Original Article

Biodegradability Improvement of Composting Leachate by Sulfate Radical-Advanced Oxidation Process followed by Aerobic and Anaerobic Treatment

Mohsen Sadani, Mohammad Mehdi Amin[1,2], Mohammad Amin Karami[3], Fahime Teimouri[4]

Department of Environmental Health Engineering, School of Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran, [1]Environment Research Center, Research Institute for Primordial Prevention of Non-Communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran, [2]Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran, [3]Department of Environmental Health Engineering, School of Health, Lorestan University of Medical Sciences, Khoramabad, Iran, [4]Department of Environmental Health Engineering, School of Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

Abstract

Aims: Comparing to strong traditional oxidation, the persulfate and sulfate radicals was characterized by relatively low cost and easy application. The present study aimed to investigate the performance of sulfate radical-based advanced oxidation process (SR-AOP) for pretreatment of compost leachate in order to improvement of its biodegradability. **Materials and Methods:** The sulfate radicals was used for pretreatment of compost leachate in the batch reactor followed by aerobic and anaerobic biological reactors. **Results:** the results of combination of SR-AOP with biological treatment showed that BOD5/COD ratio was increase. However, the different trend was observed in COD removal by sequencing batch reactor (SBR) and anaerobic sequencing batch reactor (ASBR). Comparing to SR-AOP with ASBR, the SR-AOP with SBR substantially improved final COD removal efficiency up to 70%. Although pretreatment of compost leachate with the SR-AOP clearly improved the BOD5/COD ratio of entering raw leachate into ASBR (from 0.4 to 0.65), but, the COD removal efficiency was ranging between 25% and 27%. **Conclusion:** Based on the results, it can be concluded that the BOD5/COD ratio cannot be suggested as biodegradability improvement indicator without considerations of changing of substrate nature during pretreatment.

Keyword: Aerobic sequencing batch reactor, composting leachate, sequencing batch reactor, sulfate radical

Introduction

Leachate is a relatively complex mixture and contain many compounds and its composition depends on temporal and spatial conditions.[1] Landfill leachate produced by Leachate is a relatively complex mixture and contain many compounds and its composition depends on temporal and spatial conditions. through the waste. On the other hands, the processes such as materials grinding and biological degradation can produced the leachate. Landfilled and composted leachate could contain hazardous contaminants, derived from different processes in human life; thus, the importance of its effective treatment and disposal is obvious.[2] Efficient treatment of leachate produced in composting plants is critical.[3,4] On the other hand, compost has higher organic matter content than urban solid waste; thus, the leachate produced from a compost site contains higher COD. A number of common leachate treatment techniques include recycling and combined treatment with municipal wastewater treatment, aerobic and anaerobic biological treatment processes that are used for young leachate treatment when the BOD_5/COD ratio is high, and chemical methods such as adsorption, ozonation, and advanced oxidation process (AOP).[5,6]

Recently, increasing attention has been paid to sulfate radical due to its high efficiency for oxidation of organic

Access this article online	
Quick Response Code:	Website: www.ijehe.org
	DOI: 10.4103/ijehe.ijehe_11_17

Address for correspondence: Dr. Mohammad Mehdi Amin, Environment Research Center, Research Institute for Primordial Prevention of Non-Communicable disease, Isfahan University of Medical Sciences, Isfahan, Iran.
E-mail: amin@hlth.mui.ac.ir

How to cite this article: Sadani M, Amin MM, Karami MA, Teimouri F. Biodegradability improvement of composting leachate by sulfate radical-advanced oxidation process followed by aerobic and anaerobic treatment. Int J Env Health Eng 2019;8:1.

Received: 09-12-2017, **Accepted:** 29-04-2018

pollutants. Persulfate (S_2O_8) is a strong oxidant with an oxidation potential (E_o) of 2.01 V, compaired to O_3 (2.07 V).[7] Furthermore, S_2O_8 has an ability to produce sulfate radicals that is an strong oxidant (E_o = 2.7 V) with low cost and strong oxidative capacity.[8]

Persulfate can be activated by heat, metal, elevated pH, or ultraviolet (UV) irradiation to initiate sulfate radical-based AOPs (SR-AOPs).[9] UV irradiation and metals can also activate H_2O_2 to initiate OH radicals and photocatalysts.[10,11] SR-AOPs are widely used activate some persistent organic pollutants and toxic chemicals such as 2,4-dinitrotoluene,[12] refractory organic contaminants and ammonia in landfill leachate,[13] reactive red 198,[14] dichloro-diphenyl-trichloroethane,[15] bisphenol A and phosphate,[16] and sulfaclozine.[17]

Therefore, due to the complex composition and the presence of toxic substances in leachate, SR-AOP can be a promising treatment for composting leachate.[18] Chemical oxidation processes are generally more expensive than biological treatment and are limited by requirement of corrosion-resistant equipment and high operational costs. A great reduction in costs could be achieved by combining AOPs with biological treatment. For instance, combined UV/H_2O_2 and biological treatment has decreased BOD_5, COD and adsorbable organic halides concentrations below the standard.[19] If chemical oxidation and biological processes are designed and selected to complement each other, it is possible to achieve synergetic effects. In the case that effluent is first submitted to chemical oxidation to partially degrade organic compounds, it generates a higher biodegradable effluent with less amounts of toxic compounds that are easily assimilated by the biomass in the biological process.[20] Then, the cost and the environmental impact, associated to the oxidation processes, are substantially minimized. Anaerobic processes are the most cost-beneficial biological treatments. In some cases, anaerobic processes are the most efficient processes for toxic compounds removal and might be the logical choice for combination of biological and AOP treatments.[21] It is especially applicable for the treatment of composting leachate with high BOD and COD concentrations. Literature on composting leachate treatment is relatively limited; furthermore, there are no reports that show the use of SR-AOPs as a pretreatment for biological process. The objective of this study was to evaluate the performance of an SR-AOP as a pretreatment for composting leachate. It is assumed that SR-AOP as pretreatment can increase the BOD_5/COD ratio and improve the leachate COD removals efficiency in the downstream biological processes.

Experiments

Leachate samples were collected from a non-sealed pond of composting leachate, every 10 days in 20 L plastic containers. In overall, eight samples were collected in 3 months. The collected samples were immediately transported to laboratory and homogenized, and then stored in the refrigerator (4°C) with zero headspace. The dissolved sulfate was analyzed based on standard iodometric method.[22] Figure 1 shows different configurations of SR-AOP combined with biological treatment.

Aerobic sequencing batch reactor and sequencing batch reactor

The ASBR consisted of a cylindrical vessel working volume of 1.2 L [Figure 1, B]. An impeller at a speed rate of 20 rpm was used to mix the ASBR content. Temperature was maintained at 35.0°C ± 0.5°C inside the reactor by recirculation of water from a thermostatic bath. The reactor was operated with a sludge retention time (SRT) of 10 days and fed by a peristaltic pump. The flow rate was slowly increased during the first 15 days for microbial adaptations. Only during the first 15 days of adaptations, nutrient supplementation was provided with nitrogen and phosphorus to keep ratio of COD: N:P = 500:5:1 for the anaerobic treatment process. The leachate pH was corrected to 7 ± 0.5 (the pH of composting leachate was about 5.5). The pH maintanance was carried out with 1 M sodium hydroxide solution. The ASBR was fed with composting leachate at a feeding rate of 0.1 L/m for 10 min and then operated in the batch treatment mode. After the reaction period, the reactor mixture was allowed to settle for 60 min and the supernatant was withdrawn from the reactors. In each set, ASBR supernatant was injected to SBR [Figure 1, E]. The SBR was the same as ASBR in size and operation. In SBR, during the reactor feeding, the mixed liquor was kept fully aerated and the aeration proceeded for up to 6 h (reaction stage). Aeration was then shut down for 3 h, during which the sedimentation stage proceeded. After the sludge was fully settled, the supernatant was removed from the reactor (withdrawal of treated leachate) and no sludge was wasted. Then, a new sample of leachate was fed to the reactor by a peristaltic pump.

Sulfate radical-based advanced oxidation process treatment

In a typical run, 20 mL of leachate was dispensed to a 60 mL serum vial installed in a water bath shaker (Precision, Reciprocal

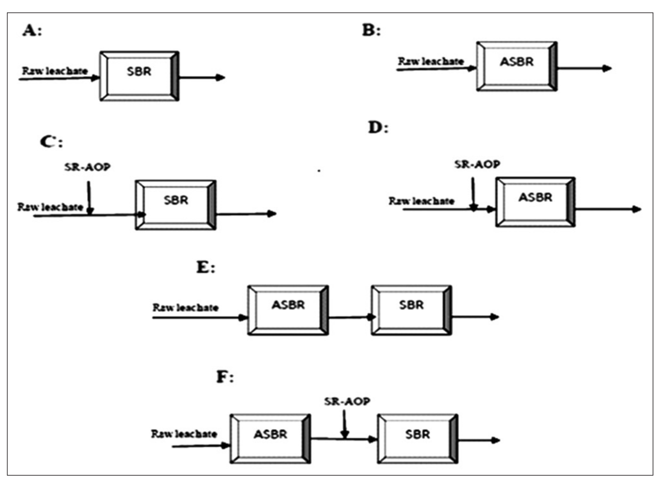

Figure 1: Different layout of combined sulfate radical-based advanced oxidation process with biological treatment

Shaking Bath Model 50, 401 Millcreek Road, Box 649. Marietta, Ohio 45750, USA) at a controlled temperature of 25°C, 40°C, or 60°C. Oxidation was initiated by addition of certain amount of sodium persulfate ($Na_2S_2O_8$, Fisher Scientific UK, Bishop Meadow Road, Loughborough, UK). The concentration of 500 mg/l sodium persulfate was selected for all tests on the basis of cost-effectiveness analysis.

Leachate pH was not adjusted in chemical oxidations by persulfate and all runs of oxidation process were performed with unchanged composting leachate pH (pH = 5.5). However, as mentioned previous stage, leachate pH was corrected to 7 ± 0.5 for biological processes.

In pretests, starch and iodine test was done as an indicator of redox titration in samples treated by persulfate and sulfate radicals. The results showed that in 2 h retention time, the persulfate was completely decomposed and oxidation processes were stopped; therefore, the reaction time 0.5, 1, and 2 h were chosen for oxidation time in all runs.

In this study, persulfate was activated only by heat without addition of chemicals. In different runs, oxidation experiments were performed in 25°C, 40°C, and 60°C.

Sulfate radical-based advanced oxidation process combined with biological treatment

In this stage, the combination of SR-AOP as pretreatment with ASBR and SBR was studied [Figure 1, C and D].

After each change or chemical treatment on leachate, biological reactors were operated for at least three hydraulic retention times (HRTs) duration (6, 10, and 12 h) and two SRT (5, 7, and 10 days) at steady state. Steady-state conditions were assumed to be attained when the soluble COD (sCOD) of reactor effluent were nearly constant for a few days. pH adjustment in raw leachate was applied before injection into biological reactors, and in some cases, it was performed after the SR-AOP. During each experiment, samples were withdrawn from the reactor to analyze initial and final sCOD and BOD_5.

Results

The properties of composting leachate samples used in this study are summarized in Table 1. The COD of composting leachate was significantly higher than typical landfill leachate (80,000–100,000 mg/L compared to 2000–10,000). Table 2 shows the BOD_5/COD ratio of raw leachate and effluents from different treatment setup [Figure 1, A to F] and its actual COD removal efficiency.

As shown in Table 2, the BOD_5/COD ratio of effluent of biological treatment including SBR and ASBR was relatively lower than raw leachate. On the other hand, by applying the combination of SR-AOP with biological treatment led to COD removal efficiency ascending [Table 2].

The variation of COD removal efficiency and also the improvement of biodegradability (BOD5/COD ratio) of composting leachate as function of persulfate dose are illustrated in Figure 2. It is notable that the percentage of COD removal was sharply increased initially rather than BOD_5/COD ratio by persulfate concentrations increases. In addition, effect of persulfate activation temperature on COD removal efficiency and BOD_5/COD ratio are summarized in Table 2.

Table 1: Characteristics of composting leachate samples

Parameter	Value
COD (mg/L)	86,000-92,000
BOD (mg/L)	41,200-47,000
pH	4.5-7
SO_4 (mg/L)	260-315
NH_4-N (mg/L)	55-70
Fe (mg/L)	88
Cr (mg/L)	50

Discussion

As illustrated in Table 2, the activation of persulfate in higher temperature causes higher COD removal efficiency and BOD_5/COD ratio. Higher temperatures could effectively activate persulfate to form more sulfate radicals, leading to higher COD removal efficiency Gao *et al*. reported that, at high temperatures, Fe^{2+} and Fe_3O_4 could effectively activate persulfate to form sulfate radicals and leading to high removal efficiency of nitric oxide.[23]

As shown in Table 2, comparing to the raw leachate, the BOD5/COD ratio of effluents of biological treatment including ASBR and SBR was relatively reduced. Thus, it is expected that the efficiency of the second biological unit is significantly reduced when the biodegradability is decreased. The BOD_5/COD ratio can be regarded as an index of biodegradability.

Some processes can improve the biodegradability such as ozonation, ultrasonic, and AOPs.[24] In some cases, ozone and ultrasonic suppose high initial costs. In this study, by comparing the price of persulfate with other oxidants used in advanced oxidation such as peroxide, it can conclude that

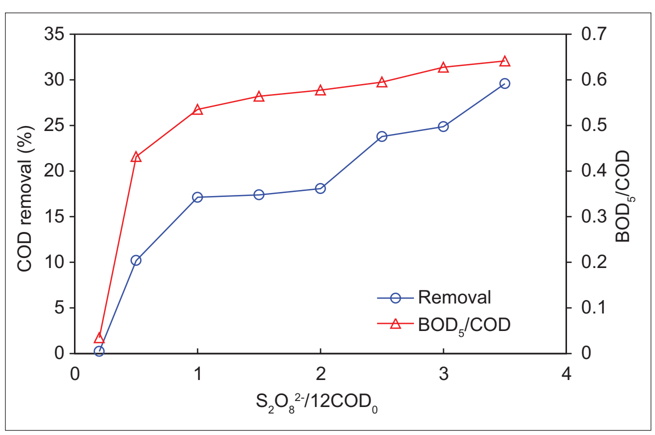

Figure 2: Effect of persulfate dose on COD removal and biodegradability improvement of compost leachate

Table 2: BOD_5/COD ratio and actual COD removal efficiency of A, B, C, D, E, and F configuration

Parameter	Operating temperature (°C)	Raw composting leachate	Reactor layout					
			A	B	C	D	E	F
BOD_5/COD	25	0.4	0.3	0.3	0.65	0.36	0.65	0.69
COD removal (%)		-	20%	9%	65%	22%	43%	96%
BOD_5/COD	40	0.4	0.34	0.36	0.65	0.43	0.61	0.65
COD removal (%)		-	25%	25%	65%	27%	45%	96%
BOD_5/COD	60	0.4	0.36	0.47	0.55	0.37	0.66	0.65
COD removal (%)		-	21%	25%	67%	22%	51%	98%

persulfate is a practical and cost-effective process to improve the biodegradability of composting leachate.

In this case, BOD_5/COD ratio was increased to 0.5, but COD removal was not acceptable to meet the environmental discharge standard. The results demonstrated that, although SR-AOP process at cost-effective concentrations increases the BOD_5/COD ratio, it cannot decrease the COD to acceptable level. After the ASBR treatment, the BOD_5/COD ratio decreased from 0.4 to 0.34, and even lower values about 0.3. This is a clear indication that most of the easy to degrade organics were removed during this step. Thus, the efficiency of subsequent SBR unit can be affected if the biodegradability is not corrected. These results are in consistent with the study results of Zaloum and Abbott, who demonstrated that after the anaerobic treatment, the BOD_5/COD ratio decreased significantly.[25] In these situations, it would be necessary to increase the retention time or HRT of the subsequent process to improve the COD removal. It is clear that this change causes higher costs for industrial purposes.

In reactor layout E, SBR used as a supplementary treatment after the ASBR. The results of Table 2 show that although the COD removal efficiency increased to 65%, still the effluent COD was approximately 32,000 mg/l and did not meet the effluent standard limits for environmental discharge. It is clear that the decreased biodegradability after the anaerobic treatment has adverse effect on COD removal efficiency of SBR in this arrangement. Uses of AOP or ozone to increase the BOD_5/COD ratio before biological reactor could be the other solution.

We used SR-AOP as a pretreatment process to increase biodegradability of the leachate. It is notable that the SR-AOP-SBR process [Figure 1, C] could improve COD removal efficiency more than the SR-AOP-ASBR [Figure 1, D]. Although pretreatment with the SR-AOP clearly improved the BOD_5/COD ratio of raw leachate before ASBR (from 0.4 to 0.65), the COD removal efficiency did not change significantly (from 25% to 27%). Results from previous studies have shown that persulfate contributed to increase sulfate concentration in the effluent of AOP as a result of the release of sulfate ions during these process ions.[26]

In this study, after SR-AOP, sulfate ions concentration increased significantly (280–560 mg/L); this increase can lead to an increase in sulfate-reducing bacteria (SRB) populations that rarely predominate in anaerobic reactors. Sulfate reducers and methanogens both live under strict anaerobic conditions with similar pH and temperature.[27] Kinetic studies have shown that sulfate reducers generally have higher maximum growth rates and higher affinity for substrates (i.e., lower half-saturation constants Ks) than methanogens.[28] Thus, sulfate reducers may dominate methanogens provided in this situation that sulfate do you mean resource? is not limited. Results from previous studies showed that the methanogens were the dominant organisms in COD removal convectional COD/SO_4 ratios for high strength leachate, and there is no advantage to the anaerobic treatment of landfill leachate by sulfate reduction pathway.[29]

Despite this, the COD removal efficiency improved significantly in SBR process pretreated with the SR-AOP. These results show that increases in sulfate ions concentration cant influence aerobic process significantly.

In the last arrangement [Figure 1, F], SR-AOP was applied after ASBR and before SBR. The results show that COD removal efficiency and BOD_5/COD ratio increased. One can hypothesize that an ASBR, applied before the SR-AOP, would remove the most biodegradable organic portion. SR-AOP promotes an increase in the biodegradability of the effluent. Thus, further aerobic treatment (SBR) may be used to complete the COD removal with reduced costs and highest efficiency. The effects persulfate activation by other methods such as high pH and iron sulfate and their effects on the efficiency of biological units can be investigated in subsequent studies.

Conclusion

The results of this study showed that pretreatment with the SR-AOP clearly improved the BOD_5/COD ratio of raw leachate before ASBR (from 0.4 to 0.65), but the removal efficiency of ASBR did not change significantly.

Acknowledgment

This study was funded by Isfahan University of Medical Sciences and was conducted in the Laboratory of School of Public Health, Isfahan University of Medical Sciences.

Financial support and sponsorship

Isfahan University of Medical Sciences, Isfahan, Iran, provided the financial support.

Conflicts of interest

There are no conflicts of interest.

References

1. Aggelides SM, Londra PA. Effects of compost produced from town wastes and sewage sludge on the physical properties of a loamy and a clay soil. Bioresour Technol 2000;71:253-59.
2. Slack RJ, Gronow JR, Voulvoulis N. Household hazardous waste in municipal landfills: Contaminants in leachate. Sci Total Environ 2005;337:119-37.
3. Baffi C, Dell'Abate MT, Nassisi A, Silva S, Benedetti A, Genevini PL, *et al*. Determination of biological stability in compost: A comparison of methodologies. Org Waste Soil EGU 2007;39:1284-93.
4. Andersen JK, Boldrin A, Christensen TH, Scheutz C. Mass balances and life cycle inventory of home composting of organic waste. Waste Manag 2011;31:1934-42.
5. Faraji M, Mehrizi EA, Sadani M, Karimaei M, Ghahramani E, Ghadiri K, *et al*. Isotherms and kinetics of lead and cadmium uptake from the waste leachate by natural and modified clinoptilolite. Int J Environ Health Eng 2012;1:26.
6. Mehrizi EA, Sadani M, Karimaei M, Ghahramani E, Ghadiri K, Taghizadeh MS. Isotherms and kinetics of lead and cadmium uptake from the waste leachate by natural absorbent. World Appl Sci J 2011;15:1678-86.
7. Liang C, Bruell CJ, Marley MC, Sperry KL. Persulfate oxidation for *in situ* remediation of TCE. I. Activated by ferrous ion with and without a persulfate-thiosulfate redox couple. Chemosphere 2004;55:1213-23.
8. Kolthoff IM, Stenger VA. Volumetric Analysis: Titration Methods: Acid-base, Precipitation, and Complex Reactions. 2nd Revised Edition., Vol. 2. New York: Inderscience Publishers, Inc.; 1947.
9. House DA. Kinetics and mechanism of oxidations by peroxydisulfate. Chem Rev 1962;62:185-203.
10. Amin MM, Jaberian B, Bina B, Sadani M, Hadian R, Bonyadinejad G, *et al*. Advanced oxidation of the endosulfan and profenofos in aqueous solution using UV/H2O22 process. Environ Asia 2014;7:57-64.
11. Amin MM, Teimouri F, Sadani M, Karami MA. Application of enhanced nZnO photocatalytic process with ultrasonic wave in formaldehyde degradation from aqueous solution. Desalination Water Treat 2016;57:9455-64.
12. Oh SY, Kang SG, Chiu PC. Degradation of 2,4-dinitrotoluene by persulfate activated with zero-valent iron. Sci Total Environ 2010;408:3464-8.
13. Deng Y, Ezyske CM. Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate. Water Res 2011;45:6189-94.
14. Karami MA, Amin MM, Nourmoradi H, Sadani M, Teimouri F, Bina B. Degradation of reactive red 198 from aqueous solutions by advanced oxidation process: O3, O3/H2O2, and persulfate. Int J Environ Health Eng 2016;5:26.
15. Zhu C, Fang G, Dionysiou DD, Liu C, Gao J, Qin W, *et al.* Efficient transformation of DDTs with persulfate activation by zero-valent iron nanoparticles: A mechanistic study. J Hazard Mater 2016;316:232-41.
16. Li Z, Zhang Y. Use of surfactant-modified zeolite to carry and slowly release sulfate. Desalination Water Treat 2010;21:73-8.
17. Ismail L, Ferronato C, Fine L, Jaber F, Chovelon JM. Elimination of sulfaclozine from water with SO 4 – Radicals: Evaluation of different persulfate activation methods. Appl Catal B Environ 2017;201:573-81.
18. Huling SG, Pivetz BE. *In-situ* chemical oxidation (EPA/600/R-06/072). United States Environmental Protection Agency. Washington Dc: Office Of Water; 2006..
19. Ferrarese E, Andreottola G, Oprea IA. Remediation of PAH-contaminated sediments by chemical oxidation. J Hazard Mater 2008;152:128-39.
20. Farré MJ, Doménech X, Peral J. Combined photo-fenton and biological treatment for diuron and linuron removal from water containing humic acid. J Hazard Mater 2007;147:167-74.
21. Van der Schroeff JA. Post-treatment of anaerobically stabilized leachate. In: Industrial Presentations Group, editor. Proceedings of Anaerobic Treatment: A Grown-up Technology. Amsterdam, Netherlands: IPG, Schiedam; 1986. p. 359-71.
22. Wahba N, El Asmar MF, El Sadr MM. Iodometric method for determination of persulfates. Anal Chem 1959;31:1870-1.
23. Gao XC, Ma XX, Kang X, Shi Y. Oxidative absorption of NO by sodium persulfate coupled with Fe^{2+}, Fe_3O_4, and H_2O_2. Environ Prog Sustain Energy 2015;34:117-24.
24. Narkis N, Schneider-Rotel M. Evaluation of ozone induced biodegradability of waste water treatment plant effluent. Water Res 1980;14:929-39.
25. Zaloum R, Abbott M. Anaerobic pretreatment improves single sequencing batch reactor treatment of landfill leachates. Water Sci Technol 1997;35:207-14.
26. Abu Amr SS, Aziz HA, Adlan MN. Optimization of stabilized leachate treatment using ozone/persulfate in the advanced oxidation process. Waste Manag 2013;33:1434-41.
27. Rinzema A, Lettinga G, Wise DL. Anaerobic treatment of sulfate-containing waste water. Biotreatment Syst 1988;3:65-109.
28. Robinson JA, Tiedje JM. Competition between sulfate-reducing and methanogenic bacteria for H2 under resting and growing conditions. Arch Microbiol 1984;137:26-32.
29. Chen C, Ren N, Wang A, Yu Z, Lee DJ. Simultaneous biological removal of sulfur, nitrogen and carbon using EGSB reactor. Appl Microbiol Biotechnol 2008;78:1057-63.