Performance of H_2O_2-assisted submerged aerated biofilter for landfill leachate treatment

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ABSTRACT

The aim of this study is to find a possible way of using Fenton's reaction for assisting biological process treating landfill leachate in a single-reactor. Considering the availability of iron in leachate, only H_2O_2 is added into a submerged aerated fix-bed (SAFB) reactor. COD and color removal was investigated subject to changes in distance from injection point to reactor, HRT and COD loading rate. The best COD and color removal was obtained at injection distance of 120 cm and HRT of 18 h. H_2O_2 assisted-SAFB reactor was able to remove 83% of COD and 76 % of color at loading rate of 2.5 kg COD/m^3/d. BOD_5/COD ratio of effluent was found to increase by 1.7 to 1.9 times. Microscopic observation of microorganisms trophically higher than bacteria in attached sludge reveals the insignificant effect of H_2O_2 on microbial populations.

KEYWORDS

H_2O_2-assisted, aerated biofilter, landfill leachate, SAFB

INTRODUCTION

Municipal landfill leachate is characterized by high concentrations of organic, nutrient as well as inorganic constituents. 'Old' leachate is dominated by refractory organic compounds and characterized by a low BOD/COD ratio.This characteristic restricts the directly biological treatment for organic removal from leachate. Accordingly, chemical oxidation with ozone or Fenton's reagent (H_2O_2/Fe^{2+}) has been intensively applied to improve the removal of the refractory organics by transforming them into biodegradable substances (Wang *et al.,* 2003). However, the common way is to carry out chemical and biological stages in separate reactors.

It is well known that obligate and facultative aerobes possess peroxidises which decompose H_2O_2 to H_2O and O_2. Therefore, if Fenton's reaction is used in combination with biological process, excessive H_2O_2 can be decomposed easily and the oxygen produced is beneficial to aerobic microorganisms. H_2O_2 was used by Houtmeyers *et al.* (1977) as oxygen source in activated sludge process, resulting in a temporary decrease of COD reduction and a marked decrease of some filamentous organisms and bacterial groups such as enterobacteria, coliforms, and streptococci. Tusseau-Vuillemin *et al.* (2006) confirmed the harmlessness of H_2O_2 addition in a COD-degradation respirometric system. As the sole source of oxygen, toxic effect of H_2O_2 in the concentration range of 100 - 200 mg/L was observed to extend the lag phase of bacteria of the genera *Pseudomonas* and *Rhodococcus* by two to three days (Tarasov *et al.*, 2004).

Considering the fact that ferrous is available in leachate, addition of H_2O_2 would create a Fenton's reaction that converts refractory into biodegradable organic compounds. These organic products, together with oxygen from the decomposition of excessive H_2O_2, are readily for aerobic microorganisms. Using an attached-growth reactor would avoid the influence of H_2O_2 on the biomass settling properties. This study was carried out to check the possibility of a treatment system in which an aerobic biofilter is assisted with H_2O_2 addition and treatability on landfill leachate.

MATERIALS AND METHODS

1. Leachate

Leachate used for study was from the Thuy Phuong Sanitary Landfill in Thua Thien Hue province. Here both leachate generated from closed and active sites was collected into a mixing tank, and then treated by a pond system. Leachate samples were taken monthly at the mixing tank from February to August 2012. Some characteristics of leachate are shown in table 1.

2. Experimental set-up

The reactor used is a submerged aerated fixed bed (SAFB) type, as shown in figure 1, with a liquid volume of 5 L. Commercial wool (Jinpai, China), prepared in net type, was used as biomass carrier. For starting-up, the reactor was seeded with activated sludge originated from wastewater treatment system of Hue Beer Company and long-term cultured in laboratory. The start-up phase lasted 29 days by feeding reactor with a synthetic medium. Dilute leachate was introduced to the reactor during next 12 days for acclimation of the system.

Table 1. Characteristics of landfill leachate

Parameter	**Unit**	**Mean ± SD** (n=6)
pH	-	8.14 ± 0.12
Temperature	^{0}C	33.8 ± 1.7
TSS	mg/L	112 ± 8.1
BOD_5	mg/L	663 ± 91
COD	mg/L	3631± 400
BOD_5/COD	-	0.182 ± 0.009
Total Fe	mg/L	30.06 ± 1.99

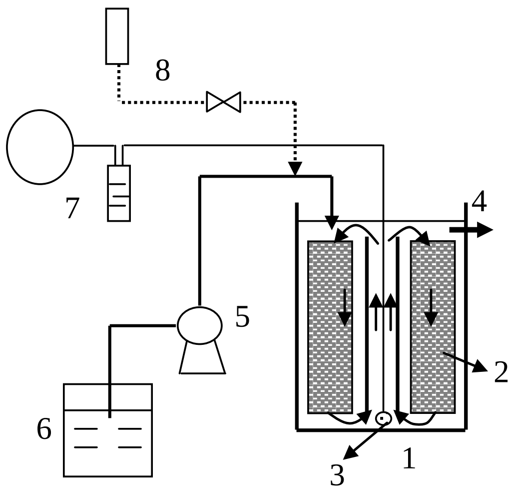


Figure 1. Scheme of H_2O_2-SAFB reactor system.

1 - SAFB reactor2 - Wool biomass carrier
3 - Air diffuser 4 - Effluent
5 - Peristaltic pump6 - Influent tank
7 - Air blower and flow meter
8 - H_2O_2 container andflow controller

In the main part of study, effects of H_2O_2 addition, H_2O_2 injection method, HRT on reactor performance were evaluated. Then, treatment performance under different organic loading rates (OLR) was investigated. Other experimental conditions included dilute leachate to COD = 250 mg/L, aeration rate = 1.0 L/min. In-line injection of H_2O_2 was done by using a hypodermic needle.

3. Sampling and sample analysis

Raw leachate was collected from landfill monthly and stored in refrigerator for preparing influent. Sample of raw leachate was analyzed for such parameters as shown in table 1. Influent and effluent samples of reactor were taken daily or every two days and analyzed for COD, BOD_5 and color. TSS, COD, BOD_5 and total iron were determined following the standard methods by APHA, AWWA and WEF (1999). Color intensity was measured spectrophotometrically. The existence of microorganisms in attached sludge was examined using a microscopy (OLYMPUS CX31, Japan). Samples were fixed with 4% formaldehyde solution before observation.

RESULTS AND DISCUSSION

1. Effects of H_2O_2 addition and injection method on treatment performance

COD and color removal data during four experimental runs without and with addition of H_2O_2 are summarized in table 2. The addition of H_2O_2 did not affect the COD removal but enhanced the color removal. The partial oxidation of humus-like compounds which are responsible for leachate color by Fenton's reagent explains for the better color removal. Fenton's reaction has positive effect on COD removal, while H_2O_2 possess inhibition to microorganisms when directly added to reactor. The balance between two opposite effects resulted in the unchanged COD removal.

Considering method of H_2O_2 addition, in-line injection seems to be better than direct injection into reactor. It is supposed that Fenton's reaction occurs in the pipe, and then the influent into reactor contains degradable organic compounds and low level of excessive H_2O_2 which is decomposed further to water and oxygen. If injection point is far from reactor, the decomposition of excessive H_2O_2 may occur in pipe and oxygen is no longer available for bio-oxidation. That is why a slight reduction of COD removal was observed when H_2O_2 was injected at 220 cm before reactor.

Table 2. Changes in COD and color removal with addition of H_2O_2

	COD removal, %	Color removal, %
Without H_2O_2 injection	83.5 ± 1.6	64.8 ± 2.3
With H_2O_2 injection, directly to reactor	83.4 ± 1.9	70.6 ± 3.0
With H_2O_2 injection, 120 cm before reactor	86.1 ± 1.3	72.7 ± 2.4
With H_2O_2 injection, 220 cm before reactor	85.0 ± 1.3	71.6 ± 2.2

(In all cells: mean ± standard deviation, n = 8)

2. Effect of HRT on treatment performance

In an H_2O_2-assisted biological system, long HRT may be adverse to microorganisms due to the longer exposure to H_2O_2. Three experimental runs with changes in HRT from 12 h to 6 h and then to 18 h were carried out to check the influence of HRT. As shown in figure 2, the longer HRT is, the better COD and color removal is.

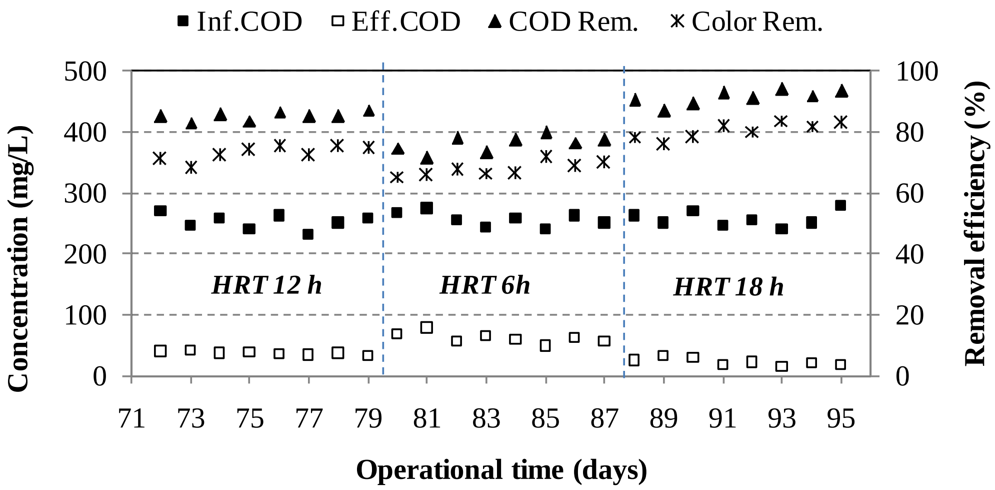


Figure 2. COD and color removal at different HRT.

3. Performance of reactor under different organic loading rates

By reducing the dilution of leachate, influent COD concentrations were increased stepwise from around 750 to 2250 mg/L, corresponding to OLRs from 1.0 to 3.0 kg $COD/m^3/d$. Removal efficiencies of COD, BOD_5 and color through H_2O_2-assisted SAFB system under increasing OLRs are presented in figure 3 and summarized in table 3. As usual, treatment efficiency decreased with increase in OLR. Increase in OLR seemed to influence BOD_5 removal more than COD removal, indicating the lesser Fenton's oxidation occurred at higher organic concentration.

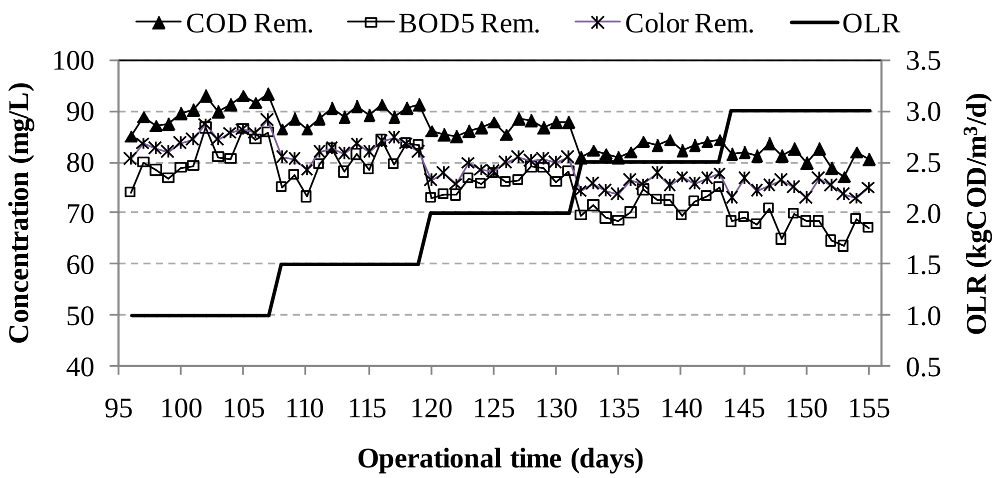


Figure 3. Changes in organic and color removal at different OLR.

Table 3. Summary of organic and color removal at different OLR

OLR, kg COD/m^3/d	**1.0**	**1.5**	**2.0**	**2.5**	**3.0**
COD removal, %	90.1 ± 2.6	89.3 ± 1.7	86.8 ± 1.2	82.8 ± 1.4	81.1 ± 1.8
BOD_5 removal, %	81.0 ± 4.0	79.8 ± 3.5	76.3 ± 2.1	71.6 ± 2.2	67.7 ± 2.2
Color removal, %	84.6 ± 2.3	82.2 ± 1.7	79.1 ± 1.7	75.9 ± 1.3	74.8 ± 1.4

(In all cells: mean ± standard deviation, n = 8)

At OLR of 2.5 kg COD/m^3/d, the treatment system resulted in an effluent with COD and BOD_5 values meeting the national discharge standard for landfill leachate (class B1, TCVN 25:2009/BTNMT).

Figure 4 shows the change in BOD_5/COD ratio of influent and effluent during five runs. It is clear that biodegradability of leachate was improved through the H_2O_2-assisted SAFB system. However, the improvement level decreased with increase in OLR. Effluent from the H_2O_2-assisted SAFB system would be suitable for further biological pond treatment.

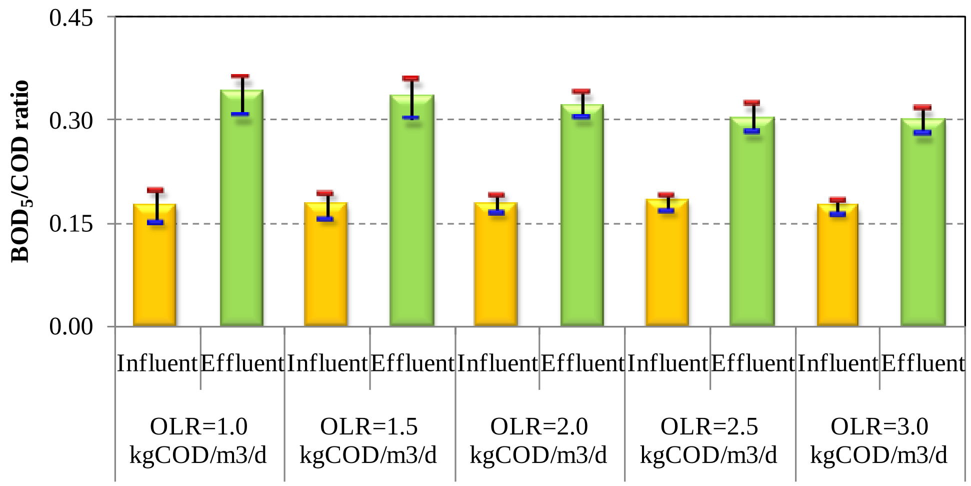
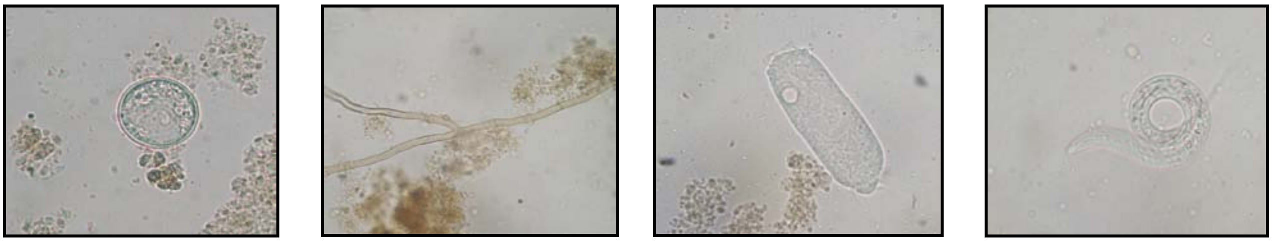


Figure 4. BOD_5/COD ratios of influent and effluent at different OLR.

4. Characteristics of biomass

Sludge production rate was calculated as 0.66 g-SS/d or 0.45 g-VSS/d, and biomass yield was estimated to be 0.13 g-SS/g-COD removed or 0.09 g-VSS/g-COD removed during 167 days of operation. These values are much lower than typical values of activated sludge (0.5 g-VSS/g-BOD removed) or biofilm systems (0.3-0.5 g TSS/g-COD removed) (di Iaconi *et al.*, 2005). Microscopic observation revealed the existence of many groups of microorganisms trophically higher than bacteria, such as algae, protozoa, fungi, rotifers (see some of them in figure 5). All of these kinds of microorganisms were well known to exist in a food chain (Gabriel, 2005). This indicates that H_2O_2 application did not destroy the food chain which drives the biological process in SAFB reactor.



Chlorophyta *Fungi* *Rotifers* *Nematoda*

Figure 5. Some microorganisms trophically higher than bacteria observed in sludge samples.

CONCLUSIONS AND PERSPECTIVES

It is feasible to use H_2O_2 for assisting the biological process in a submerged aerated fixed bed reactor for treating landfill leachate. Using in-line injection of H_2O_2 at a concentration of 200 mg/L, organic and color removal from and biodegradability of leachate was improved. Addition of H_2O_2 did not affect the food chain created by microorganisms attached on biomass carrier. The H_2O_2-assisted SAFB system developed could result in effluent meeting discharge standard for leachate (at OLR of 2.5 kg COD/m^3/d) or being suitable for further conventional biological treatment (at higher OLR). Application of higher H_2O_2 concentrations for leachate containing higher COD concentrations should be further investigated.

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Contents

1. Background
2. Experimental description
3. Results and discussions
4. Conclusions and perspectives

1. Background

- Rationale of study problem
  - Difficulty in biological treatment of landfill leachate due to refractory organic compounds
  - Separate pre-treatment by chemical oxidation with O_3 or Fenton's reagent (H_2O_2/Fe^{2+}) is normal practice
  - Question: is it possible to apply H_2O_2 assistance in a bioreactor?

1. Background

- Advantages of direct application:
  - Only a single reactor
  - Excessive H_2O_2 can be decomposed by enzymes available in bioreactor
  - O_2 from H_2O_2 decomposition can supply for bacteria
- Problems to be solved:
  - What is a safe level of H_2O_2?
  - How to add H_2O_2 to bioreactor?
  - What kind of bioreactor is suitable?
  - What are operational conditions for reactor?
  - etc.

$\Rightarrow$ ***Our study idea and approach***

1. Background

- **Experience from other studies:**
  - Houtmeyers *et al.* (1977) used H_2O_2 as oxygen source in activated sludge process
  - Tusseau-Vuillemin *et al.* (2006) confirmed the harmlessness of H_2O_2 addition in a COD-degradation respirometric system
  - Tarasov *et al.* (2004) determined 100 - 200 mg/L of H_2O_2 possessing toxic effect on bacteria of the genera *Pseudomonas* and *Rhodococcus* when used as the sole source of oxygen

1. Background

- **Landfill and leachate in Hue city**
  - MSW collected: ~ 200 tons/day
  - Before 2005: only landfilling (at Thuy Phuong Sanitary Landfill)
  - Since 2005: landfilling (~30%) and recycling+composting+incinerating (~70%) alternatively
  - Landfill: site 1 (1998~2007), site 2 (2007~present)
  - Leachate: mixing 'old' leachate from site 1 and 'young' leachate from site 2; treatment by a pond system

1. Background

Landfill sites and leachate treatment in Hue

2. Experimental description

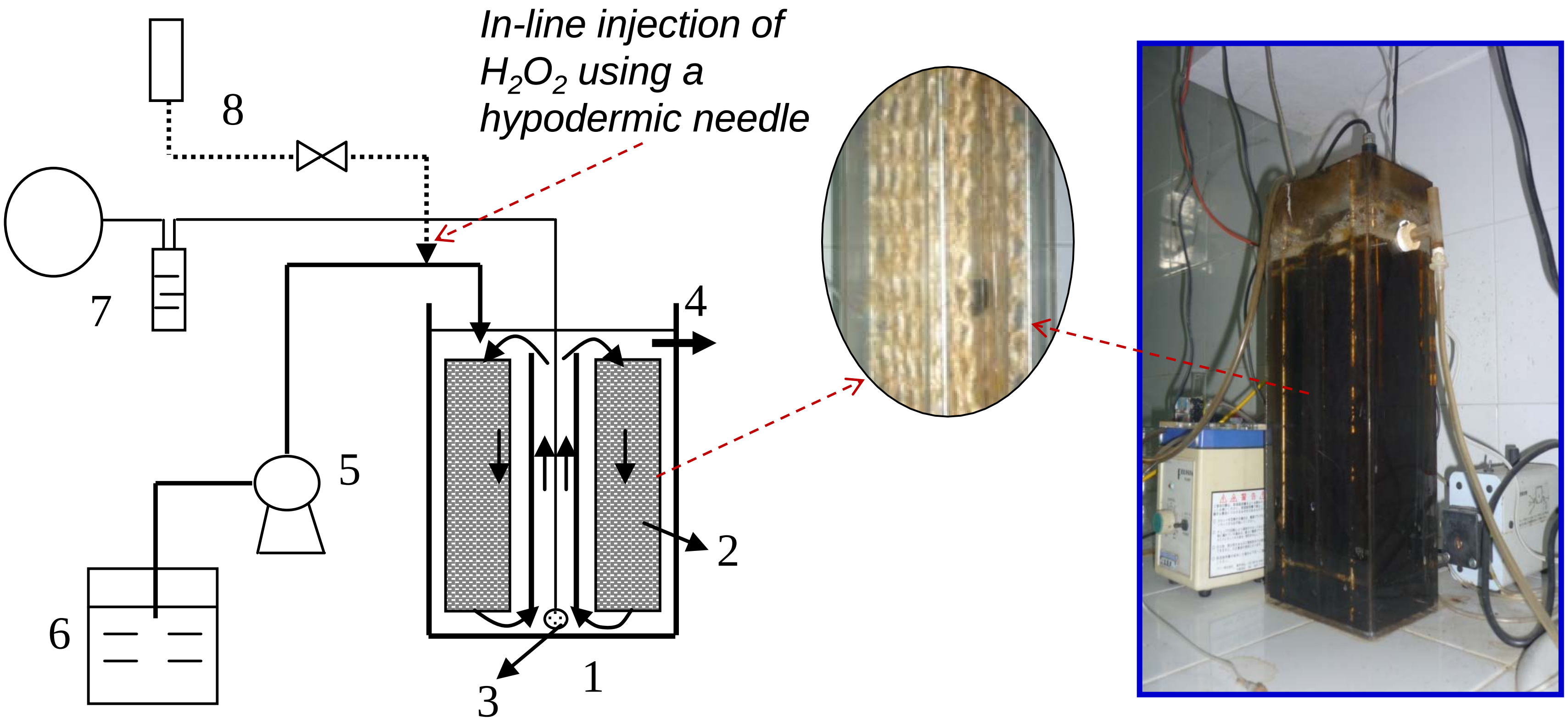


Figure 1. Scheme of H_2O_2-SAFB reactor system.

1 - SAFB reactor 2 - Wool biomass carrier
3 - Air diffuser 4 - Effluent
5 - Peristaltic pump 6 - Influent tank
7 - Air blower and flow meter 8 - H_2O_2 container andflow controller

2. Experimental description

Table 1. Characteristics of leachate from Thuy Phuong landfill

Parameters	Unit	Mean ± STDEV (n=6)
pH	-	8,14 ± 0,12
Temperature	^{0}C	33,8 ± 1,7
TSS	mg/L	112 ± 8,1
BOD_5	mg/L	663 ± 91
COD	mg/L	3631 ± 400
BOD_5/COD ratio	-	0,18 ± 0,01
Total iron	mg/L	30,1 ± 1,9

2. Experimental description

- Experimental phases
  - Reactor start-up *(not included in this presentation)*
  - Reactor acclimation to leachate *(not included in this presentation)*
  - Main investigation *(in this presentation)*
    - Effects of H_2O_2 addition and injection method
    - Effect of HRT
    - Treatment performance under different OLR
- Experimental conditions:
  - Dilute leachate to various COD conc.
  - Aeration rate = 1.0 L/min
  - Applied H_2O_2 conc. = 200 mg/L
  - pH ~ 6.0
- Evaluation: COD, BOD5, color removals; microorganisms populations of sludge

3. Results and discussions

3.1. Effects of H_2O_2 addition and injection method

Table 2. Changes in COD and color removal with addition of H_2O_2

	COD removal, %	Color removal, %
Without H_2O_2 injection	83.5 ± 1.6	64.8 ± 2.3
With H_2O_2 injection, directly to reactor	83.4 ± 1.9	70.6 ± 3.0
With H_2O_2 injection, 120 cm before reactor	86.1 ± 1.3	72.7 ± 2.4
With H_2O_2 injection, 220 cm before reactor	85.0 ± 1.3	71.6 ± 2.2

- Addition of H_2O_2 did not affect COD removal but enhanced color removal
- In-line injection better than direct injection into reactor
- Distance of injection point slightly influenced treatment

3. Results and discussions

3.2. Effect of HRT on treatment performance

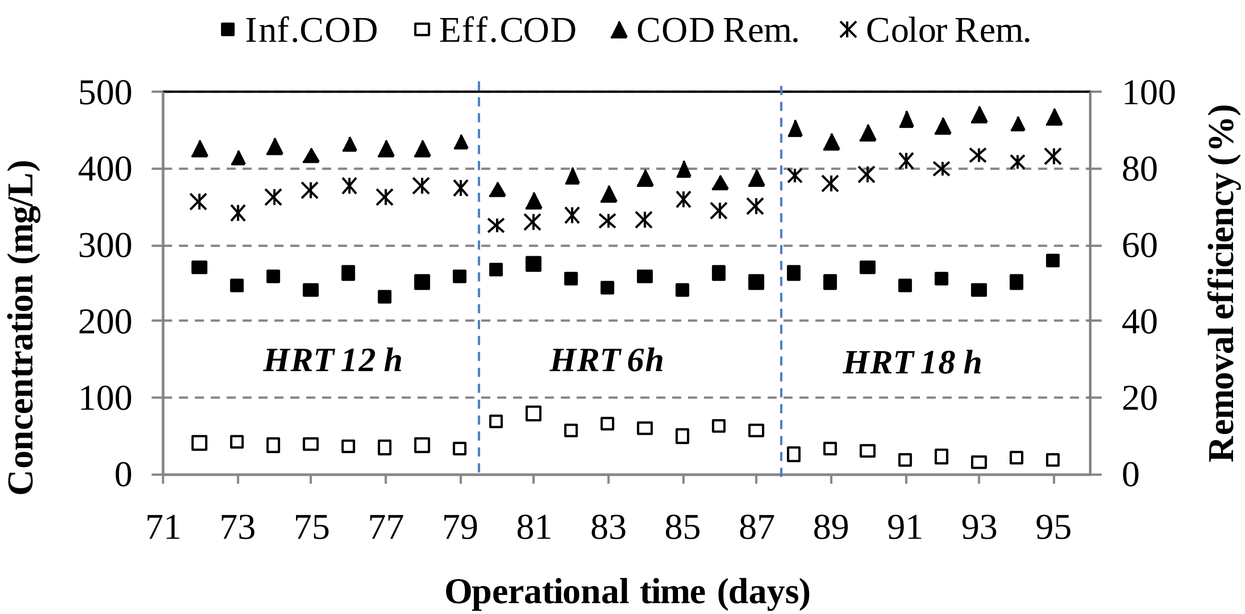


Figure 2. COD and color removal at different HRT.

- Longer HRT, better COD and color removal
  → long HRT may be adverse to microorganisms due to the longer exposure to H_2O_2

3. Results and discussions

3.3. Performance of reactor under different OLRs

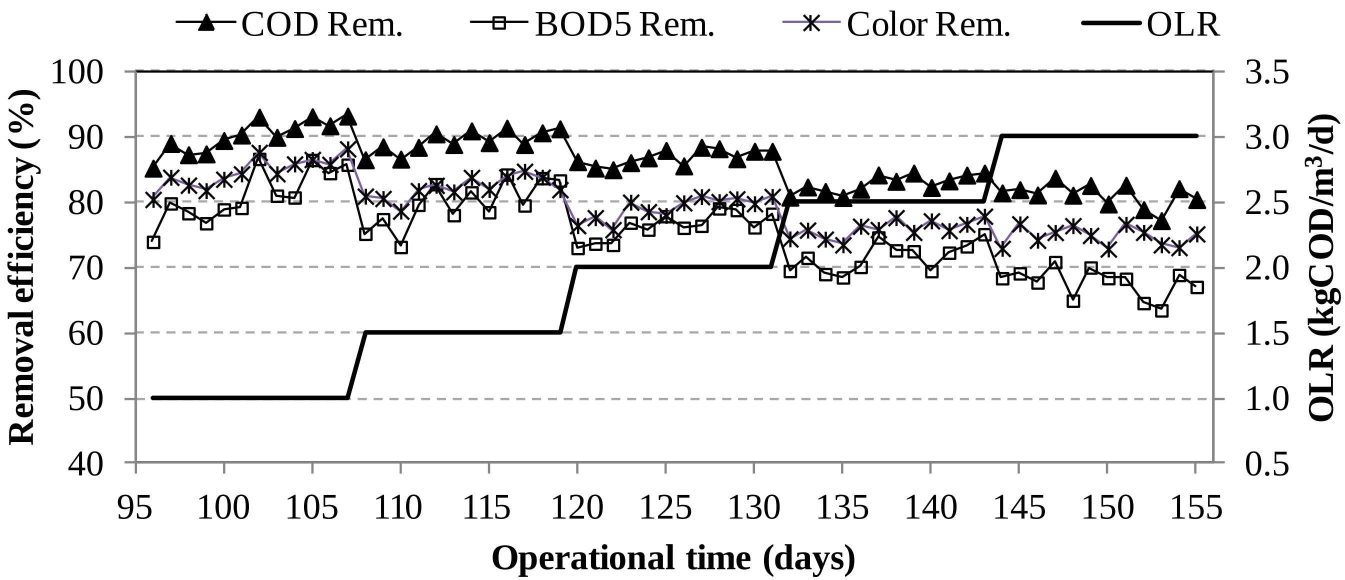
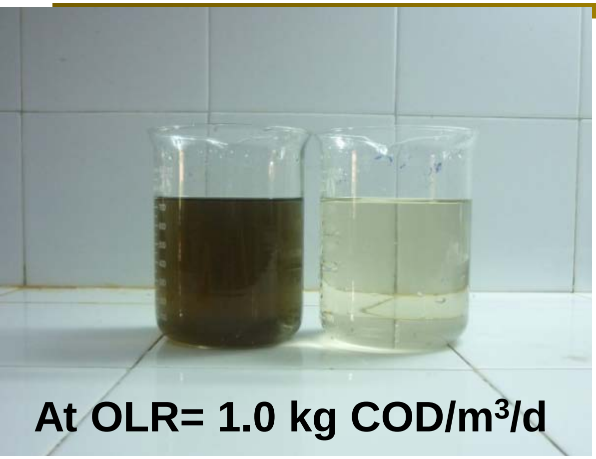
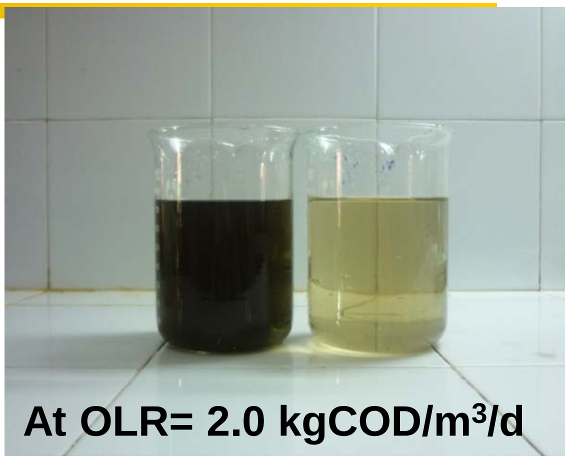


Figure 3. Changes in organic and color removal at different OLRs.

- As usual, treatment efficiency decreased with increase in OLR.

3. Results and discussions





Leachate color removal at increasing OLRs

3. Results and discussions

Table 3. Summary of organic and color removal at different OLRs

OLR, kg COD/m^3/d	**1.0**	**1.5**	**2.0**	**2.5**	**3.0**
COD removal, %	90.1 ± 2.6	89.3 ± 1.7	86.8 ± 1.2	82.8 ± 1.4	81.1 ± 1.8
BOD_5 removal, %	81.0 ± 4.0	79.8 ± 3.5	76.3 ± 2.1	71.6 ± 2.2	67.7 ± 2.2
Color removal, %	84.6 ± 2.3	82.2 ± 1.7	79.1 ± 1.7	75.9 ± 1.3	74.8 ± 1.4

- Increase in OLR influenced BOD_5 removal more than COD → lesser Fenton's oxidation occurred at higher organic concentration.
- At 2.5 kg COD/m^3/d, effluent COD (326.4±27.3 mg/L) and BOD_5 (98.5±7.9 mg/L) meet the national discharge standard for landfill leachate (COD ≤ 400 mg/L,BOD_5≤ 100 mg/L, respectively of class B1, TCVN 25:2009/BTNMT)

3. Results and discussions

- Leachate biodegradability improved through H_2O_2-assisted SAFB system

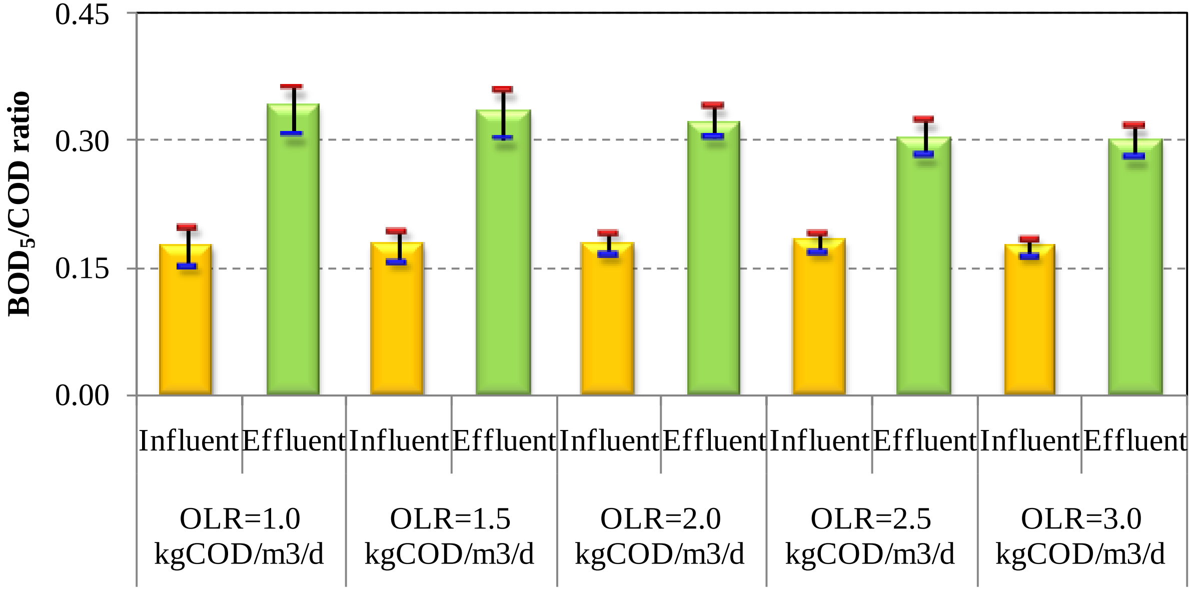


Figure 4. BOD_5/COD ratios of influent and effluent at different OLR.

- BOD_5/COD ratio of effluent = 1.7-1.9 times of influent
- Improvement level decreased with increase in OLR

3. Results and discussions

3.4. Characteristics of biomass

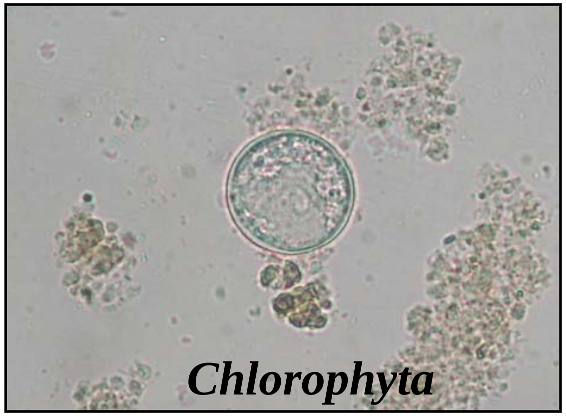
- Sludge production rate = 0.66 g-SS/d or 0.45 g-VSS/d

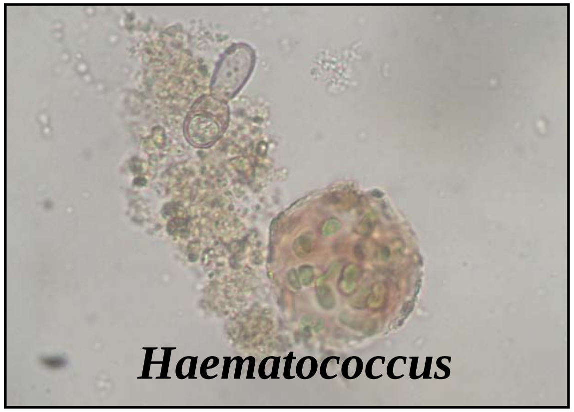
  Biomass yield = 0.13 g-SS/g-CODrem. or 0.09 g-VSS/g-CODrem.

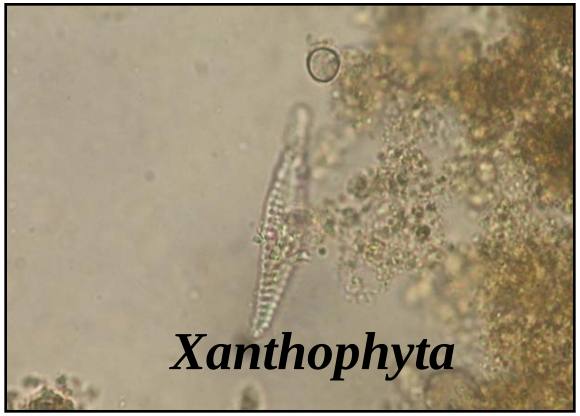
  →much lower than typical values of activated sludge or biofilm systems (0.3-0.5 g TSS/g-COD removed).

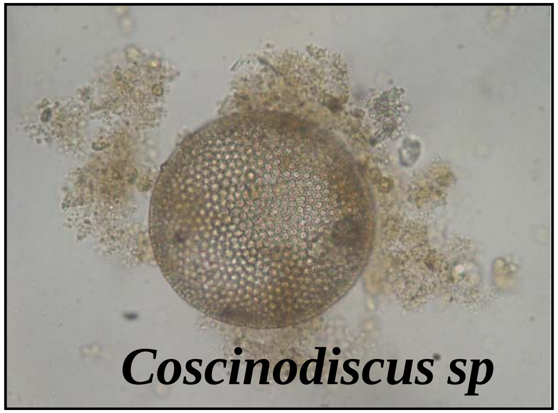
- Microscopic observation revealed the existence of microorganisms trophically higher than bacteria
- H_2O_2 application did not destroy food chain which drives the attached-growth biological process

3. Results and discussions



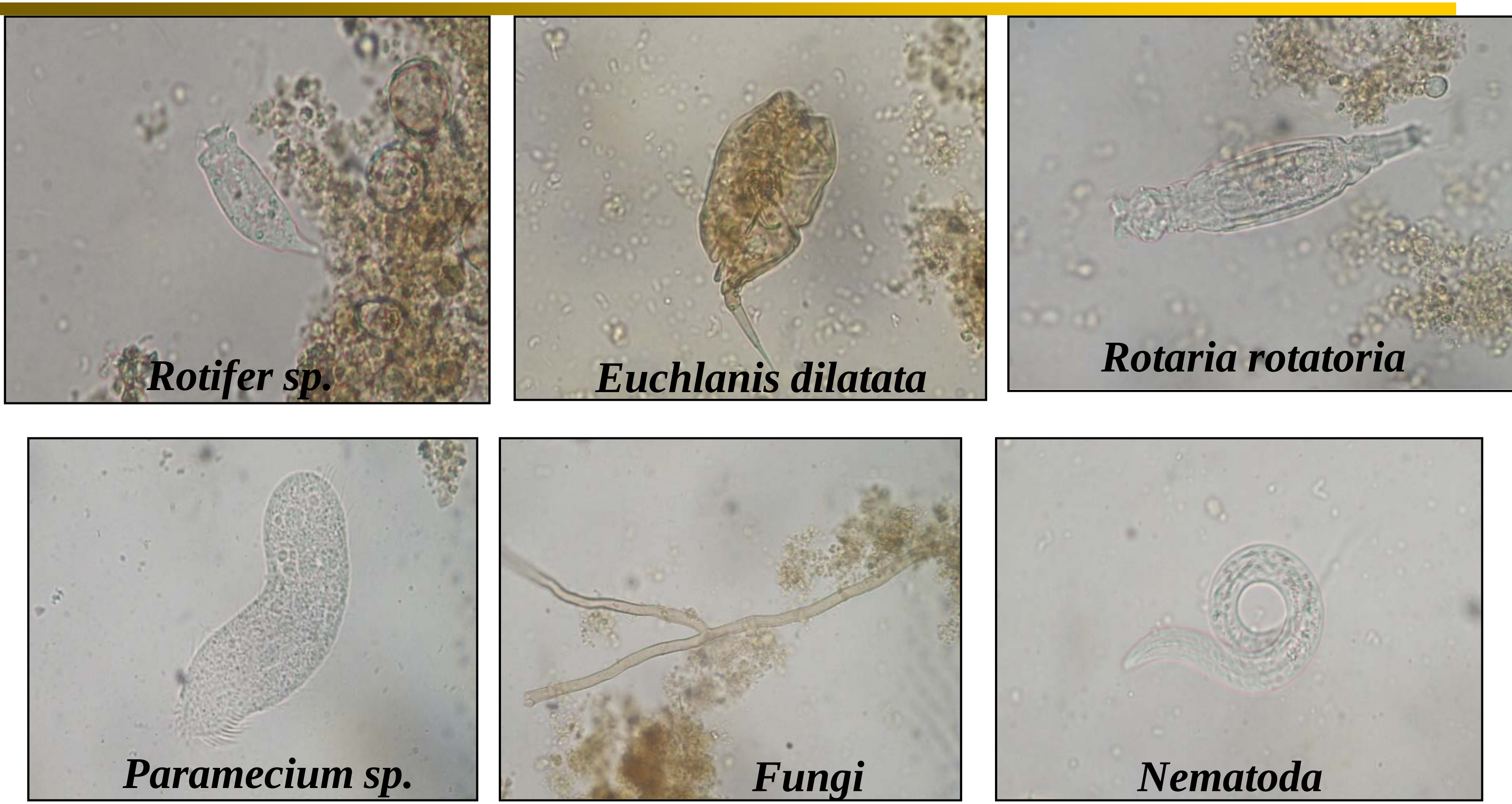






Examples of microalgae observed in attached sludge (microscopy, x40)

3. Results and discussions



Examples of other microorganisms observed in attached sludge

(microscopy, x40)

4. Conclusions and perspectives

- It is feasible to use H_2O_2 for assisting the biological process in SAFB reactor for treating landfill leachate.
- Using in-line injection of H_2O_2 organic and color removal from and biodegradability of leachate was improved.
- Addition of H_2O_2 did not affect the food chain created by various microorganisms attached on biomass carrier.
- H_2O_2-assisted SAFB system could result in effluent meeting discharge standard (at 2.5 kg COD/m^3/d) or being suitable for further biological treatment (at higher OLR).
- Application of higher H_2O_2 concentrations for leachate containing higher COD concentrations should be further investigated.
- Treatment at larger scale should be investigated.


Thank you very much for your kind attention