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Abstract:

Monoethanolamines (MEA) are commonly used as adsorbent in CO_2 capture plants. MEA are degraded when used and become a waste product. 3 series of BOD test as well as 9 cases of syringe batch experiments under anaerobic, micro-aerobic and aerobic conditions were conduced to examine the biodegradation of waste amines. BOD and syringe batch experiments indicate that waste amines are successfully degraded and degraded with high reaction rates under all anaerobic, micro-aerobic and aerobic conditions, removing more than 90 % of amine COD. Almost all amine COD was removed in the micro-aerobic case. The BOD experiments show that the amine degradation is in first order reaction, and the highest reaction rate 1.08/d was obtained in reactors with 125 mg/l of initial amine. Even high concentration of amines (2000 mg/l) can be degraded if pH is maintained neutral. Small and compact biological treatment plants therefore can be built to treat waste amines at low cost and meanwhile recover energy as CH_4.

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1. INTRODUCTION

Monoethanolamines (MEA, C_2H_7N) are commonly used as a scrubbing agent for gas purification in many oil refineries and natural gas conditioning plant (nature gas sweetening) basically intended for removing H_2S (Hydrogen sulphide) and CO_2 (Shao, 2002; Espita et al., 2004). Almost all of the major CO_2 capture plants (from flue gas) currently operating in the world are using MEA as their chemical solvent (Strazisar et al., 2001). MEA has remarkable features including high loading capacity for CO_2, fast reaction kinetics and high remove efficiencies (Goff, 2005).

Amines are degraded when used and becomes a waste product. It contains both liquid and solid fractions of wastes generated by amine degradation and by other additives. The disposal regulations on this type of amine waste are very stringent because they are considered as a hazardous waste for their compositions, toxicity and volumes are still not well understand (CCR Technologies, Technical Bulletin). Amine reclaimer is the unit in the process used for separating or reclaiming usable amine from its degradation products. There are three types of reclaimer technologies available such as (vacuum) Distillation, Anion exchange and Electrodialysis.

The options which could be used for treatment/disposal for amine reclaimer wastes include incineration or thermal decomposition (Kumagai et al., 2006; Chapel and Mariz, 1999; Espita et al., 2004, etc.), disposing in Cement kilns as a NO_X reduction agent to reduce NO_X emissions (Dangtran and Butt, 2001; French Agency for Environment and Energy Management, 2002; US department of Energy, 2002) and as a PCDD/Fs formation inhibitor to reduce the formation of dangerous and persistent air pollutants, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs and PCDFs) (Ruokojarvi et al., 2004; Botheju, 2006), using as a sludge solubilising agent (Kumagi et al., 2006), land disposal (Espita et al., 2004; IEA report, 2006) and biological treatment (Ohtaguchi et al., 1995; lai and Shieh, 1996; Anne et al., 2004 etc.).

Biological treatment is a very constructive idea due to the fact that MEA is an organic substance embodied with a rich amount of carbon and nitrogen, and both of these elements are essential in microbial metabolism (Botheju, 2006). Lai and Shieh (1996) reveal that MEA is highly degradable via nitrate respiration, using NO_3^- as an electron acceptor and ammonia was formed as an end product. More than 70 % of the mixed liquor TOC could be removed within 4 h after the addition of MEA when the initial TOC/MLVSS ration used in a batch experiment was below 0.30-0.35.

Ohtaguchi et al. (1995) demonstrated the MEA degradation via aerobic degradation using pure cultures of Escherichia coli K 12. They found that the biodegradation rate was higher for waste amine solutions than the pure MEA solutions. Amine degradation compounds present in the waste had a positive effect on the biodegradation process. The authors suggest the following degradation pathways to explain their observation (Eq. 1.1 to Eq. 1.4):

$$H_3N^+CH_2CH_2OH \rightarrow NH_4^+ + CH_3CHO \qquad (1.1)$$

$$CH_3CHO + CoA + NAD^+ \rightarrow CH_3CO - CoA + NADH + H^+ \quad (1.2)$$

$$CH_3CO - CoA + Pi \rightarrow CH_3CO_2PO_3^{-2} + CoA + 2H^+ \quad (1.3)$$

$$CH_3CO_2PO_3^{2-} + 2H^+ + ADP \rightarrow CH_3COOH + ATP \quad (1.4)$$

MEA is first degraded to ammonium ion and acetaldehyde, and then further transformed into acetic acid while most of the ammonium was assimilated as a nitrogen source. In addition to Escherichia coli K 12, Ohtaguchi and Yokoyama (1997) also demonstrate other metabolic alternatives for MEA degradation.

Ndegwa et al. (2004) elucidate degradation pathways of MEA in soil under aerobic and anaerobic conditions. They indicate that MEA in soil is biodegraded to ammonium and acetaldehyde by a mean of hydrolysis process. Under aerobic conditions, ammonium can be oxidized to nitrite and then nitrate, the acetaldehyde is then hydrolyses to ethanol and acetic acid. Ethanol and acetic acid can be consumed by bacteria and turned to CO_2.

Acetic acid is the major end product in most of metabolic pathways of MEA aerobic degradation together with other end products like ethanol, acetaldehyde, amine acids, H_2 they are all have potential for further anaerobic degradation, therefore it is possible to redirect the process anaerobically towards CH_4 generation (Botheju, 2006).

1.1 Aim

The objective of this project is to investigate the potential of biological degradation of used amines. The long term aim is to develop a theoretical and experimental platform for the design of biological treatment processes for such waste streams. The present study is designed to obtain information about degradation extent and rates under aerobic, micro-aerobic and anaerobic conditions.

2 MATERIALS AND METHODS

This chapter is organized by 6 sections. Section 1, 2 and 3 describe sources and composition of inoculum, waste amine and nutrient used in this project, respectively. Experimental matrix, initial compositions and labels of BOD and syringe reactors are shown in section 4. Section 5 lists the experimental procedures for both BOD and syringe experiments. At last, analytical methods used in this project are presented in section 6.

2.1 Inoculum

Inoculum used for this study is a mixture from five different sources (Table 3). It is assumed that a “multi-microorganism Inoculum” will make the reaction more efficient and/or more likely to take place because it increase the probability that adequate organisms are available in the inoculum.

2.2 Waste amine

The amine samples are taken from the Aker Kvaerner pilot plant at Kårstø (Norway). They are used for capturing CO_2 from natural gas. The amine waste for this study was sampled when the whole system was emptied. It is not representative of waste as it would come from a reclaimer. The samples contain relatively more MEA (about 21 %), and less degradation products, than what would be typical for reclaimer waste (Joh Hovland, 2008).

2.3 Nutrients

The nutrients used for this study consists a mineral solution and a vitamin solution. The composition of the mineral solution (Hariklia et al., 2005) is shown in Table 1. The vitamin solution used in this study is a 10 times concentrated vitamin solution as described by Wolin et al., (1963)

Table 1

Composition of raw waste amine used in this study, tested in ALS Scandinavia NUF (2008).

ELEMENT	Content
Sulfate (SO_4) (mg/l)	<144
Ammonium (NH_4) (mg/l)	14320
Al (µg/l)	275
As (µg/l)	<0.7
B (µg/l)	30.2
Ba (µg/l)	230
Ca (mg/l)	3.54
Cd (µg/l)	3.98
Co (µg/l)	4.25
Cr (µg/l)	17.7
Cu (µg/l)	860
Fe (mg/l)	4.43
Hg (µg/l)	0.0816
K (mg/l)	2.2
Mg (mg/l)	0.909
Mn (µg/l)	135
Mo (µg/l)	14.1
Na (mg/l)	20.2
Ni (µg/l)	78.6
P (µg/l)	1280
Pb (µg/l)	24.4
S (mg/l)	3.47
Si (mg/l)	1.13
Sr (µg/l)	41.7
Zn (µg/l)	2130
Nitrate (NO_3) (mg/l)	186
pH	10.9
Monoetanolamine (mg/l)	210000
N-Kjeldahl (mg/l)	40000

Table 2
Composition of mineral solution used in this study.

Chemical	Content (g/L)
$MnSO_4.H_2O$	0.04
$FeSO_4.7H_2O$	2.8
$CuSO_4.5H_2O$	0.06
$NiCl_2.6H_2O$	0.092
$ZnSO_4.7H_2O$	0.09
$CoCl_2.6H_2O$	0.05
H_3BO_3	0.05
$(NH_4)_6Mo_7O_{24}$	0.05
$AlCl_3$	0.05
$Na_2SeO_3.5H_2O$	0.1
HCl (37 %)	1 ml

Table 3

Sources and composition of inoculum, a mixture from 5 sources, used in this study.

Type of Source	Description	percentage	Treatment process
Bed sediment from Lilleelva stream	Re-suspended river sediment (expected to be contaminated by petrochemicals to a certain degree)	25 %	Re-suspended, add 1.6L water, add 1 ml waste amine, kept at in room temperature.
Anaerobic digester at Knardalstrand waste water treatment plant	Liquid phase of filtered digestate (from filter-press)	35 %	Kept at room temperature.
Micro-aerobic hygenization reactor at Knardalsrand waste water treatment plant	Micro-aerobic culture containing mostly facultative organisms	12.5 %	Kept at room temperature
Petrochemical reactor	Effluent from lab scale anaerobic digester operating on a petrochemical feed	2.5 %	Add 25 ml waste amine
Sludge from a Refinery waste water treatment plant	Activated sludge from refinery wastewater treatment	25 %	Kept in room temperature.

2.4 Experimental design

The experiments are carried out in two types of batch reactors: 60 ml syringes on a shaker, as shown in Figure 1 and standard BOD analysis equipment (Hach BOD Trak™ DR 2000 BOD analyzer).

The experimental matrix is shown in Table 4, showing the oxygen levels and amine concentrations tested and the numbers of parallels for each case. The main variables for syringe experiments were MEA and O_2 concentrations, the initial contents and labels of the 28 syringe batch reactors are shown in Table 4. Initial composition and labels of the 3 series of BOD test are shown in Table 6.

Fig. 1. ***Syringes as batch reactors fixed onto a shaker by adhesive tape.***

Table 4

Experimental matrix for all experiments showing the numbers of parallels for the different oxygen levels and amine concentrations tested.

O_2 level (reactor)	Amine content			
	0 mg/l	≈125 mg/l	≈500 mg/l	≈2000 mg/l
Anaerobic (syringe)	2	2	2	0
Micro—aerobic assisted anaerobic (syringe)	2	10	2	0
Aerobic (syringe)	2	2	2	0
Aerobic (BOD)	2	4	2	2

Table 5
Initial compositions and labels of the 28 syringe batch reactors.

No.	Condition	Amine content (mg/l)	Initial air head space (ml)	Total liquid volume (ml)
1A	anaerobic	0	0	20
1B	anaerobic	0	0	20
2A	anaerobic	≈125	0	20
2B	anaerobic	≈125	0	20
2C	anaerobic	≈125	0	20
2D	anaerobic	≈125	0	20
3A	anaerobic	≈500	0	20
3B	anaerobic	≈500	0	20
4A	Micro-aerobic	0	2.5	20
4B	Micro-aerobic	0	2.5	20
5A	Micro-aerobic	≈125	2.5	20
5B	Micro-aerobic	≈125	2.5	20
5C	Micro-aerobic	≈125	2.5	20
5D	Micro-aerobic	≈125	2.5	20
5E	Micro-aerobic	≈125	2.5	20
5F	Micro-aerobic	≈125	2.5	20
5G	Micro-aerobic	≈125	2.5	20
5H	Micro-aerobic	≈125	2.5	20
5I	Micro-aerobic	≈125	2.5	20
5J	Micro-aerobic	≈125	2.5	20
6A	Micro-aerobic	≈500	10	20
6B	Micro-aerobic	≈500	10	20
7A	aerobic	0	16	20
7B	aerobic	0	16	20
8A	aerobic	≈125	16	20
8B	aerobic	≈125	16	20
9A	aerobic	≈500	16	20
9B	aerobic	≈500	16	20

Table 6

Initial compositions and labels for the 3 series of BOD tests.

Series	Sample label	Amine (mg/l)	PH adjust	sample source
1	#1	0	No	B0[a]
1	#2	0	No	B0
1	#3	125	No	B1[b]
1	#4	125	No	B1
1	#5	500	No	B2[c]
1	#6	500	No	B2
2	#1	0	No	B0 refrigerate 12 days
2	#2	0	No	B0 refrigerate 12 days
2	#3	125	No	B1 refrigerate 12 days
2	#4	125	No	B1 refrigerate 12 days
2	#5	1000	No	B1 refrigerate 12 days + waste amine
2	#6	1000	No	B1 refrigerate 12 days + waste amine
3	#1	0	No	Dilute #1 and #2 samples of series 2 BOD test for 4 times + proper amount of waste amine
3	#2	0	No	
3	#3	500	No	
3	#4	500	No	
3	#5	2000	Yes	
3	#6	2000	Yes	

[a, b, c] B0, B1 and B2 are three containers for mixing inoculum and waste amine. Amine concentrations of them are about 0 mg/l, 125 mg/l and 500 mg/l, respectively.

2.5 Experimental procedure

The experiments were carried out through the following steps:

1. Mix inoculums in a 5000 ml beaker according to Table 1. The inoculums are taken from the top liquid part of each five inoculum containers.
2. Remove the liquid part in the 5000 ml beaker to 3 1000 ml beakers. The three beakers are labeled B0, B1 and B2, respectively.
3. Add 0.5 ml waste amine in beaker b1 and 2 ml waste amine in beaker b2. Measure and record pH in each beakers.
4. Put 2 ml nutrient in each beaker.
5. Purging the beakers with argon until the oxygen levels drop below 0.2 mg/l.
6. Suck 20 ml liquid from the beakers into the appropriate syringes. Put on needles and rubber stoppers
7. Put all syringe reactors in incubator on the shaker and at 35℃.And leave for 5 hours to stabilize temperature.
8. Take 95 ml liquid from the beakers (B0 in #1 and #2 BOD reactors, B1 in #3 and #4 BOD reactors and B2 in #5 and #6 BOD reactors)(BOD series 1). Follow BODTrak test procedures to set BOD test
9. After temperature has stabilized in the incubator: Draw back the pistons and leave 2.5 ml headspace in the syringes of micro-aerobic 125 mg/l amine and micro-aerobic 500 mg/l cases, leave 10 ml headspace in the syringes of micro-aerobic 500 mg/l amine case for O_2 for micro-aerobic digestion. Put rubber stoppers back on.
10. Draw back the pistons and leave 16 ml headspace in the syringes of aerobic 0 mg/l amine and aerobic 125 mg/l amine cases, leave 64 ml headspace in the syringes of aerobic 500 mg/l amine case for O_2 for aerobic digestion. Put rubber stoppers back on
11. Keep the rest inoculum of B0, B1 and B2 in capped bottles in the refrigerator.
12. Perform the second series BOD test (BOD series 2) by using the left liquid in B0, B1 and B2 which are kept in the refrigerator for 12 days. The amine concentration in #1 and #2 bottles are 0 mg/l, and #3 and #4 bottles are 500 mg/l, and #5 and #6 bottles are 2000 mg/l, respectively.
13. Perform the second series BOD test (BOD series 3). The inoculum used in BOD series 3 is from the #1 and #2 bottles (0 mg/l amine) of BOD series 2, but, by diluted it for 4 times. The amine concentration in #1 and #2 bottles are 0 mg/l, #3 and #4 bottles are 500 mg/l, and #5 and #6 bottles are 2000 mg/l, respectively. pH value in the #5 and #6 bottles were adjusted to 7 using sulfuric acid.
14. Measure biogas production volumes about every 24 hours.
15. Empty and add new air in the headspace in syringes of all three aerobic cases.
16. Collect biogas samples for composition analyses.
17. Sacrifice the some syringes at some intervals depending on biogas production and measure pH, COD, NH_4^+ and VFA

2.6 Analytical Method

Biogas volumes were read directly from the scale on the syringe reactors. To analyze the gas composition, biogas in the headspace was firstly transferred to other syringes

then measured by HP Hewlett Packard 5890A gas chromatograph.

About 5 ml samples were taken out from the syringes to measure COD. pH was measured first. The samples were then filtered by “mill pore” 36s filter and then COD measurements were perform using Hach DR 2000, method 962, modified method 8000. pH is measured by MT-00010 pH meter (744 pH meter).

3 RESULTS AND DISCUSSION

This chapter includes two main parts. The first part first presents BOD results and then investigates kinetics of BOD reactions. The Second part is syringe experiment results and discussion. COD measurements and COD removal, CH_4 and biogas production are presented and discussed. The last section shows the measurement results of NH_4-N, alkalinity and pH.

3.1 BOD results and discussion

BOD measurements and reaction stoichiometry are presented first and then analyzed in terms of reaction kinetics.

3.1.1 BOD results

Three series of BOD test were carried out one after another. Fig. 2 shows the results of BOD test series 1, showing apparently difference in BOD value between reactors with different amine concentrations. The reactors with 125 mg/l amine have the highest BOD and BOD removal rate (4 days to reach their ultimate BOD) in BOD series 1. The standard deviation for the two parallels of 0 mg/l amine samples are big, perhaps due to leakage from the cap which had a small crack on it for the #1 BOD bottle.

Inoculum has dominant effect on BOD degradation in BOD series 2 and there are no significant differences in BOD values among those reactors in series 2 (Fig. 3). Solutions for the second series BOD test had been kept in refrigerator for 12 days. The explanation hence could be that nitrification occurs in the BOD test. When nitrification occurs in the BOD test, erroneous interpretations of treatment operating data are possible (Tchobanoglous et al., 2003).

There is remarkable inhibition in the reactors with 2000 mg/l amine in BOD series 3. Microorganisms can't overcome the inhibition by themselves in the experiment period (about 1 week) until pH was adjusted to 7 by adding sulfuric acid in the samples. When pH was adjusted, the reaction rate became fast (about 6 days to reach their ultimate BOD value) despite high concentration of amine in the reactors.

Theoretical MEA BOD/COD is calculated by assuming that MEA reduced to N_2, CO_2 and H_2O:

$$2NH_2CH_2CH_2OH + 13/2O_2 \rightarrow N_2 + 4CO_2 + 7H_2O$$

Accordingly, Maximum theoretical MEA BOD/COD = 104 g O_2/mol MEA.

Table 7 shows theoretical and measurement amine BOD and BOD transfer efficiency. All waste amine present in the reactors with 125 mg/l amine in series 1 (S1-125) was removed within 4 days (Fig. 2), indicating that S1-125 case was running under more favorable conditions compared with the conditions of reactors in other cases. Reactors with 2000 mg/l amine in series 3 (S3-2000) showed a high amine

degradability when pH was adjusted to about 7. It can be seen that 38 % of the amine BOD was removed in only 4 days (Fig. 4) despite the high amine concentration (≈ 2000 mg/l). According to this observation it appears that amine is not very inhibitory to the amine degradation process even at quite high concentrations. The amine concentration in a continuous low bioreactor for amine degradation should never reach such high levels as tested here.

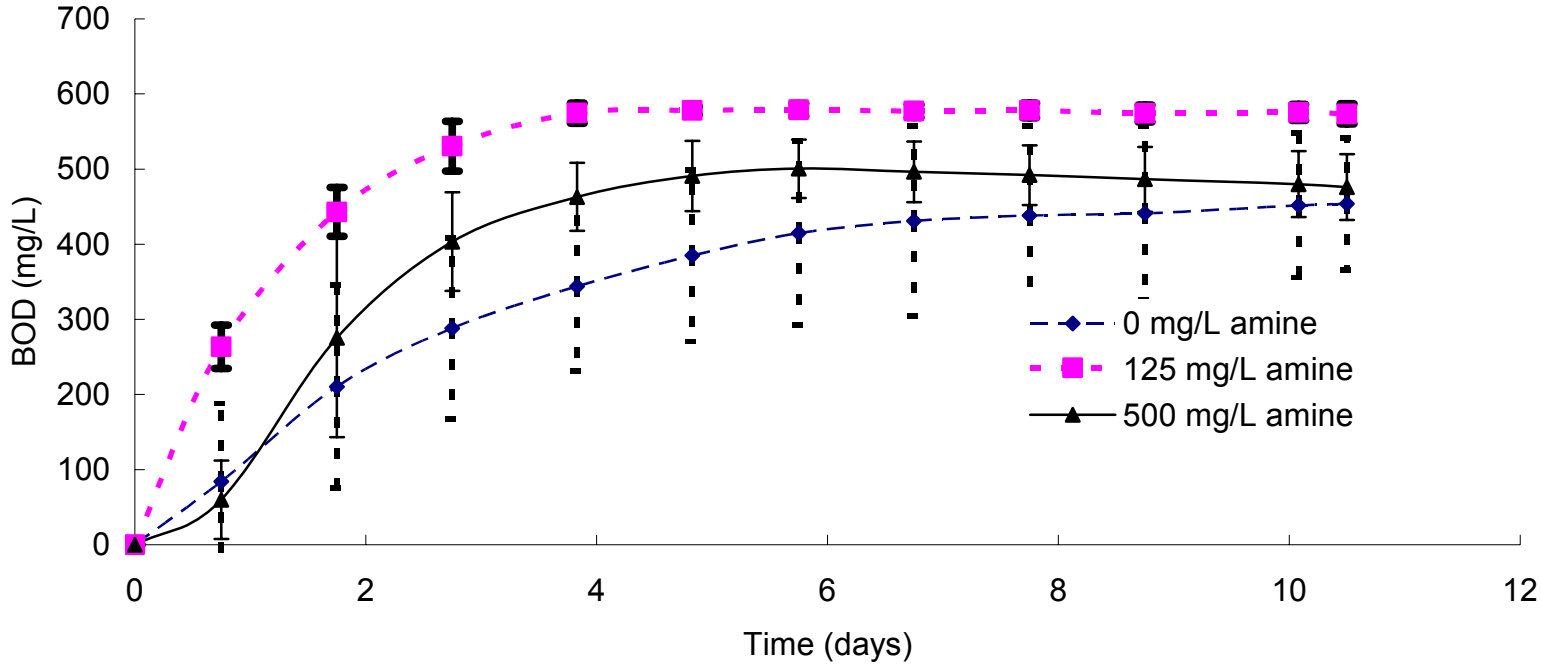

Fig. 2. ***Results of BOD test series 1 showing consumed oxygen as average of two parallels for 3 amine levels, as a function of time.***

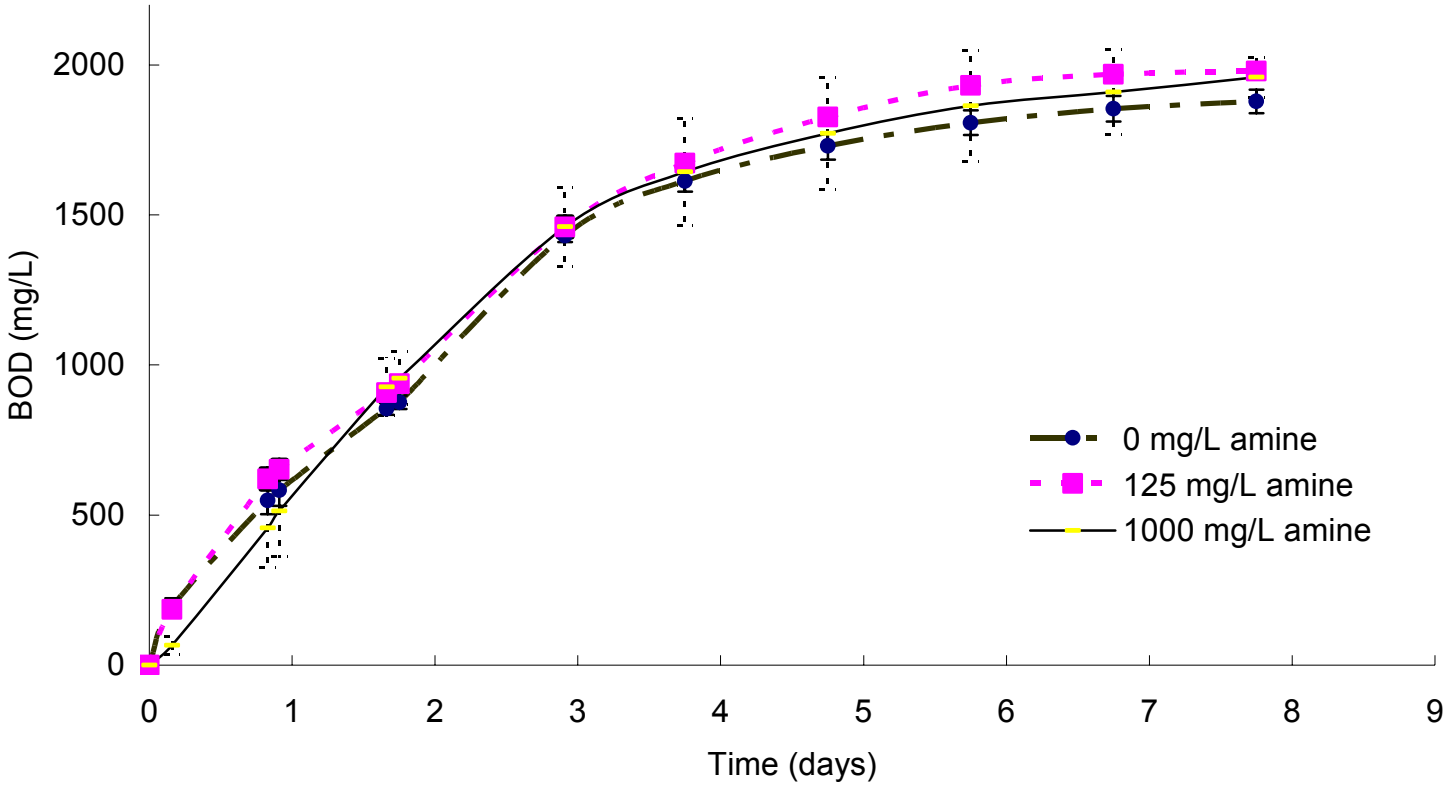

Fig. 3. ***Results of BOD test series 2 showing consumed oxygen as average of two parallels for 3 amine levels, as a function of time.***

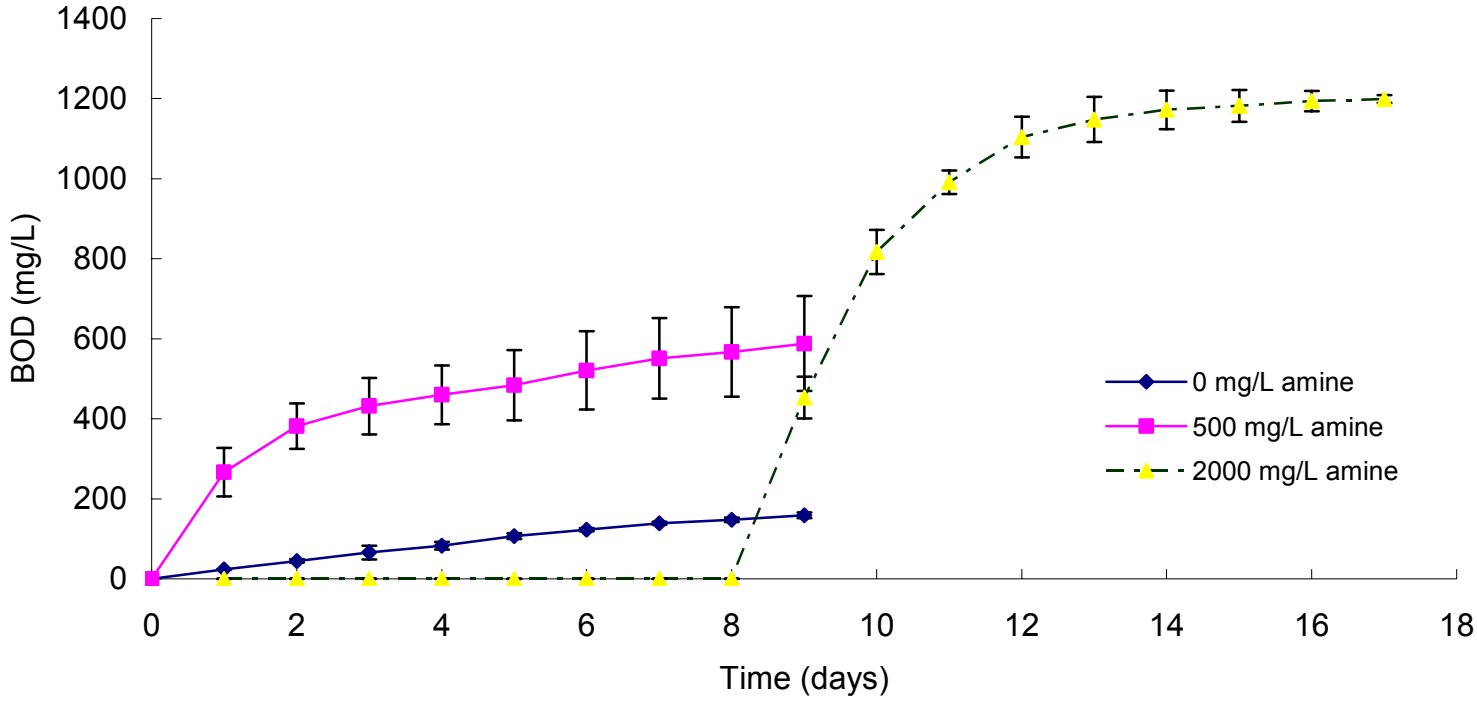

Fig. 4. ***Results of BOD test series 3 showing consumed oxygen as average of two parallels for 3 amine levels, as a function of time.***

Table 7
Theoretical and measured amine BOD and BOD transfer efficiency for reactors in series 1 and 3.

Samples	S1-0	S1-125	S1-500	S3-0	S3-500	S3-2000
Ultimate overall BOD (mg/l))	492	698	558	278	615	1359
Amine concentration (mg/l)	0	≈125	≈500	0	≈500	≈2000
Theoretical maximum amine BOD (mg/l)	--	179	715	--	715	2860
Ultimate amine BOD (mg/l)	--	206	66	--	337	1081
BOD transfer efficicency	--	115 %	9 %	--	47 %	38 %

3.1.2 Kinetics of BOD reaction

The BOD curve can be described by a first- order kinetic equation (Tchobanoglous et al., 2003).

$$\frac{dL}{dt} = -kL \tag{3.1}$$

Eq. (1.1) can be converted to Eq. (1.2):

$$y = L_0(1-10^{-k_{10}t}) \tag{3.2}$$

Thomas method (Thomas, 1950) is used to find k and L_0 values. This method is based on the following equation:

$$(t/y)^{1/3} = 1/(2.3kL_0)^{1/3} + [(2.3k_{10})^{2/3}/6L_0^{1/3}]\cdot t \tag{3.3}$$

Plot of $(t/y)^{1/3}$ as ordinate vs. t as abscissa gives slope as $(2.3k_{10})^{2/3}/6L_0^{1/3}$ and intercept as $1/(2.3k_{10}L_0)^{1/3}$. The parameters are then calculated using the slope and intercept:

$$k_{10} = 2.61(slope/\mathrm{int}ercept) \tag{3.4}$$

$$k = 2.303k_{10} = 6(slope/\mathrm{int}ercept) \tag{3.5}$$

$$L_0 = 1/(6\cdot a\cdot b^2) \tag{3.6}$$

Where:

y = amount of oxygen (BOD) consumed at time t, mg/l;

t = time, d;

L_0 = total or ultimate BOD, mg/l;

k(base e), k_{10} (base 10) = first order reaction rate constant, 1/d

The calculations were carried out in the Microsoft excel and the results are shown in Fig. 5 to Fig. 7.

The BOD series 2 was not included in this analysis since it appears that the BOD values were significantly disturbed by nitrification.

The first order reaction rates for all reactors with waste amine in series 1 and 3 are higher than reactors without waste amine (Fig. 5 and Fig. 6). Indicating that amine degradation compounds present in the reactor had a positive effect on the biodegradation. This is also discovered by Ohtaguchi et al., (1995). The highest first order reaction rate of 0.54/d was obtained in the reactors with 125 mg/l amine (Fig. 5 b). Inhibition in the 2000 mg/l amine samples is enormous, so that no oxygen was consumed initially. Sulfuric acid was therefore added in the samples to try to reach ≈ neutral pH and eliminate inhibition. The BOD degradation then started and it turned out to have quick reaction rate of 0.42/d in reactors with 2000 mg/l amine (Fig. 6 c), which is only 0.02 less than the 500 mg/l amine reactors in the same series when their pH values are maintained close to neutral (pH≈7). This suggests that the high pH caused by amine can inhibit the process, while amine, nor the ammonium, is inhibitory to amine degradation, even at quite high concentrations.

The inoculum used in BOD series 3 was 4-time diluted of inoculum from #1 and #2 reactors in BOD series 2 to decrease the interfere of inoculum for the BOD values and to study effects of biomass concentration on reaction kinetics. The reaction rate k values significantly decreased from 0.31/d (Fig. 5 a) in series 1 to 0.10/d (Fig. 6 a) in series 3. Fig. 6 compares the net reaction rate k of amine in four cases of reactors in series 1 and 3 with two different concentration of inoculum. For reactors with 500 mg/l amine (Fig. 7 b and c), the reactors in series 1 which have higher inoculum concentration have higher net reaction rate k (0.78/d) than the reactors that have the same concentration of amine in series 3 (0.54/d). Therefore, high inoculum concentration in reactors has a positive effect on waste amine degradation rate. The net reaction rate for 125 mg/l reactors in series 1 is as high as 1.08/d, indicating the degradation rate could be very fast if proper condition is maintained. A efficient treatment plant is always designed and operated in such a way that high biomass concentration is maintained, implying that high reaction rates can always be maintained in an amine degrading plant.

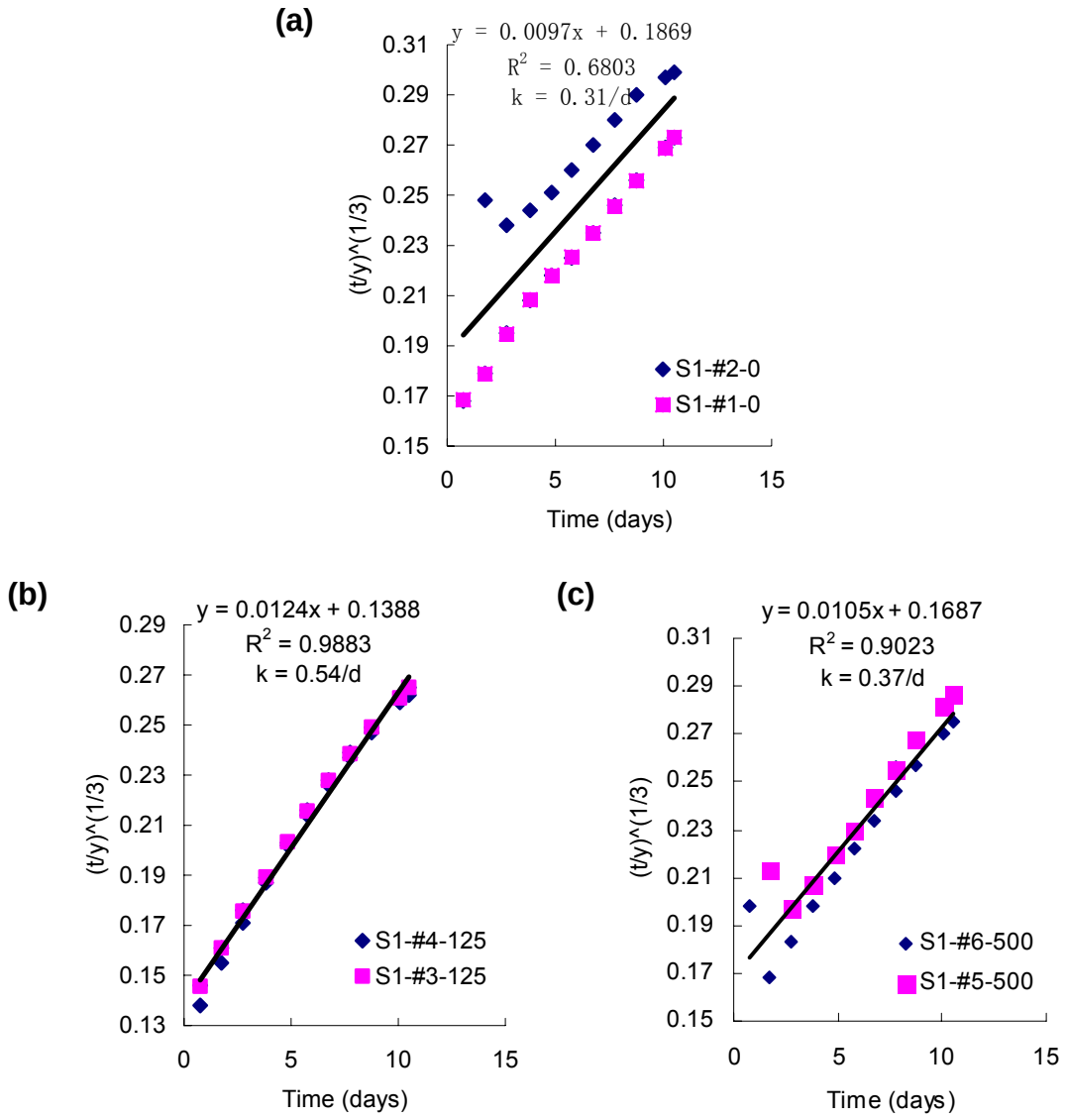

Fig. 5. ***First order BOD removal rate k and linearization of data for reactors with 3 amine levels in BOD test series 1.***

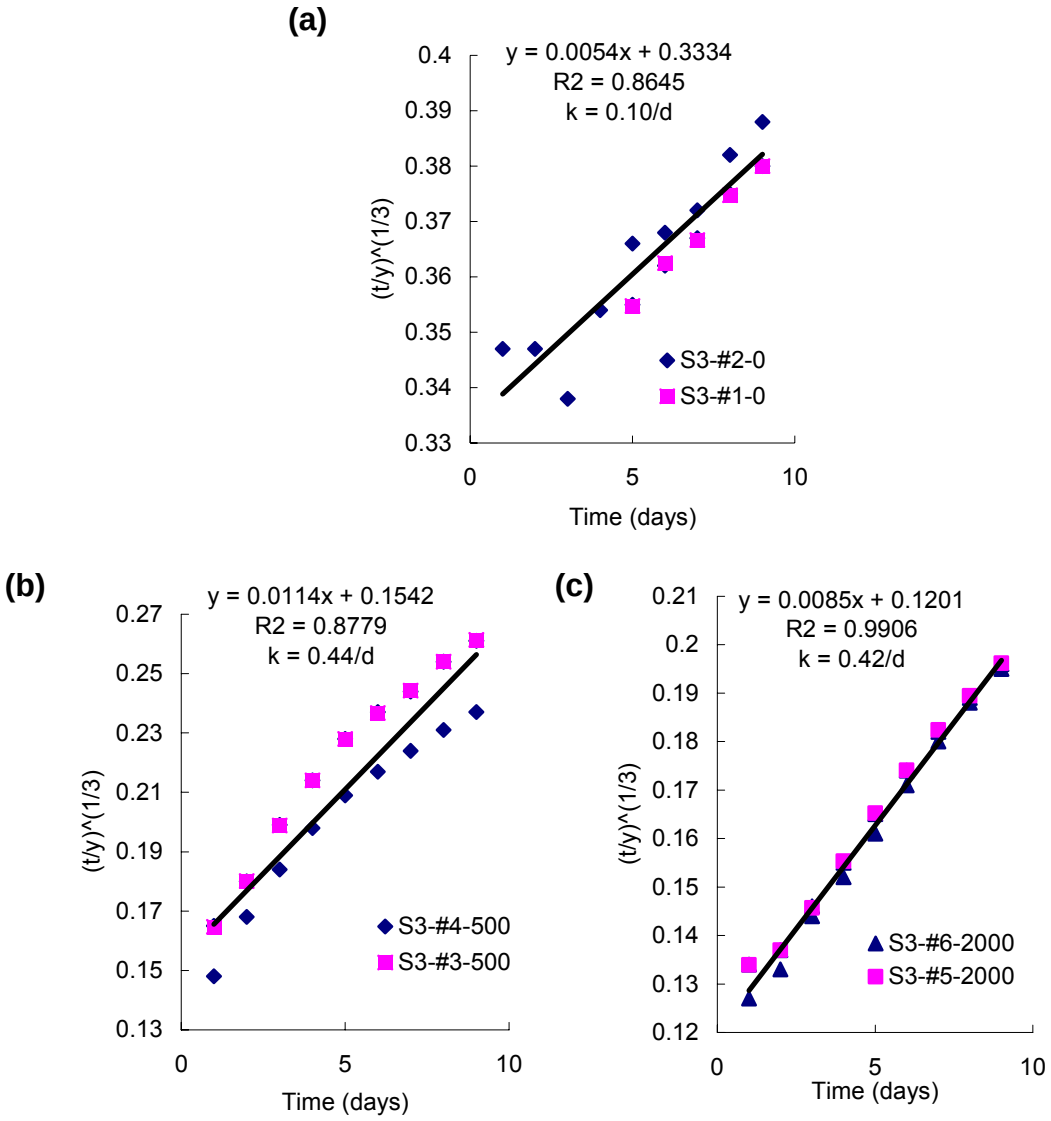

Fig. 6. ***First order BOD removal rate k and linearization of data for reactors with 3 amine levels in BOD test series 3.***

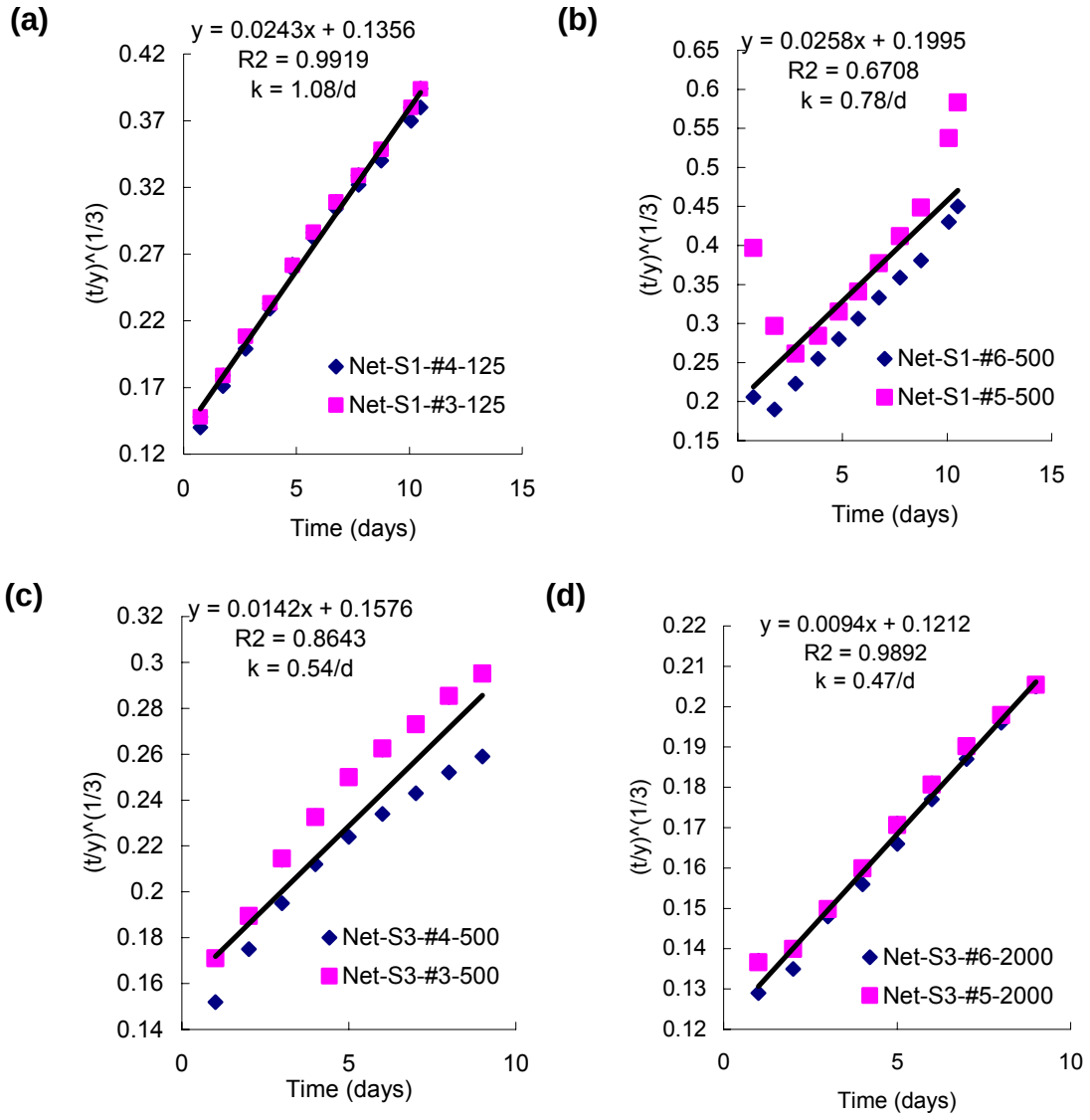

Fig. 7. ***Net reaction rate k and linearization of data for reactors in BOD test series 1 and 3.***

3.2 Syringe experiment results and discussion

Biogas produced is presented first, followed by COD measurement and removal, CH_4 and biogas production presentation and discussion. Then measurements results of NH_4-N, alkalinity and pH are analyzed.

3.2.1 Syringe experiment results

Biogas volumes were measured by reading scales on the syringe reactors everyday from the first day of the experiment to the 21st day, when all of the reactors in anaerobic and micro-aerobic cases stop producing biogas (Fig. 8 to Fig. 10). All 28 syringe batch reactors testing 9 different conditions (Table 4) produced CH_4, CO_2 and N_2

Fig. 8 shows the biogas production of three anaerobic cases. Anaerobic-125 and anaerobic-500 cases produced average about 17 ml and 19 ml biogas respectively, significantly more biogas than the anaerobic-0 case of 13 ml, indicating that waste amine can be degraded in anaerobic condition without any oxygen. Inhibition in anaerobic-500 case probably significantly influenced its gas production and hence not significantly larger than the anaerobic-125 case.

The three figures, Fig. 8, Fig. 9 and Fig. 10 show that waste amine in anaerobic, micro-aerobic and aerobic reactors have different degradation approaches. Reactors under anaerobic conditions have the highest degradation rate, finishing biogas producing in about 150 hours. The gas producing in the micro-aerobic cases can be seen to be divided into two stages. From the beginning to about the 158th hour is the first stage. The three micro-aerobic cases produced almost the same amount of biogas (15 ml). In the second stage from 158th hour on, the micro-aerobic-500 case produce more biogas than the125 case and the 0 amine cases produced no significant gas. The 500 case produced more biogas than the125 and the 0 amine cases in the aerobic syringe experiments also (Fig. 10). These experiments were, however, not fully aerobic as intended, as can be seen by the fact that some methane was produced (Table 9). Fresh air was added into syringe reactors whenever it was assumed needed. Sometimes the oxygen in the reactors apparently had been already depleted and the reactors were already in the anaerobic conditions before fresh air was added in.

There was a remarkable delay in gas production in micro-aerobic-500 case (Fig. 9), and the same phenomenon is observed in all 3 aerobic-0 cases (see Fig. 10). The delay can be explained by the aerobic digestion in the beginning because of the 10 ml air in the headspace of the reactors. In aerobic digestion, the gas volume that is consumed (O_2) is more than that produced (CO_2 etc.) (Metcalf & Eddy, Inc.).

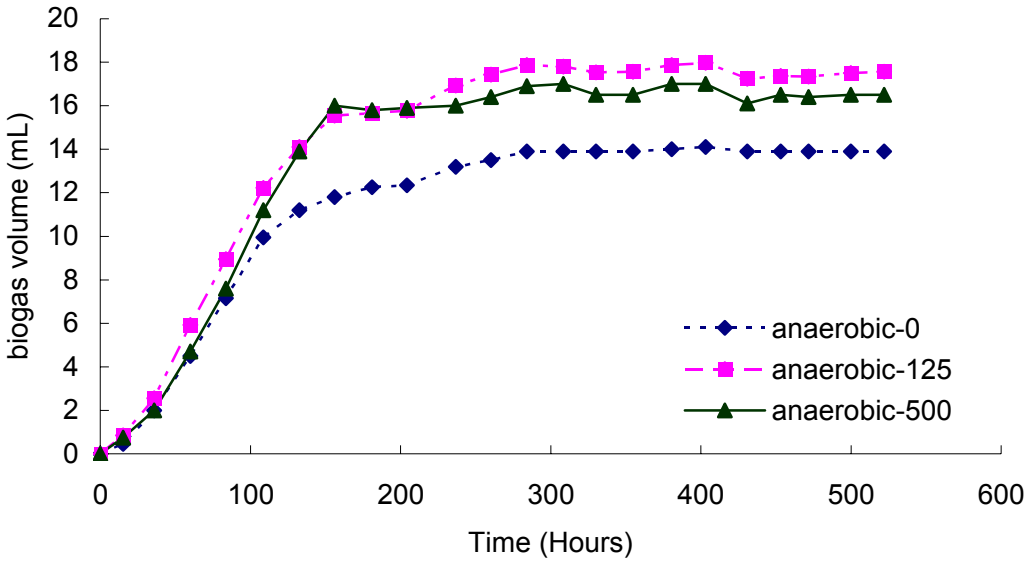

Fig. 8. ***Biogas production in anaerobic reactors showing accumulated biogas produced as average of parallels for 3 amine levels, as a function of time.***

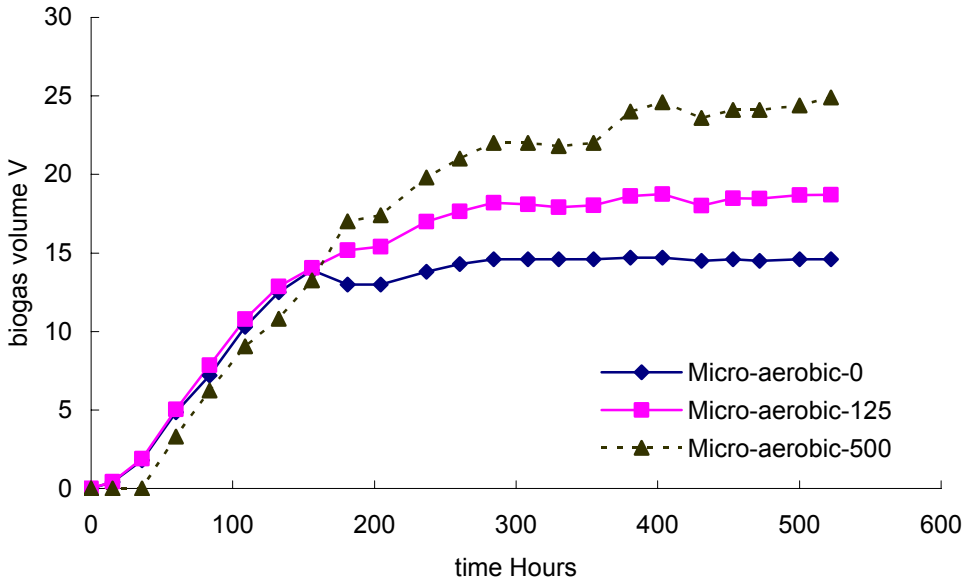

Fig. 9. ***Biogas production in micro-aerobic reactors showing accumulated biogas produced as average of parallels for 3 amine levels, as a function of time.***

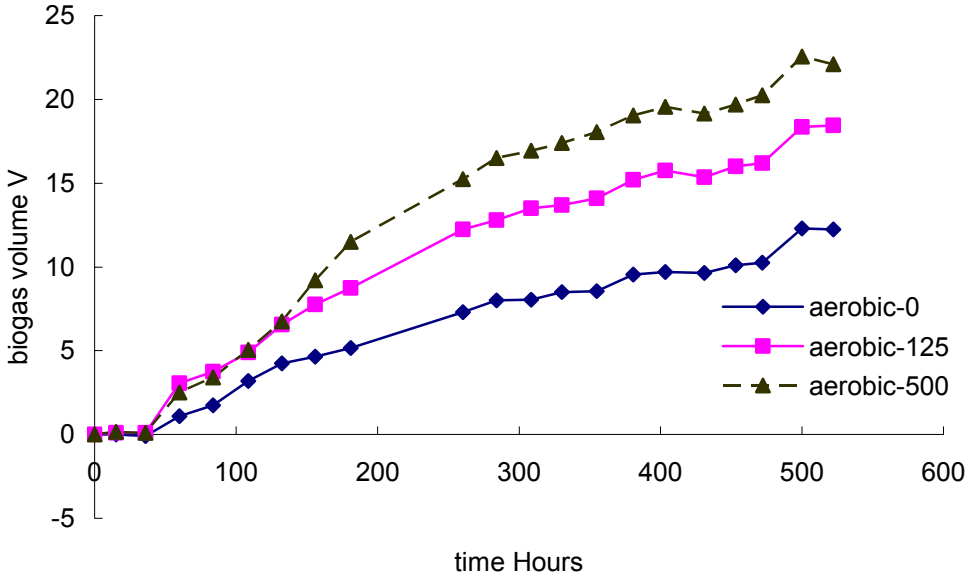

Fig. 10. ***Biogas production in aerobic reactors showing accumulated biogas produced as average of parallels for 3 amine levels, as a function of time.***

3.2.2 COD measurement and removal efficiency

COD removal efficiencies of waste amine in syringe reactors are presented in Fig. 12 and Table 8. Waste amines are highly degradable in the reactors under anaerobic, micro-aerobic and aerobic conditions, especially in the reactors under the micro-aerobic conditions (micro-aerobic-125 and micro-aerobic-500), removing almost 100 % of waste amine COD. This fact reflects that existence of small amount of air in the beginning of the reactions has a positive effect on amine degradation. The anaerobic-500 and aerobic-500 reactors also have high COD remove efficiencies, removing more than 90 % of amine COD.

The COD for MEA calculated based on pure theoretical formula (170 mg/l for anaerobic-125 and micro-aerobic-125) (Table 8) is less than the MEA COD based on measurement of raw MEA (115 mg/l for anaerobic-125 and micro-aerobic-125). The low COD in the second case could represent the already degraded COD of MEA in waste amine. The relation between amine concentrations and COD measurements based on measurement of B0, B1 and B2 (See B0, B1 and B2 description in Table 6) is non-proportional (i.e. 125/500 ≠ 430/820), it could be caused by non-uniformity in mixing of amine inoculum sludge.

Their COD degradation status in reactors of anaerobic-125 and micro-aerobic-125 cases are shown in Fig. 11 (a) and (b), reflecting the reduced COD level in the reactor liquid phases. COD for anaerobic-125 case quickly decreased from 1470 mg/l to 900 mg/l in the 21st days and relatively slowly decreased to 585 mg/l after 68th days. The micro-aerobic-125 case has a very similar COD curve where the COD first drops down to 889 mg/l in the 21st day and finally come to 688 mg/l. The anaerobic-125 case has higher total COD removal in 68 days.

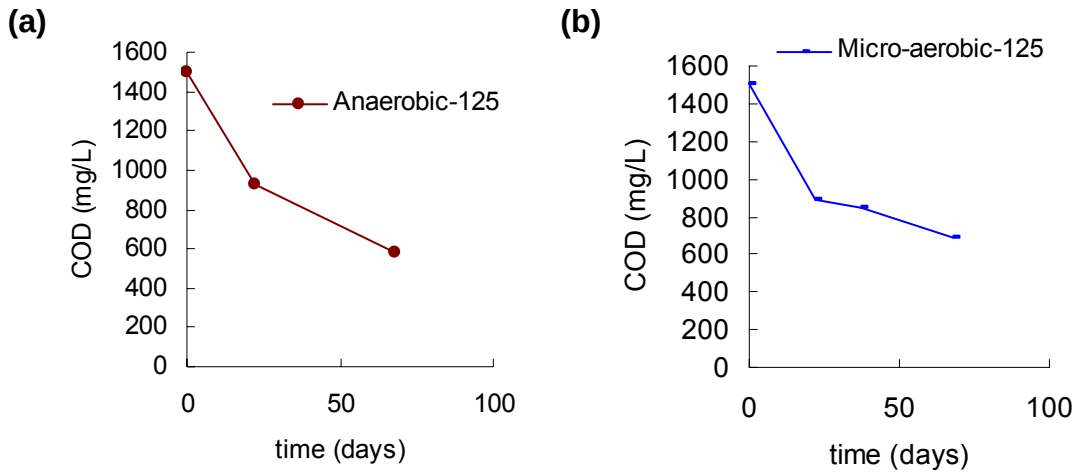

Fig. 11. ***COD degradation in anaerobic-125 and micro-anaerobic-125 reactors showing COD degradation as average of parallels, as a function of time.***

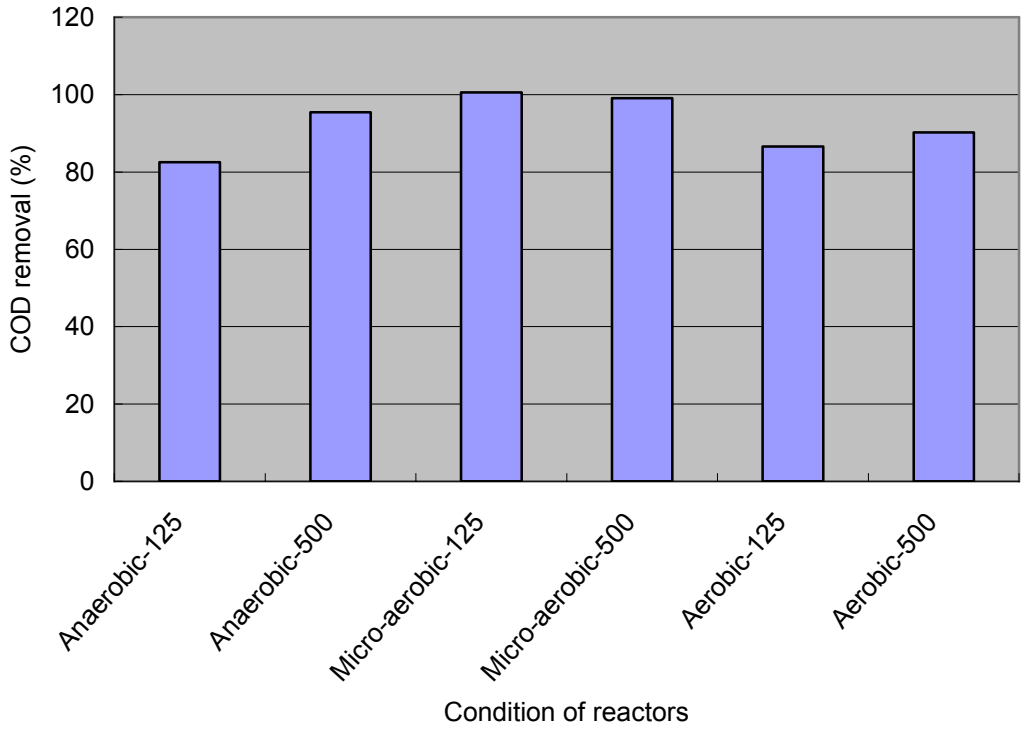

Fig. 12. ***COD removal by the 21st day of the syringe experiment in reactors under 6 different conditions.***

Table 8

Measured and theoretical COD results and related calculations.

	Anaerobic_125	Anaerobic_500	Micro-aerobic_125	Micro-aerobic-500	Aerobic-125	Aerobic-500
MEA concentration(mg/l)	≈125	≈500	≈125	≈500	≈125	≈500
Theoretical MEA COD (mg/l)	179	719	179	719	--	--
Final net CH_4 COD (mg/l)	290	205	292	627	--	--
MEA COD based on measurement of raw MEA (mg/l)	115	465	115	465	--	--
Net amine COD removed based on measurement of reactor COD in the end of reaction (mg/l) [g]	355	782.5	432.5	812.5	372.5	740
Net original amine COD based on measurement of B0, B1 and B2 COD (mg/l) [h]	430	820	430	820	430	820
COD remove efficiency [i]	82.6 %	95.4 %	100.6 %	99.1 %	86.6 %	90.2 %

[g, h] The over-predicted part of COD could came from the inoculum instead of amine itself due to non uniform mixing.

[i] COD remove efficiencies were calculated by Net amine COD removed / Net original amine COD.

3.2.3 CH_4 and biogas production

Fig. 13 shows the net biogas productions of two anaerobic cases and two micro-aerobic cases. Anaerobic-125 and micro-aerobic-125 cases produce almost the same volume of net biogas, about 4 ml in 21 days. Their biogas yield is 0.37 L biogas/g amine waste and 0.410 L biogas/g amine waste, respectively. Their CH_4 yields are the same; 0.23 L CH_4/g amine waste (Table 9). The micro-aerobic-500 case produced the most volume of biogas from amine waste. However, its biogas yields (0.26 L biogas/g amine waste) and CH_4 yield (0.13 L CH_4/g amine waste) are much lower than the anaerobic-125 and micro-aerobic-125 cases.

It is possible to build anaerobic treatment plants in industry to treat waste amine and meet its discharge limits meanwhile recycle useful energy from biogas produced. Reactors of anaerobic-125 and micro-aerobic-125 cases gave the highest CH_4 yield and they both have quick degradation rates (See section 3.2.1), however, micro-aerobic-125 case has higher COD removal. Hence, a bio-treatment process, i.e. an aeration tank and followed by an anaerobic treatment process, could be the best design to treat waste amine and recycle CH_4, a single reactor operating under micro-aerobic or anaerobic conditions could also be feasible after further study.

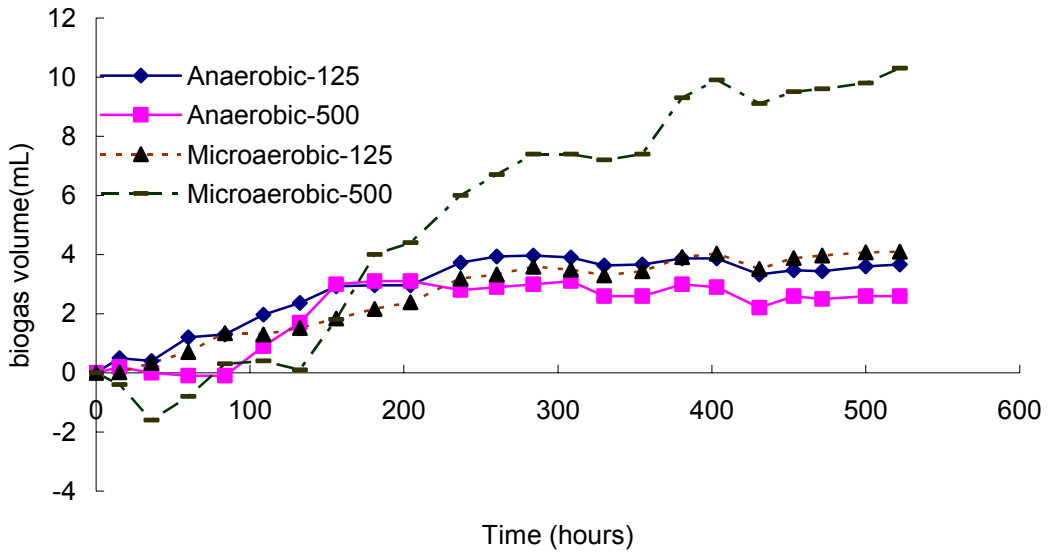

Fig. 13. ***Net biogas production showing net biogas production as average of parallels in two anaerobic and two micro-aerobic cases with 2 amine levels of each case, as a function of time.***

Table 9

Biogas yield and CH_4 yield of syringe experiments based on biogas composition, biogas measurement and waste amine measurement.

	Anaerobic_ 125	Anaerobic_ 500	Micro-aerobic_125	Micro-aerobic-500
Biogas yield (L biogas/g waste amine)	0.367	0.065	0.41	0.26
CH_4 yield (L CH_4/g amine waste)	0.23	0.04	0.23	0.13

Table 10

COD measurements for raw MEA, B0, B1 and B2.

Samples	MEA	B0	B1	B2
COD (mg/l)	232400	1050	1480	1870

3.2.4 Biogas Composition of syringe experiment

All reactors in 9 cases produced CH_4, CO_2 and N_2, even including the 3 aerobic cases (Table 9). The N_2 percentages are unexpectedly high in all reactors. N_2 in the biogas of this project could come from the N_2 present in the air that was added in the reactors (Hence not truly biogas). Denitrification of NO_3-N present in the waste amine is another source but it can only account for a small percentage and can be neglected (Table 9). The percentage of N_2 from other sources are of the same magnitude level in all reactors, around 20 %, even in the reactors with 0 mg/l amine, indicating that this part of N_2 in the biogas could from the denitrification of NO_3-N present in the inoculum or that there is some systematic error in sample handling and analysis. More analysis of NO_3-N and NH_4-N should be carried out in future work to find the N balance.

In anaerobic and micro-aerobic cases, CH_4 is 48 % to 63 % of the biogas while CO_2 is just about 10 % of the biogas. The percentages of CO_2 in the biogas from the syringe reactors in this project are lower than typical in other anaerobic processes (normally > 20 %). Part of the CO_2 could have dissolved in the liquid due to the relatively higher pH conditions caused by higher alkalinity in the present study.

Table 11

Gas compositions of the gas samples collected on the 21st day of the syringe experiment and probable N_2 sources.

Case	CH_4 (%)	CO_2 (%)	N_2 total (%)	N_2 from air (%)	N_2 from NO_3-N denitrification (%)	N_2 from other source (%)
Anaerobic-0	61.14	9.95	28.86	0.00	0.00	28.86
Anaerobic-125	63.16	10.83	25.89	0.00	0.21	25.68
Anaerobic-500	63.06	9.55	27.34	0.00	0.91	26.43
Microaerobic-0	55.49	9.86	34.60	11.42	0.00	23.18
Microaerobic-125	56.87	10.19	32.91	9.21	0.17	23.53
Microaerobic-500	48.65	10.30	41.02	22.38	0.43	18.21
Aerobic-0	9.41	10.40	79.96	58.67	0.00	21.29
Aerobic-125	11.98	11.01	76.87	53.28	0.06	23.53
Aerobic-500	17.72	11.30	70.87	50.54	0.22	20.11

3.2.5 NH_4-N, Alkalinity and pH

The results of alkalinity analyses (shown in Table 12) reveal that adding of waste amine caused significant increasing of alkalinity. The alkalinity of samples from B0 1450 mg/l increased to 1597 mg/l and 1752 mg/l in B1 and B2, respectively.

The initial pH for all 125 mg/l and 500 mg/l cases are higher than the favorable pH range for anaerobic and aerobic digestion (6.5 - 7.8) due to the waste amine (Table 12), but pH gradually decreased while the reaction was going. pH values in the 9th day are significantly decreased compare with the beginning even in the reactors with 500 mg/l amine. Inhibition caused by pH is probably significant in the beginning of the reaction but will disappear along with the degradation reactions. NH_4-N, as an amine degradation product, accumulated in all reactors (Table 13). The three anaerobic cases accumulated the most quantity of NH_4-N while three aerobic cases accumulated the least amount of NH_4-N (comparing reactors with same amine concentration of 9 cases). Part of accumulated NH_4-N could have been consumed by nitrification in the aerobic reactors.

Table 12
Alkalinity measurements for 3 samples which represent samples taken from B0, B1 and B2.

Samples	B0	B1	B2
Alkalinity (mg $CaCO_3$/L)	1450 (7A)[d]	1597 (5D)[e]	1752 (3B)[f]

[d, e, f] 7A, 5D and 3B are syringe reactors with 0 mg/l, 125 mg/l and 500 mg/l amine concentrations, and they represent samples taken from B0, B1 and B2

Table 13

Results of NH_4-N and pH measurements showing initial and 21st day's NH_4-N measurement data as well as initial and 9th day's pH measurement data.

Reactors	Amine concentration(mg/l)	Initial NH_4-N (mg/l)	NH_4-N at 21th day (mg/l)	NH_4-N changed/accumulated (mg/l)	Initial pH	pH at 9th day
Anaerobic-0	0	177.6	251.6	74	7.68	7.34
Anaerobic-125	≈125	187.8	279	91.2	7.99	7.79
Anaerobic-500	≈500	267	342.4	75.4	8.47	8
Micro-aerobic-0	0	177.6	256.6	79	7.68	7.73
Micro-aerobic-125	≈125	187.8	269.2	81.4	7.99	7.4
Micro-aerobic-500	≈500	267	326.8	59.8	8.47	8.06
aerobic-0	0	177.6	239.6	62	7.68	--
aerobic-125	≈125	187.8	264.6	76.8	7.99	--
aerobic-500	≈500	267	323.6	56.6	8.47	--

4 CONCLUSIONS

In this project we demonstrate that waste amine can be successfully degraded under anaerobic, micro-aerobic and aerobic conditions. It is possible to remove all of the waste amine in the solution if operate under proper conditions.

For the removal of waste amine under aerobic conditions, amines are degraded by first order reaction and quick reaction rate can be obtained under proper condition. Amine, nor the ammonia produced, are inhibitory to amine degradation, even at the high concentrations of amine solution tested (2000 mg/l), and can be degraded if pH is maintained neutral.

High biomass concentrations of the mix-source inoculum and the degradation components in waste amine have positive effects on amine degradation. Since both of these two factors, especially the inoculum contains certain amount of NO_x^-, it appears that the NO_x^- can have positive effects on the amine degradation. However, more research is needed to prove it.

Both of anaerobic and micro-aerobic reactors have high COD removal from waste amine and obtain high CH_4 yields. The reaction rates are fast and most of initial waste amines are degraded in about 1 week. Small amounts of air in the beginning stage of the anaerobic digestion have positive effects on COD removal.

In general, biodegradation of waste amine can become a practical technique. Compact, high rate biological treatment plants can be built to treat waste amine at low cost and meanwhile recover energy as CH_4.

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APPENDIX

Telemark University College
Faculty of Technology

Master Thesis - F4299
Thesis Proposal

Thesis title: Biological amine degradation

Responsible professor (from HiT): Professor Rune Bakke

Assistant advisor(s): Hans Aksel Haugen (Tel-Tek), Carlos Dinamarca and Deshai Botheju

Detailed text:
Study degradation of used amines from a CO2 capture process in lab batch reactors. Mix the used amine solution with an active culture from wastewater treatment, soil and anaerobic digestion and measure biogas generation and other relevant parameters to estimate degradation extent and rates under aerobic, micro-aerobic and anaerobic conditions.

Background for the thesis:
Amines are used as adsorbent in CO2 capture plants. Amines are degraded when used and becomes a waste product. Biological degradation to CH4 and/or CO2 of partly degraded amines from CO2 capture plants is a possible solution to this waste problem. There is not much experience and data available for such solutions.

Category of students (and special demands, eg. subject combinations): EET student with relevant lab experience.

Practical conditions (work place, work form, equipment, etc.): The work will mainly be carried out at TUC.

Document name (use initials, eg. fh1.rtf): YL-Thesis.rtf

Date for proposal: 1. Feb. 2008

Yuan Li

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