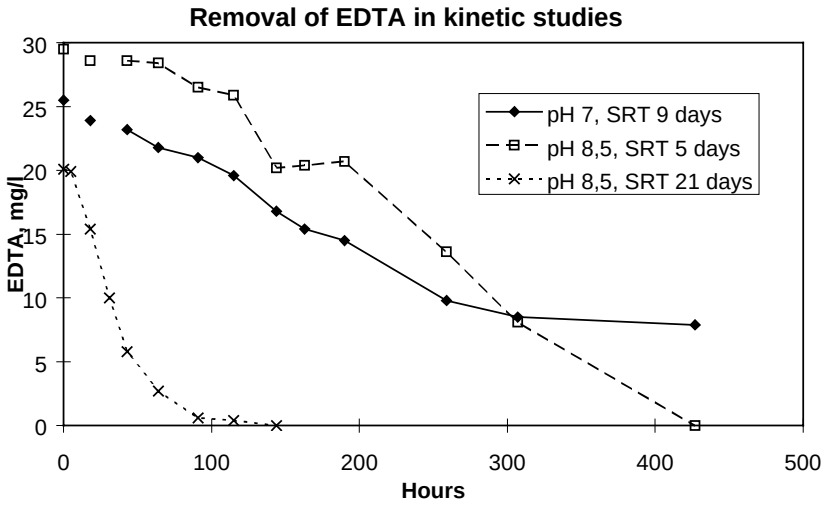

Figure 4. EDTA removal versus time in batch experiment.

Degradation of EDTA was slow in reactor 2 with pH 8,5 and with sludge from the experiment with low sludge age or SRT. No degradation was observed until after 64 hours, and after this the degradation was just about 2 mg EDTA/g SS*day. The rate seems not to be influenced by the residual concentration of EDTA.

At pH 7 , in reactor 1, the degradation seemed to start faster, but the overall rate was even lower than in reactor 2, about 1,5 mg EDTA/g SS*day. At the end of the experiment, the sludge concentration had fallen from 1,0 to 0,2 g/l. This massive death and lysis of the sludge probably explains the levelling off of the EDTA curve.

EDTA removal at pH 8,5 with the high age sludge (reactor 3) shows a typical curve with substrate limited degradation. It is shown in more detail in figure 5. From 5 to 43 hours the mean degradation rate was 11 mg EDTA/g SS*day.

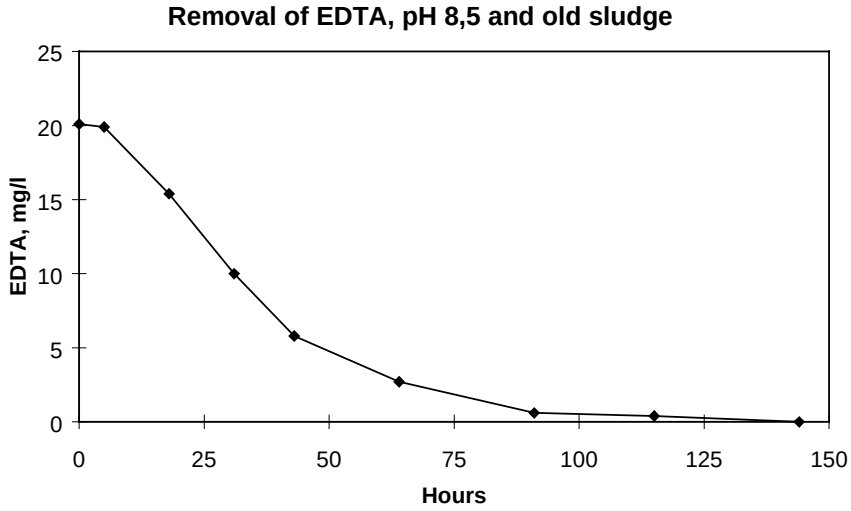

Figure 5. EDTA removal in reactor 3 at pH 8,5 and high SRT.

After drawing a smooth curve through the data points, v (degradation rate) can be measured for different S (substrate concentrations) and 1/v and 1/S can be calculated, table 3.

Table 3. Kinetic data for the Lineweaver-Burk diagram, pH 8,5, high SRT.

S	v	1/S	1/v
mg/l	mg/l*h	l/mg	l*h/mg
15,5	0,491	0,065	2,04
10	0,374	0,100	2,67
6,3	0,246	0,159	4,07
4	0,160	0,250	6,25
2,7	0,120	0,370	8,33
1,5	0,078	0,667	12,82

From these data a Lineweaver-Burk diagram (9) can be constructed, figure 6.

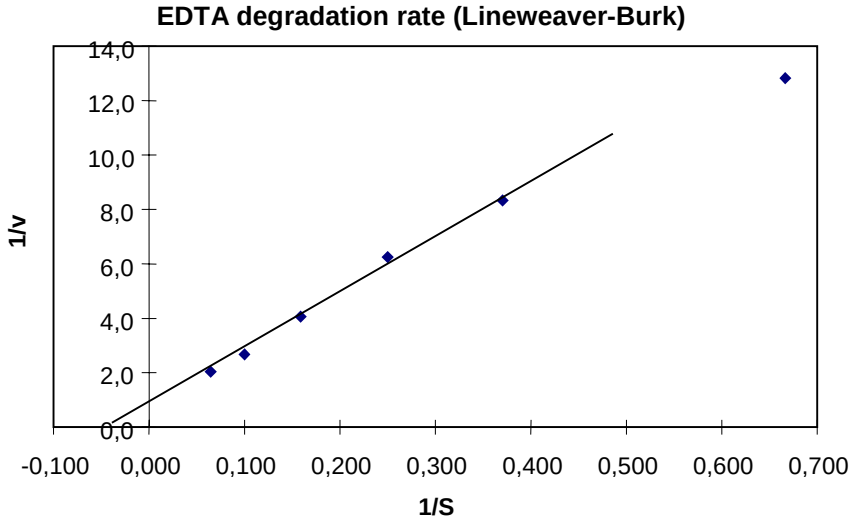

Figure 6. Lineweaver-Burk diagram for EDTA degradation at pH 8,5 and long SRT.

The line is based upon the first 5 data points. It is not surprising that the last point seems to fall out of the line, it is very difficult to measure this low slope on the hand drawn curve. From the line (r^2 = 0,995) the kinetic constants can be calculated to be: v_{max} = 1,5 mg EDTA/l*h and K_M = 31 mg EDTA/l (K_M is the substrate concentration where the degradation rate is $v_{max}/2$) (9). Since the sludge concentration was 1,0 g/l, v_{max} was determined to 35 mg EDTA/g SS*day.

5. Discussion

Part of the results from continuous treatment in laboratory scale are surprising. It was expected that COD degradation would be dependent on the sludge load, as shown in figure 1. However, the better COD removal at pH 8,5 than at pH 7 was unexpected. Just a part of the difference can be explained by the higher content of suspended solids (probably bacteria and flagellates) in the supernatant from pH 7. This difference was in itself not expected, since the general opinion would be that you have less protozoa at pH 8,5 than at pH 7, giving more free bacteria at pH 8,5. On the other hand, very high concentrations of flagellates may give high suspended solids in the supernatant. The reason may also be specific to this kind of waste water with a lot of fatty acids and resin acids. They are possibly less toxic at higher pH. Lignin residues are also more soluble and possibly more degradable at higher pH.

The really surprising result was that EDTA degradation in this system was not obviously dependent on pH, but just on sludge load, figure 2. To try to validate this with the waste

water from Hallsta, EDTA was determined into and out from the first aeration unit in Hallsta. No degradation was found at pH close to 7 and sludge load about 1,5 g COD/g SS*d. This was in agreement with the laboratory results, but samples from the final aeration at Hallsta were also analysed. In this case almost no degradation was found, in spite of just 550 mg COD/g SS*d and SRT 10 days. This cannot be explained by figure 2, not even if the dotted line for pH 7 is true. One possible explanation is that the suggested lines in figure 2 are not relevant at all, and the data almost random.

The kinetic experiments again gave new results concerning EDTA, but the same situation for COD removal. Figure 3 indicates both a slower degradation of organic material at pH 7 than at pH 8,5, and a more complete degradation with sludge of higher age. The two curves for pH 8,5 have interesting differences. The SRT 5 days sludge gave a very fast initial degradation of COD, but the rate decreased fast and the final value was not reached until after 31 hours. The SRT 21 days sludge gave a somewhat slower initial degradation, but the final concentration was reached already after 18 hours.

One explanation to the fast final degradation of COD can be that in the low age sludge bacteria's adapted to the most readily degradable part of COD dominated, while those able to degrade more recalcitrant material were less abundant. In the high age sludge the bacteria's able to degrade most of the COD were found in higher concentration, thus giving a faster final degradation.

The difference in final concentration of COD is probably a result of the experimental procedure, with different mixtures of sludge with treated waste water with full strength, and new waste water with half strength.

The kinetics of EDTA degradation were very different at different pH and with different sludges. In both reactors with low sludge age inoculum, the degradation rate of EDTA was low and not obviously influenced by the concentration of EDTA. This means that the rate was probably restricted by the amount of suitable bacteria, rather than by EDTA concentration, at least at higher concentrations. The degradation rate was about the same as that found in the continuous experiment in reactors 1 and 2 (1,5-2,8 mg EDTA/g SS*day).

It is also similar to the degradation rate that can be calculated from experiments in a Finnish pulp mill (3). In that case 8 mg EDTA/l was removed during 2 days, that is 4 mg EDTA/l*day. If the sludge concentration was 2 g/l, this would mean 2 mg EDTA/g SS*day. However, in other cases much higher degradation rates have been found (4).

The degradation of EDTA in reactor 3, with pH 8,5 and high sludge age, was much faster. Typical Michaelis-Menten kinetics (9) gave v_{max} 35 mg EDTA/g SS*day and K_M 31 mg EDTA/l. With these constants the expected degradation rate in the continuous

reactor 3 can be calculated. With residual EDTA around 10 mg/l the rate would be about 9 mg EDTA/g SS*day, that is much higher than the 3 mg EDTA/g SS*day that was measured.

One possible explanation to this is a toxic effect of the waste water. In the kinetic experiment the waste water was diluted, while it had full concentration in the continuous experiment.

The only logical explanation to all the data seem to be at least two different kinds of bacteria that degrade EDTA. One of them degrades EDTA both at pH 7 and 8,5, and has a slow degradation rate v_{max} but a low half rate constant K_M. This bacteria seem to be present also at low sludge age (5 days) and not sensitive to toxic compounds in the waste water.

The other bacteria has a much higher degradation rate, but also a higher K_M. It is only found in sludge with a sludge age over 9 days (21 days), active at pH 8,5 but sensitive to some toxic effect in the waste water.

Though this is a possible explanation to the laboratory results, it does not explain that no degradation of EDTA was seen in the full scale treatment at Hallsta paper mill or in other measurements at pH 7. There are still many questions to be answered concerning degradation of EDTA.

About 1,5 kg NaOH/m^3 of waste water was needed in this case to keep pH at 8,5. In this pH region this should correspond roughly to about 1 kg CaO or about 1,5 kg $Ca(OH)_2$, which should be used in practice.

It is obviously very important to know the extra cost for a biological treatment that not only removes COD, but also EDTA. However, this can not be properly calculated from the data available. They are still too contradictory, and a long term test in pilot scale is needed to give reliable data about retention times (aeration volumes) and sedimentation properties (settling area and residual suspended solids).

The direct cost for caustic lime would be about 15 SEK per ton of TMP, with a water like the one investigated here. This can vary a lot dependent on starting pH and buffering capacity. Costs for addition of nitrogen source could probably be omitted, but this is normally not more than 1-2 SEK per ton of TMP. The extra need for oxygen in the treatment would not be more than some percent, but may be important if oxygen is limited.

A substantial extra cost would be if the aeration volume has to be increased. According to the best results from the kinetic study, this would not be needed in an extended aeration activated plant with 2 days HRT and sludge concentrations of 2-3 g/l. At lower

HRT an increase could be necessary, unless the sludge concentration can be increased. To some extent this can be possible, since the sludge properties may be improved at higher pH.

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