

SDBS inhibition to Activated Sludge OUR and Nitrification in Batch and SBRs systems

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Abstract—Wastewater treatment plants (WWTPs) commonly use activated sludge systems to remove organics and nitrogen. Nitrogen is removed through two processes: nitrification and denitrification. Many WWTPs experience poor nitrification with drops in weather temperatures and changes to the influent characteristics, as nitrifying bacteria are generally sensitive and susceptible to inhibition. The case study selected for this project is a WWTP that usually experiences poor nitrification at the beginning of the cold season. During this period, an increased level of surfactants in the influent and effluent were observed. This study assessed the effect of the surfactant sodium dodecylbenzenesulfonate (SDBS) on nitrification using batch and sequencing batch reactors (SBRs).

The effect of SDBS on oxygen uptake rate (OUR) and ammonia removal in batch tests was carried out according to standard methods. The SBRs were operated at 8 hours/cycle and received SDBS in the influent at each cycle. Batch experiments performed according to standard methods showed 10% and 20% inhibition to OUR and nitrification respectively, for an influent spiked with 20 mg/L SDBS. The presence of 40 mg/L SDBS showed a slight increase in inhibition to OUR, at 22%, whereas inhibition to nitrification increased by 5%. However, no inhibition to nitrification was detected in the SBRs up to 20 mg/L. This was because the mixed liquor suspended solids (MLSS) of SBRs were higher than the batch experiments, resulting in reduced sensitivity to the inhibitor.

Keywords— Surfactant inhibition, nitrification, OUR, SDBS

I. INTRODUCTION

MUNICIPAL wastewater generally contains high concentrations of carbon and nitrogen-based compounds that need to be removed before it can be released into receiving water bodies. Hence, wastewater treatment plants (WWTPs) usually utilise biological nutrient removal (BNR)-activated sludge processes to remove organics (measured as BOD) and nitrogen. A medium size WWTP in Australia of 6 ML/day capacity currently faces difficulties meeting the effluent licence limits, especially at the beginning of the cold season. The poor nitrification observed during this period necessitated the dosage of nitrifying culture for a quick recovery. The WWTP utilises the Modified Ludzack-Ettinger (MLE) process (i.e. activated sludge with pre-anoxic zone for denitrification). Monitoring of the WWTP showed high concentrations of surfactants in the influent during the period in which poor nitrification was observed. This study investigated the likelihood of surfactant

being the cause of poor nitrification.

Nitrification is a biological reaction that according to most published literature occurs in two steps by a group of aerobic autotrophic bacteria called nitrifiers. The first step is performed by ammonia-oxidising bacteria (AOB), for instance the *Nitrosomonas* oxidise ammonium to nitrite. The second step is performed by nitrite-oxidising bacteria (NOB), the *Nitrobacter*, which oxidises nitrite to nitrate. Due to the low energy yield of these reactions, nitrifiers have lower growth rates compared to other heterotrophic bacteria in the system [1]. Nitrifiers are also more sensitive to changes in pH, temperature, alkalinity and the presence of inhibitors. Therefore, achieving nitrogen removal can be a significant problem for some treatment plants.

Surfactants are the active agents used in most laundry and other cleaning products. Linear alkylbenzene sulfonates (LAS), otherwise known as sodium dodecylbenzenesulfonate (SDBS), is a widely applied anionic surfactant in domestic and industrial detergents, it has been extensively used for more than 30 years [2].

Previous studies generally assessed the level of biodegradation and removal of LAS from wastewater based on its concentration in the influent and final effluent [3], [4] and [5]. The aim of this study is to assess the effect of SDBS on the nitrification process and on nitrogen removal in activated sludge systems using sequencing batch reactors (SBRs).

II. MATERIALS AND METHODS

Activated sludge for seeding of SBRs and batch experiments were all obtained from the aeration tank of Sunbury WWTP, Melbourne.

The surfactant SDBS of 80% SDBS was obtained from Aldrich (D-2525). The antifoam 1402 was obtained from Dow Corning and was used to spike both the SBRs and batch reactors to control excessive foaming.

A. Batch experiments

Batch oxygen uptake rate (OUR) tests were carried out according to the ISO 8192:1986 Standard Test 'inhibition of oxygen consumption by activated sludge'. The dissolved oxygen (DO) probe YSI Model 5100 was used to measure DO. The procedure involved the addition of the surfactant SDBS to a flask that contained activated sludge of mixed liquor suspended solids (MLSS) of 1500 mg/L. This study assessed the effect of adding 20, 40 and 60 mg/L SDBS on OUR. Duplicate flasks were used for each concentration. Two additional flasks of the same MLSS concentration were

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used as a control (i.e. received no SDBS) and another two flasks received the reference inhibitor allylthiourea (ATU) and no SDBS.

Batch inhibition to nitrification tests were carried out according to the ISO 9509:1989 'standard method for assessing the inhibition of nitrification of activated sludge micro-organisms by chemicals and wastewaters'. The effect of SDBS at 20 and 40 mg/L was assessed using 1500 mg/L MLSS; the effect of 30 mg/L SDBS was assessed using 3000 mg/L MLSS. All experiments were conducted in duplicate at 20°C.

B. SBRs set-up

Two SBR reactors, each of 4L effective volume, were fed with synthetic wastewater and operated at room temperature (25°C ± 2°C). The reactors were operated until a stabilised performance was observed, at least for two sludge retention times (SRTs), before spiking the feed with the surfactant SDBS commenced. The SBRs were operated at 8 hours/cycle, including 30 minutes feeding (no aeration), 4 hours aeration, 2 hours anoxic, 1 hour settling, and 30 minutes decanting. The decant percentage is 50%, making hydraulic retention time (HRT) 16 hours and the SRT was approximately 11 days.

One of the SBRs was used as a control and the second SBR was used as a test reactor. The synthetic wastewater was spiked with the surfactant SDBS at the designated concentration before being fed into the test reactor. The SBRs were operated and monitored for two SRTs.

The effect of SDBS on SBR performance was assessed at 5, 10, 20 and 30 mg/L. The parameters measured to assess performance included chemical oxygen demand (COD) total (for synthetic wastewater), filtered CODs (using 0.45 µm filter paper), SDBS concentration, NH₄-N, NO₃-N, turbidity, MLSS and MLVSS.

The composition of the synthetic wastewater consisted of sucrose (0.4 g/L), beef extract (0.2 g/L), ammonium chloride (NH₄Cl) 0.13 mg/L, and sodium bicarbonate (NaHCO₃) for alkalinity. Solutions of nutrients and trace metal were prepared according to composition reported by [6]. The synthetic wastewater was prepared fresh every day and final characteristics are shown in Table I.

TABLE I
CHARACTERISTICS OF SYNTHETIC WASTEWATER FED INTO THE SBRs

Parameter	Concentration (mg/L)
COD	668 ± 5
NH ₄ -N	39.6 ± 1.7
NO ₃ -N	< 0.1
PO ₄	17.3
PO ₄ -P	5.6
BOD	555 ± 3

C. Analytical method

Samples were immediately collected after completion of the test, then filtered through 0.45µm membrane and stored at 4°C until analysed. The MLSS and MLVSS were measured according to Standard Method 2540 [7].

COD was measured using high range HACH COD reagents according to Method 8000; NH₄-N was measured using HACH AmVer™ Salicylate Test 'N Tube™ (Method 10031); nitrate nitrogen was measured using HACH Chromotropic Acid Test 'N Tube (Method 10020). The concentration of SDBS was measured according to the methylene blue method published by [8]. Turbidity was measured using HACH 2100P Turbidimeter.

III. RESULTS AND DISCUSSION

A. Effect of SDBS on OUR

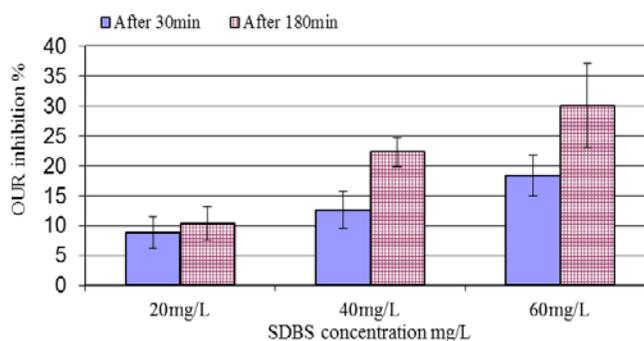


Fig. 1 OUR at different SDBS concentrations after 30 and 180 minutes (sludge MLSS 1500 mg/L)

The effect of SDBS on OUR, using batch tests, at 20, 40 and 60 mg/L is shown in Fig. 1. The results show that inhibition exhibited a proportional relationship with the concentration of SDBS added into the batch reactors. The inhibition increased from 10 to 30% with increased concentration from 20 to 60 mg/L, respectively.

Moreover, higher inhibition was detected after 180 minutes compared to after 30 minutes, and the effect intensified with time for concentrations of 40 and 60 mg/L SDBS. This might be due to the accumulative effect of SDBS as it was adsorbed onto the sludge. The results at the end of four-hour batch nitrification experiments according to the ISO method showed 19.6 and 24.9% inhibition at 20 and 40 mg/L SDBS, respectively. This shows a proportional relationship of SDBS concentration and inhibition to nitrification (results not shown).

B. Effect of SDBS on SBRs performance

The SBR was operated until a steady state was achieved, then the feed to the SBR was spiked with 5, 10 and 20 mg/L SDBS. The SBR was monitored for the removal of COD, and concentrations of NH₄ and NO₃ in the effluent, for each cycle, for one SRT. The results showed that SDBS had no significant effect on nitrification, measured in terms of changes to NH₄ removal (not shown). These results are not in agreement with the inhibition levels measured using batch tests where 20% inhibition to nitrification was measured in

the presence of 20 mg/L SDBS. These results indicate that batch tests cannot be used as reliable tests for assessing the potential effect of SDBS on activated sludge nitrification under continuous operation conditions.

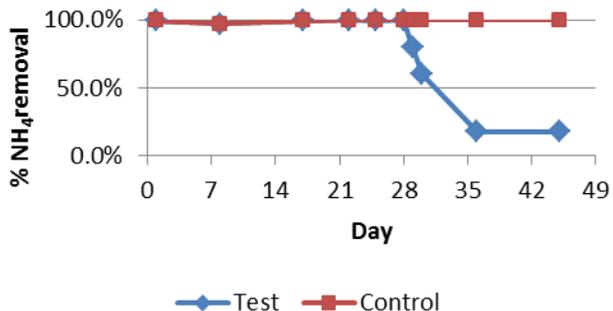


Fig. 2 Ammonia removal in the control and test SBR (surfactant added on test SBR after 28 days)

On the other hand, inhibition was detected at 30 mg/L SDBS. Fig. 2 shows that there was an immediate inhibition to NH₄ removal after adding 30 mg/L of SDBS to the influent to the test reactor on the 28th day. NH₄ removal dropped to 80% within the first cycle and deteriorated further within the first week, staying at less than 20% for the remainder of the experiment.

These results can be explained in terms of the high MLSS in the SBR, which was more than double the MLSS used in the batch test.

To establish a potential relationship between MLSS and SDBS inhibition to nitrification, another standard batch inhibition to nitrification test was carried out at MLSS 3000 mg/L.

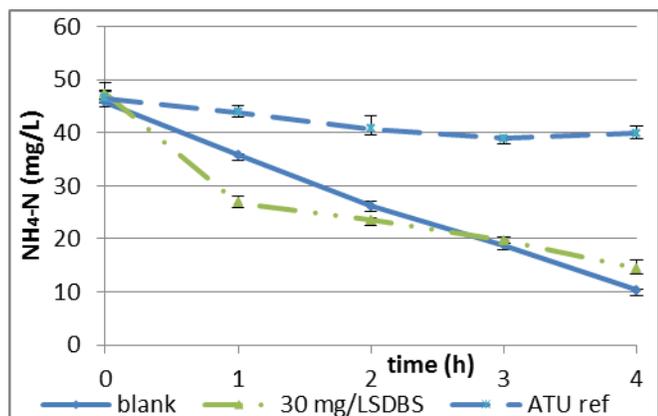


Fig. 3 Nitrification in the presence of SDBS using batch test (MLSS of 3000 mg/L)

During the first hour of the test, the mixture had not stabilised completely and ammonia was removed at a faster rate when exposed to SDBS, but with time, inhibition started to occur. This increase in inhibition over time is in agreement with the different inhibition of OUR after 30 and 180 minutes as discussed for Fig. 1.

In Fig. 3, overall inhibition was only 9% but after the first hour, inhibition to nitrification was 70% for the remaining three hours. Comparing the overall inhibition in four hours

with previous nitrification experiments, it was evident that increasing MLSS could reduce surfactant's inhibition to activated sludge nitrification. Another study also reported similar findings, observing that the inhibition effect of SDBS on OUR using batch tests at 1500 mg/L MLSS diminished compared with the inhibition observed at MLSS concentration of 100 mg/L [9].

TABLE II
CHANGES IN SBR PARAMETERS OVER TIME (MEASURED AT THE END OF AERATION)

	1 st cycle	24 hour	1 week	1 SRT
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
NH ₄ -N	5.9	11.7	24.5	24.7
NO ₃ -N	3.6	1.4	0.6	0.9
SDBS	22.2	10.0	24.6	34.0
MLSS	4400	4400	1900	2400

The concentration of SDBS was monitored and the results showed 7.8 mg/L SDBS removal during the first cycle of the SBR operation (Table II). Although SDBS concentration in the effluent dropped to 10 mg/L after one day, it increased considerably after one week (24.6 mg/L) and exceeded 30 mg/L after 11 days (34 mg/L). In comparison with the batch OUR tests, 6–7 mg/L of SDBS was removed after 180 minutes exposure (i.e. approximately 20% removal) whereas under continuous conditions 66 and 18% SDBS removal was observed after one and seven days of exposure.

Further, after seven days, the SDBS concentration exceeded the influent concentration, which indicates that SDBS adsorbed onto sludge desorbed under the experiment conditions.

After one week of spiking the feed to the test SBR with 30 mg/L SDBS, MLSS also dramatically reduced. It was found that the sludge had poor settling properties as indicated by the turbidity of the test-SBR effluent, 44.6 NTU, whereas the control SBR effluent turbidity was 9.06 NTU. This poor settling and loss of sludge through the decant of effluent was similar to that reported by [10] and [11]. Effluent suspended solids of the test reactor were measured to be 260 mg/L after one week and the loss of sludge decreased the SRT, causing a detrimental effect on the operation of the SBRs as well as nitrification process. This could be the main reason for the high drop in NH₄ removal after one week of exposure to SDBS (Fig. 2 and Table II).

Continuous monitoring of the SBRs for a further four days showed no improvement to nitrification or any signs of recovery in the removal performance.

IV. CONCLUSION

The surfactant SDBS has inhibition effects on activated sludge OUR and nitrification. The level of inhibition to OUR observed using batch tests ranged from 10 to 30% for SDBS concentrations of 20 to 60 mg/L. Whereas, the level of inhibition to nitrification ranged from 20 to 25% for SDBS concentrations of 20 to 40 mg/L.

The exposures of activated sludge to SDBS had negative effects on its settling properties and led to increased effluent suspended solids concentration.

In general, SDBS inhibition threshold to nitrification under continuous conditions, as measured using SBRs, was higher than that measured using batch OUR tests.

This study showed that the low concentration of MLSS recommended by the standard methods might lead to invalid results and recommends that batch and continuous reactors be operated using the same MLSS to be applied in the pilot and/or large WWTP.

REFERENCES

- [1] Metcalf & Eddy Inc., Tchobanoglous, G, Burton, F & Stensel, HD 2004, *Wastewater Engineering: Treatment and Reuse* (international edition), 4th edn, McGraw-Hill, New York.
- [2] Verge, C, Moreno, A, Bravo, J & Berna, JL 2001, 'Influence of water hardness on the bioavailability and toxicity of linear alkylbenzene sulphonate (LAS)', *Chemosphere*, vol. 44, no. 8, pp. 1749-57.
[http://dx.doi.org/10.1016/S0045-6535\(00\)00574-9](http://dx.doi.org/10.1016/S0045-6535(00)00574-9)
- [3] Brandt, KK, Hesselsoe, M, Roslev, P, Henriksen, K & Sorensen, J 2001, 'Toxic effects of linear alkylbenzene sulfonate on metabolic activity, growth rate, and microcolony formation of *Nitrosomonas* and *Nitrosospira* strains', *Applied and Environmental Microbiology*, vol. 67, no. 6, pp. 2489-98.
<http://dx.doi.org/10.1128/AEM.67.6.2489-2498.2001>
- [4] Temmink, H & Klapwijk, B 2004, 'Fate of linear alkylbenzene sulfonate (LAS) in activated sludge plants', *Water Research*, vol. 38, no. 4, pp. 903-12.
<http://dx.doi.org/10.1016/j.watres.2003.10.050>
- [5] Ying, GG 2006, 'Fate, behavior and effects of surfactants and their degradation products in the environment', *Environment International*, vol. 32, no. 3, pp. 417-31.
<http://dx.doi.org/10.1016/j.envint.2005.07.004>
- [6] Hu, Z, Zhang, J, Li, S, Xie, H, Wang, J, Zhang, T, Li, Y & Zhang, H 2010, 'Effect of aeration rate on the emission of N₂O in anoxic-aerobic sequencing batch reactors (A/O SBRs)', *Journal of Bioscience and Bioengineering*, vol. 109, no. 5, pp. 487-91.
<http://dx.doi.org/10.1016/j.jbiosc.2009.11.001>
- [7] Clesceri, LS, Greenberg, AE & Eaton, AD 1999, *Standard Methods for Examination of Water and Wastewater*, 20 edn, American Public Health Association, the American Water Works Association, and the Water Environment Federation, USA.
- [8] Jurado, E, Fernandez-Serrano, M, Nunez-Olea, J, Luzon, G & Lechuga, M 2006, 'Simplified spectrophotometric method using methylene blue for determining anionic surfactants: Applications to the study of primary biodegradation in aerobic screening tests', *Chemosphere*, vol. 65, no. 2, pp. 278-85.
<http://dx.doi.org/10.1016/j.chemosphere.2006.02.044>
- [9] Jiao, Y 2009, 'The effect of sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulphonate (SDBS) on activated sludge oxygen uptake rate (OUR) and nitrification', Master Thesis, RMIT.
- [10] Oviedo, MDC, Marquez, DS & Alonso, JMQ 2004, 'Influence of linear alkylbenzene sulphonates (LAS) on microbial activity of activated sludge', *Chemical & Biochemical Engineering Quarterly*, vol. 18, no. 4, pp. 409-15.
- [11] Xiong, X, Hirata, M, Takanashi, H, Lee, M-G & Hano, T 1998, 'Analysis of acclimation behavior against nitrification inhibitors in activated sludge processes', *Journal of Fermentation and Bioengineering*, vol. 86, no. 2, pp. 207-14.
[http://dx.doi.org/10.1016/S0922-338X\(98\)80115-3](http://dx.doi.org/10.1016/S0922-338X(98)80115-3)