

Performance of A-stage process treating combined municipal-industrial wastewater.

Antoine Prandota Trzcinski^{a*}, Chong Wang^b, Dongqing Zhang^b, Wui Seng Ang^e, Li Leonard Lin^e, Terutake Niwa^f, Yasuhiro Fukuzaki^g and Wun Jern Ng^{c,d}

^a School of Civil Engineering & Surveying, Faculty of Health, Engineering and Sciences, University of Southern Queensland, 4350 Queensland, Australia.

^b Advanced Environmental Biotechnology Centre (AEBC), Nanyang Environment and Water Research Institute (NEWRI), Nanyang Technological University, 1 Cleantech Loop, CleanTech One, #06-10, Singapore 637141, Singapore.

^c Division of Environmental and Water Resources, School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

^d Nanyang Environment and Water Research Institute (NEWRI), Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore.

^e Public Utilities Board, Water Reclamation (Plants) Department, 40 Scotts Road, #15-01 Singapore 228231, Singapore

^f Meiden Singapore Pte Ltd, 5 Jalan Pesawat, Singapore 619363, Singapore

^g Meidensha Corporation, Nishibiwajima Kiyosu Aichi, Japan 4528602, Japan

* Corresponding author. Email: antoine.trzcinski@usq.edu.au

Tel: +61 7 4631 1617

Abstract

A biosorption column and a settling tank were operated for 6 months with combined municipal and industrial wastewaters (1 m³/hr) to study the effect of dissolved oxygen (DO) levels and Fe³⁺ dosage on removal efficiency of dissolved and suspended organics prior to biological treatment. High DO (>0.4 mg/L) were found to be detrimental for soluble COD removals and iron dosing (up to 20 ppm) did not improve the overall performance. The system performed significantly better at high loading rate (> 20 kg COD.m⁻³.d⁻¹) where suspended solids and COD removals were greater than 80% and 60%, respectively. This is a significant improvement compared to conventional primary sedimentation tank (PST) and the process is a promising alternative for the pre-treatment of industrial wastewater.

Keywords: Carbon capture; Biosorption; Waste Activated Sludge (WAS); anaerobic digestion; A-stage.

1. Introduction

Conventional wastewater treatment plants include a primary sedimentation tank (PST) to remove suspended solids and organics. These units operate typically at 2-3 hours hydraulic residence time and suffers from low efficiencies. This results in high aeration costs in the subsequent biological tanks to degrade the organic matter. A possible alternative to PST is the A/B (Adsorption/Bio-oxidation) process which comprises high rate activated sludge (HRAS) process (A-stage), which removes chemical oxygen demand (COD) primarily by bioflocculation, adsorption, bioaccumulation and settling, followed by biological nutrient removal (BNR) (B-stage). In the A-stage COD removal by activated sludge is preceded by rapid physicochemical adsorption of organic matter on active sites of bioflocs (biosorption) and intracellular storage depending on the pH, dissolved oxygen (DO), residence time, organic loading, type of organics (particulate, colloidal or soluble) and microorganisms (Lim et al., 2015). In some circumstances up to 60% of incoming COD can be removed by intracellular mechanism versus 40% by surface sorption mechanism at 15 minutes contact time. Table 1 lists typical performances of A-stage processes obtained with municipal wastewaters.

Table 1. Typical parameters of A-stage processes

Influent COD (mg/L)	Parameters (biosorption/settling) tanks					Chemical Aid	References
	HRT (h)	SRT (day)	DO (mg/L)	Volume	COD removal		
400-700	0.9/1.8	0.3-0.5	2	3/6 L	80%	20 mg Fe ²⁺ /L	(Diamantis et al., 2013)
171 (COD) 107 (SS)	0.58/1.5	NR	1.9-3.2	1.2 m ³	68% 91%	Al ₂ O ₃ Fe ₂ O ₃	(Zhang et al., 2007)
450-800 (COD) 200-600(SS)	0.5/1.5	1.1-2	2-4	2.64/6.11 L	70-80% 80-95%	no	(Zhao et al., 2000)
700	1/1	-	NR	1L (batch)	70%	no	(Yu et al., 2014)
NR	0.21- 0.61/1.47-	0.5-0.7	NR	644/4540 m ³	40-85%	FeCl ₃ + polym.	(Wett et al., 2014)

The advantages realized by operating the A/B process is the overall reduction of the total biological reactor and clarifier volumes, reduced aeration requirement, and the redirection of more sewage carbon to anaerobic digestion for biogas generation. The main objective of an A-stage is to produce large amounts of raw waste sludge that can be converted to biogas by anaerobic digestion and reduce the organic load on the subsequent BNR process. As a result of reducing the organic load and providing a more stable influent to the BNR process, aeration capacity and tank volume of the B-stage can be reduced. The A-stage can also be a buffer against shock loads and inhibitory industrial inputs to the B-stage biological process.

Biosorption has been reported to be suitable for wastewaters containing high suspended solids and colloids concentration. The main parameters to consider are the SRT, HRT, aeration control, velocity gradient inside the contact tank, settling time, concentration of suspended solids (MLSS), sludge recycle ratio and temperature. Under low SRT and HRT the COD removal is due to adsorption and bio-flocculation and the degradation of organic compounds by metabolism is avoided. Biodegradation of organic matter typically represents less than 10% of the incoming COD load (Guellil et al., 2001, Haider et al., 2003, Hernández Leal et al., 2010). Furthermore, coagulant dosage to the influent of A-stage may enhance the removal of the carbon by precipitation onto bioflocs.

Biosorption does not exceed 10-15 minutes to reach equilibrium (Guellil et al., 2001). Yu et al. (2014) reported that biosorption of the colloidal fraction in batch tests reached equilibrium after 10 minutes, while 45 minutes were required for the soluble fraction. Under optimal conditions and with municipal wastewater, COD removal can reach 70-80% (30% of it is SCOD) and about 80 to 95% of TSS can be removed (Zhao et al., 2000).

Biosorption sludge contains aggregates of microorganisms, adsorbed organic matter and Extracellular Polymeric Substances (EPS). EPS are highly charged polymers (proteins, polysaccharides, lipids, glycolipids and glycoproteins) which are excreted by microorganisms or produced by cell lysis and hydrolysis. The main mechanisms include charge neutralization, hydrophobic interactions and bridging (Vogelaar et al., 2005). The effectiveness of bridging depends on the molecular weight of EPS, the charge of polymer and the particle, the ionic strength and the mixing. Divalent cations may improve the biosorption efficiency of activated sludge due to the negative charge of EPS (Keiding and Nielsen, 1997). These authors showed that small particles in wastewater have a negative surface charge density and a change in the repulsive forces due to calcium concentration and ionic strength can cause floc disintegration.

Diamantis et al. (2013) operated a biosorption step as pre-treatment to ultrafiltration at laboratory-scale with diluted (<300 mg/L COD) and concentrated (\approx 400-700 mg/L COD) municipal wastewater to study the removal of organics (particulate and soluble COD) and recovery of nutrients (TKN, ammonia and phosphorus). The HRT was 0.9h and 1.8h in the biosorption and sedimentation tanks, respectively, and the SRT in the system was 0.3-0.5 days. They found that removal of particulate COD was significantly higher when concentrated wastewater (400-700 mg/L COD, on average 524 mg/L) was used while soluble COD removal was improved with iron supplementation (FeSO_4 at 20 mg Fe^{2+} /L). The addition of coagulant is known to enhance the biosorption capacity by co-precipitating iron phosphate and soluble carbon onto bioflocs.

In this study, the objective of the A-stage pilot plant with capacity of 1 m³/hour was to evaluate the removal of particulate and soluble organics from a combined municipal-industrial wastewater and to study the effect of dissolved oxygen, solid residence time (SRT), organic loading rate (OLR) and

ferric chloride dosage. Conventional **PST** operate at 2-4 hours hydraulic residence time (HRT) and achieve typically 30-35% BOD removals and 50-60% MLSS removals ~~at 2 hours HRT~~ (Metcalf and Eddy, 2014). There is therefore a need to study other technologies capable of removing more organics at similar residence time. Compared with municipal sewage, the combined municipal-industrial wastewater has an unknown composition and large fluctuation in water quality and there is currently a lack of data on the applicability of A-stage treatment for high-strength industrial wastewater, especially at pilot scale. The objective was to determine the organics removals (MLSS, Soluble and Total COD) of the novel A-stage process operating **at lower HRT** than **most** conventional **PST**.

2. Material and Methods

2.1. Combined municipal-industrial wastewater

Sewage **and industrial wastewaters were collected** from various local industries including petrochemical, chemical, electroplating, food processing and pharmaceuticals industries—~~was combined with municipal wastewaters~~. The wastewater parameters were determined from a composite sample collected by auto samplers over a period of 24 hours.

2.2. A-stage Pilot Plant

The pilot plant comprised a sorption column ($V = 0.5 \text{ m}^3$; cylindrical; $D = 0.4 \text{ m}$; Water depth = 4 m) followed by a clarifier ($V = 1.5 \text{ m}^3$; circular; $D = 1.1 \text{ m}$; Surface loading $1 \text{ m}^3/\text{m}^2/\text{hr}$). The simplified schematic diagram is depicted in Figure 1. The influent flow rate was fixed at $1 \text{ m}^3/\text{hr}$ and the **overall** hydraulic retention time was 2 hours.

A fraction of the settled solids was returned to the sorption column through the Return Activated Sludge (RAS) line. The sludge volume of the RAS was estimated at 330 L including the conical part (320L) and the RAS pipe (10L). The sludge concentrations in the sorption column were controlled by adjusting the return activated sludge and waste activated sludge rates. The influent and effluent samples were composite samples collected automatically every hour over a period of 24 hours. The sorption column and Return Activated Sludge (RAS) samples were grab samples from the sorption column and clarifier bottom, respectively. The excess sludge's Total Solids (TS), Volatile Solids (VS), TCOD, SCOD, calorific value and anaerobic biodegradability of the clarifier sludge samples were analyzed throughout the study.

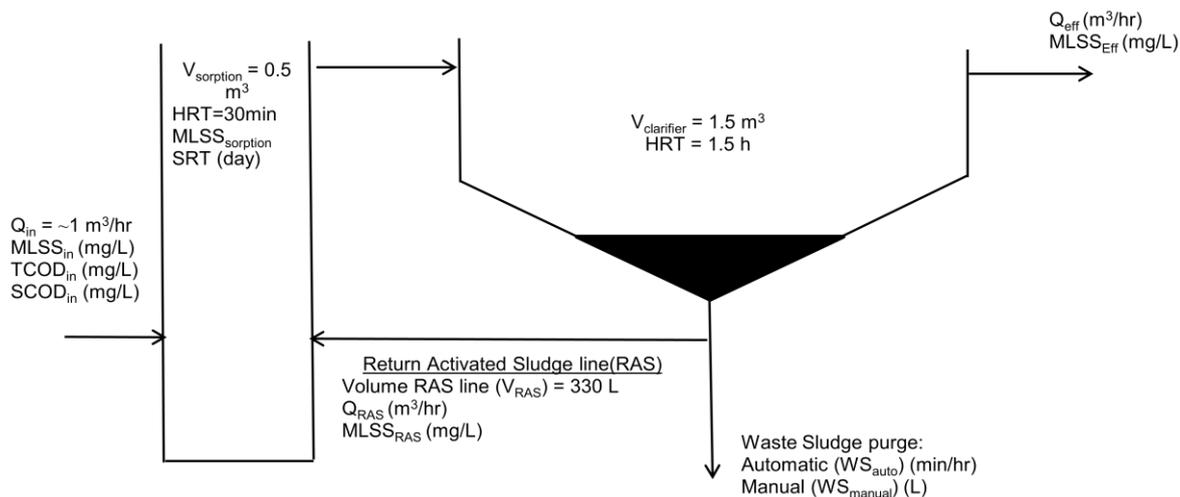


Figure 1. Schematic diagram of the A-stage pilot plant.

2.3. Effect of Dissolved oxygen

The pilot plant was operated for about 200 days. During the first 144 days, various dissolved oxygen (DO) levels were tested in the sorption column during tests 1 to 6. DO was controlled at 0.2, 0.4, 0.5, 0.7 and 1 mg/L through adjustment of the blower flowrate with PID control. The experimental plan is shown in Table 2.

Table 2. Summary of conditions tested on the A-stage process.

Test	Days	Date	No. of Run	Experimental conditions						Influent			Reactor	RAS
				Influent m ³ /h	DO SP mg/L	RAS m ³ /h	WAS kg/d	SRT day	FeCl ₃ ppm	SS mg/L	T-COD mg/L	S-COD mg/L	MLSS mg/L	MLSS mg/L
1	14-71	4-9-13 to 18-10-13	6	0.95	0.20	0.21	10.8	0.52	0.0	1155	1553	527	5272	20069
2	74-96	6-11-13 to 20-11-13	5	1.03	0.40	0.47	18.2	0.21	0.0	1338	1873	565	3733	10533
3	110-112	4-12-13 to 6-12-13	2	1.00	0.70	0.49	18.2	0.20	0.0	3032	3026	262	4246	8994
4	117-119	11-12-13 to 13-12-13	2	1.04	1.00	0.49	16.0	0.16	0.0	2883	3214	462	3276	7866
5	124-126	18-12-13 to 20-12-13	2	0.95	0.50	0.29	9.8	0.31	0.0	846	1425	726	2092	21872
6	132-144	26-12-13 to 8-1-14	3	1.06	0.40	0.50	14.1	0.24	0.0	687	1375	304	3355	8873
7	151-160	15-1-14 to 24-1-14	4	1.04	0.40	0.50	12.7	0.24	5.0	3725	2266	712	3304	7942
8	186-194	20-2-14 to 28-2-14	4	1.13	0.40	0.49	15.8	0.22	10.0	2559	2082	748	3800	10057
9	201-203	5-3-14 to 7-3-14	3	1.13	0.40	0.50	13.0	0.21	20.0	2148	2649	619	3114	8126
10	208-210	12-3-14 to 14-3-14	3	1.10	0.70	0.50	13.4	0.26	20.0	1876	2296	680	4559	8112
		<i>Average</i>	34	<i>1.04</i>			<i>14.20</i>	<i>0.26</i>		<i>2025</i>	<i>2176</i>	<i>561</i>	<i>3675</i>	<i>11244</i>

2.4. Solid Residence Time (SRT)

The Solid Residence Time (SRT) was controlled by withdrawing sludge in the recirculation line. To adjust the amount of sludge withdrawn, the opening time of the automatic sludge discharge valve was adjusted to 5 – 10 min every hour. The SRT in the A-stage process was calculated as follows:

$$SRT = \frac{\text{mass MLSS in the process (g MLSS)}}{\text{daily MLSS removal in effluent and WS automatic and manual removal } \left(\frac{\text{g MLSS}}{\text{day}} \right)}$$
$$= \frac{V_{sorption} \cdot MLSS_{sorption} + V_{RAS} \cdot MLSS_{RAS}}{Q_{Eff} \cdot 24 \cdot MLSS_{Eff} + WS_{auto} \cdot Q_{RAS} \cdot 24 \cdot MLSS_{RAS} + WS_{manual} \cdot MLSS_{RAS}}$$

2.5. Ferric chloride dosage

From day 145 to day 210, the addition of coagulant was considered to further enhance the sorption capacity by entrapment of dissolved organic matter in iron phosphates precipitates. In this study, ferric chloride (FeCl_3 , 38%) was used as coagulant. The dosage rates were adjusted at 5 ppm (Test 7), 10 ppm (Test 8) and 20 ppm (Tests 9) as Fe^{3+} in order to determine the optimum value while keeping a constant DO of 0.4 mg/L (Table 2). In test 10, 20 ppm Fe^{3+} was tested together with DO of 0.7 mg/L.

2.6. Analytical methods

2.6.1. Influent, sorption column and effluent samples

The Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS), Soluble Chemical Oxygen Demand (SCOD) and Total Chemical Oxygen Demand (TCOD) of the influent, sorption column and clarifier effluent were measured in triplicate as described in Standard Methods (APHA, 2012). Their coefficient of variation (COV) for ten identical samples was 4%, 3.1%, 1.9% and 1.6%, respectively. Biochemical Oxygen Demand (BOD), Total Kjeldahl Nitrogen (TKN), NH₃-N, Total phosphorus (TP) and PO₄-P of the influent, sorption column and clarifier effluent were measured in triplicate as described in Standard Methods (APHA, 2012).

2.6.2. Clarifier sludge samples

The Total Solids (TS), Volatile Solids (VS), Soluble Chemical Oxygen Demand (SCOD) and Total Chemical Oxygen Demand (TCOD) of the clarifier sludge samples were measured in triplicate as described in Standard Methods (APHA, 2012). Their coefficient of variation (COV) for ten identical samples was 2.7%, 3.8%, 1.9% and 1.6%, respectively.

Biochemical methane potential (BMP) assay was conducted on the clarifier sludge samples in triplicate using the Automatic Methane Potential Test System (AMPTS model 2) from Bioprocess Control (Sweden) in 500 mL bottles. For the assays 100 mL of excess sludge, 200 mL of degassed acclimated inoculum and 50 mL Owens' biomedium (Owens et al., 1979) were added to the bottles and purged with N₂ gas for five minutes to create absolute anaerobic environment. Two blanks containing the inoculum and the biomedium were run in parallel, and the methane produced was subtracted from the methane produced in the bottles containing excess sludge. All bottles were incubated at 35°C and mixed automatically (1 min

on and 30 seconds off). The methane volumes were automatically recorded by the AMPTS. The composition of biogas was analyzed with gas chromatography as previously reported (Tian et al., 2014). Calorific value was analyzed with a IKA bomb calorimeter (Model C200). The sample was freeze-dried at -80°C for 24 hours prior to analysis (Trzcinski et al. 2016).

3. Results and discussion

3.1. Influent characteristics and process performance

Influent MLSS is normally less than 700 mg/L in municipal wastewaters. The influent MLSS in this study ranged from 360 to 5,370 mg/L and its average was 1,690 mg/L, demonstrating the industrial nature of the influent. The exact ratio of municipal and industrial wastewater was variable and unknown. The influent characteristics varied over a wide range as shown in Table 3. Oil and grease and extremely high suspended solids were frequently found in the influent. Typical effluent characteristics are shown in Table 3 during a baseline test at 0.2 mg/L DO.

Table 3. Influent characteristics, mixed liquor properties in the sorption column and effluent parameters.

Parameter (Influent)	#samples	Units	Min	Max	Average \pm standard deviation
pH	29	-	6.8	8.53	7.09 \pm 0.3
TCOD	29	mg/L	750	4,120	1,790 \pm 830
SCOD	23	mg/L	300	840	490 \pm 130
BOD	35	mg/L	200	1,225	775 \pm 510
MLSS	29	mg/L	360	5,370	1,690 \pm 1,240
MLVSS	29	mg/L	190	3,115	770 \pm 590
TKN	35	mg/L	40.3	184	73.2 \pm 29.6
NH ₃ -N	35	mg/L	29.4	84	47.7 \pm 12.8
Total Phosphorus (TP)	35	mg/L	9.2	75.7	20.8 \pm 12.3

PO ₄ -P	35	mg/L	1.7	12.6	6 ± 2.7
Parameter (sorption column)					
MLSS	28	mg/L	760	17,930	5,300 ± 3,420
MLVSS	28	mg/L	440	8,570	2,640 ± 1,625
Parameter (clarifier effluent)					
TCOD	37	mg/L	290	1,715	814 ± 310
BOD	35	mg/L	102	1,636	479 ± 320
TKN	35	mg/L	33.1	117	65.5 ± 18.4
NH ₃ -N	35	mg/L	27.4	89.4	49.2 ± 13
Total Phosphorus (TP)	35	mg/L	1.5	18.6	12.1 ± 4.2
PO ₄ -P	35	mg/L	1	9.8	4.5 ± 2.4

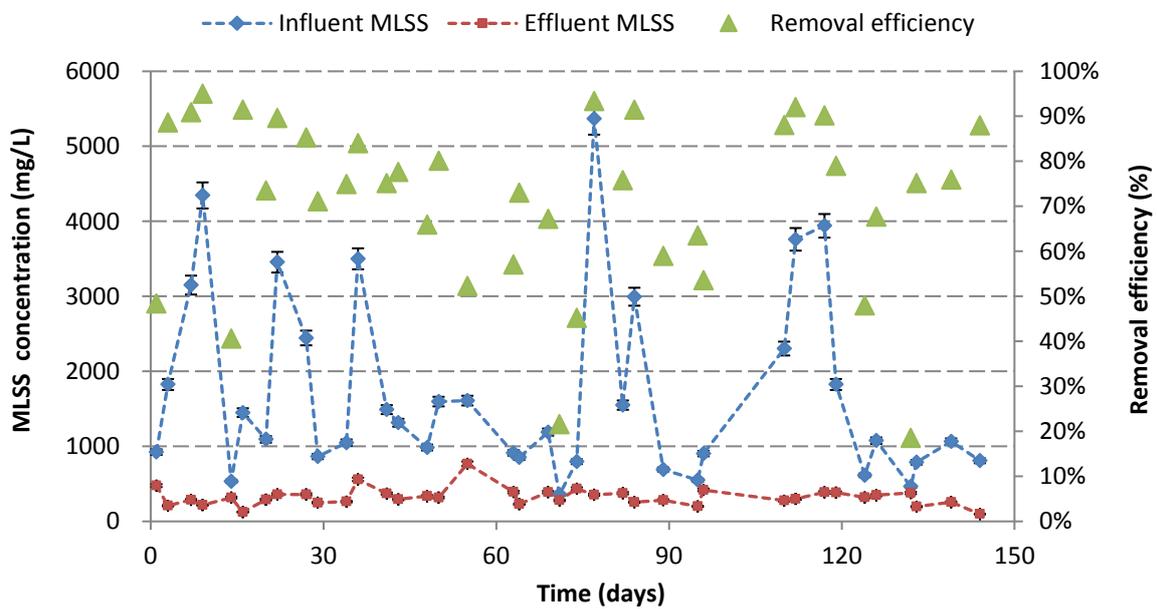
The incoming MLSS was in the range 360-5,370 mg/L. The incoming SCOD and TCOD were very high in the range 300-840 mg/L and 750-4,120 mg/L, respectively. The SCOD to TCOD ratio percentage was below 35% in the influent, whereas and it increased to above 60% in the effluent, indicating that most of the effluent was soluble and particulate COD were effectively removed in the clarifier sludge despite the high fluctuations of raw wastewater. The A-stage could also remove some phosphorus as shown by a decrease in TP (Table 3), while the removal of TKN, NH₃-N and PO₄-P were not consistent. The BOD concentration decreased from 775 mg/L to 479 mg/L on average which shows the potential of the A-stage to remove organics at a high rate despite the fluctuations in the influent which will considerably reduce the aeration costs in the subsequent biological stage. The BOD concentration in the clarifier effluent was in the range 102-1,636 mg/L, which indicates that there would still be sufficient biodegradable matter for nutrient removal in the B-stage.

3.2. Effect of DO

Low DO environment can lead to growth of filamentous bacteria which would affect the settling (Li et al., 2010). Yu et al. (2014) showed that the biosorption capacity of sludge decreased when it was mixed with anaerobic sludge. Air must therefore be provided during

biosorption in order to reactivate the sludge and maintain its adsorption capacity. Higher DO would require greater air supply, and therefore higher operating costs. It is therefore important to investigate its impact on the process.

Figure 2 shows the incoming MLSS, TCOD and SCOD, effluent MLSS, TCOD, SCOD and MLSS, TCOD and SCOD removal percentages at various DO tested during tests 1 to 6.



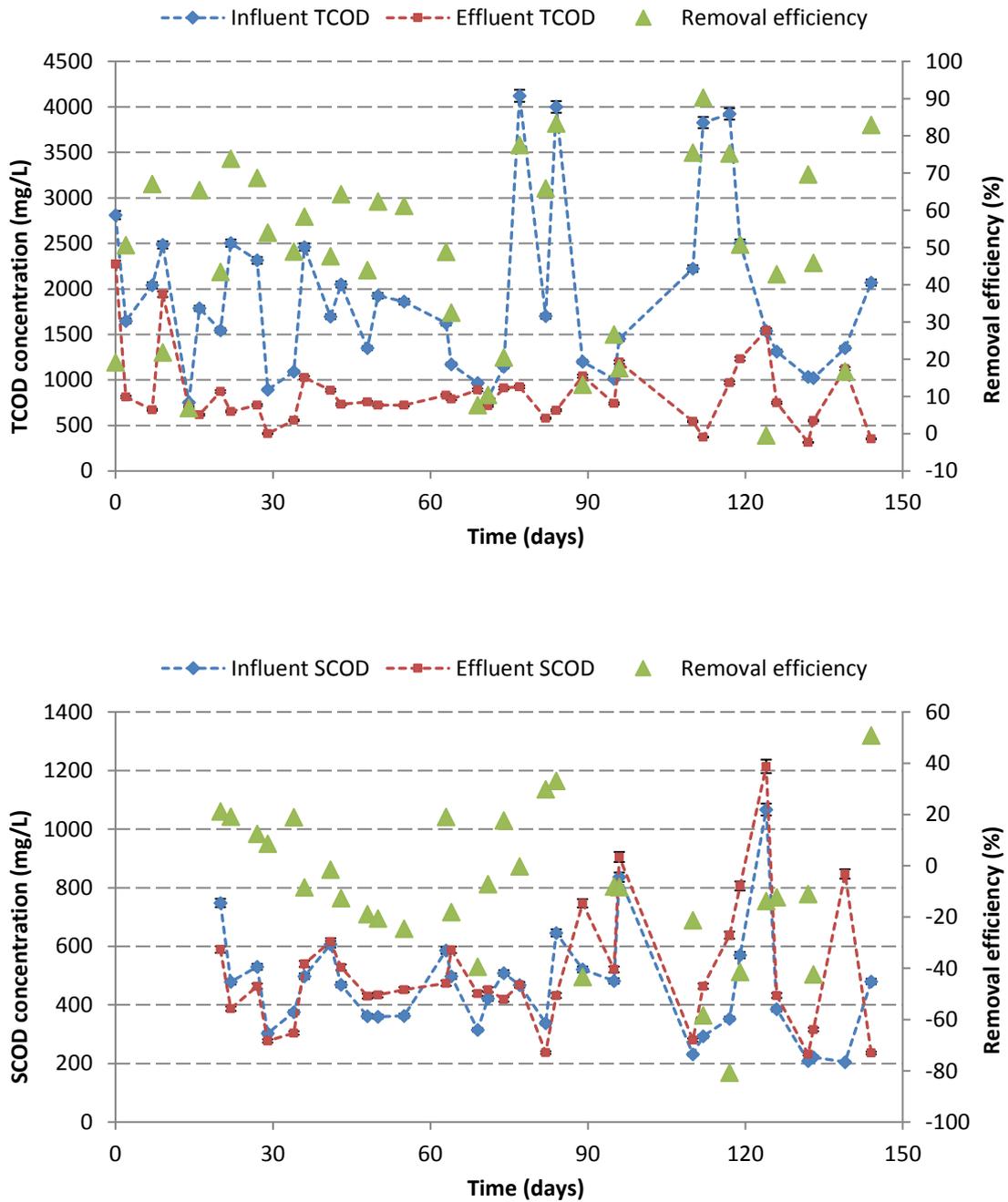


Figure 2. Evolution of MLSS (top), TCOD (middle) and SCOD (bottom) and the respective removal efficiency during continuous operation of the A-stage process (tests 1 to 6). **Error bars indicate standard deviation. The error bars were omitted when smaller than the marker.**

Between 50 and 90% MLSS could be removed in the A-stage process demonstrating the applicability of this compact treatment for industrial wastewater, which was not shown before. Furthermore, at influent MLSS greater than 2,000 mg/L, 80 to 90% of MLSS could

be removed regardless of the DO level. Despite the high fluctuation and presence of oil and grease the A-stage process performs significantly better than conventional PST that can only remove 50-55% of MLSS from raw sewage. This significant improvement was expected because the adsorption properties of activated sludge floc are favorable for wastewater with high concentrations of MLSS and colloidal particles (Diamantis et al., 2013, Zhao et al., 2000) and this was verified in this study with industrial wastewater. Entrapment of larger particles in the open structure of sludge flocs can also take place in carbon capture systems (Lim et al., 2015).

As it can be seen from Figure 2 (bottom) the SCOD removal efficiency in the A-stage process was low and Figure 3 showed that it decreased as DO in the sorption column was increased from 0.2 to 1 mg/L. When DO was 0.5 mg/L or higher, SCOD removal percentage was systematically negative. These results are very different from previous studies on municipal wastewater that reported 30% SCOD removal under optimum conditions (Zhao et al., 2000). The presence of oil and grease in the influent may have inhibited the adsorption of SCOD and entrapment of colloids in this study. High DO may also have caused hydrolysis of particulate COD to soluble COD or the shear effect caused by vigorous aeration may have resulted in the breakage of bioflocs leading to the release of soluble components. From the results, DO greater than 0.4 mg/L are therefore not recommended.

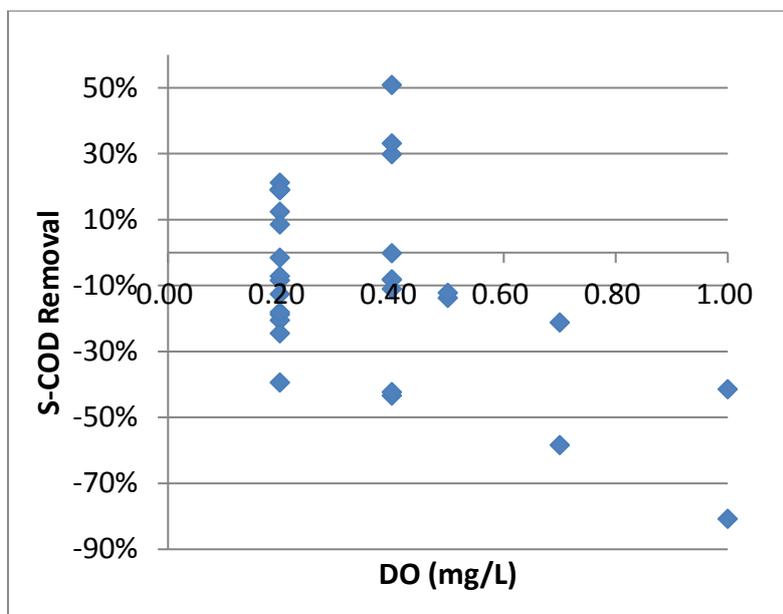


Figure 3. Effect of Dissolved Oxygen on SCOD removal percentage at DO in the range 0.2-1 mg/L (tests 1 to 6).

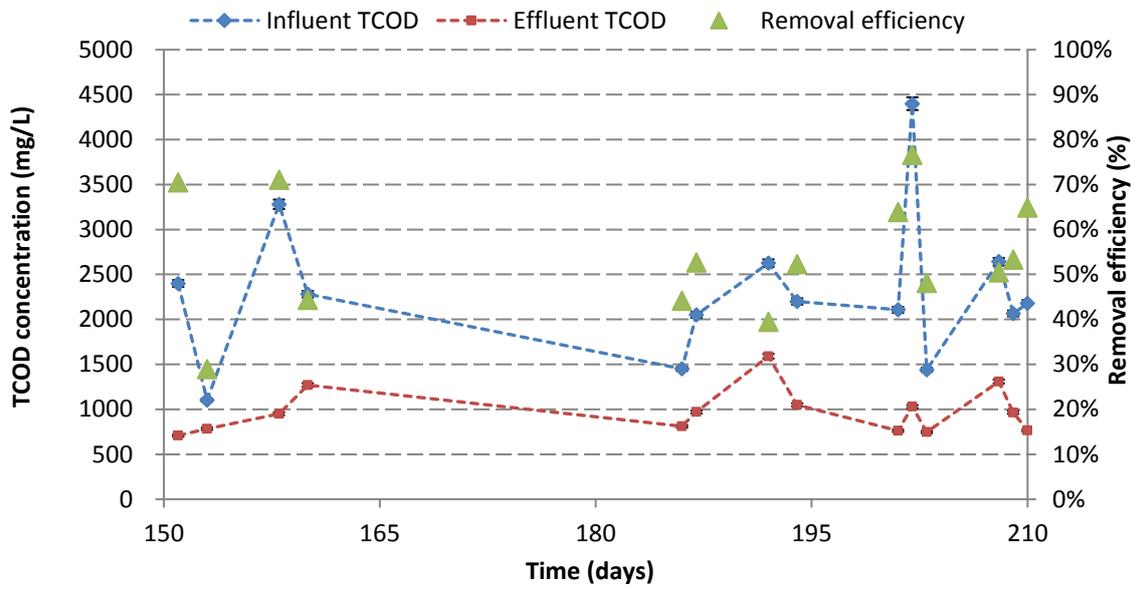
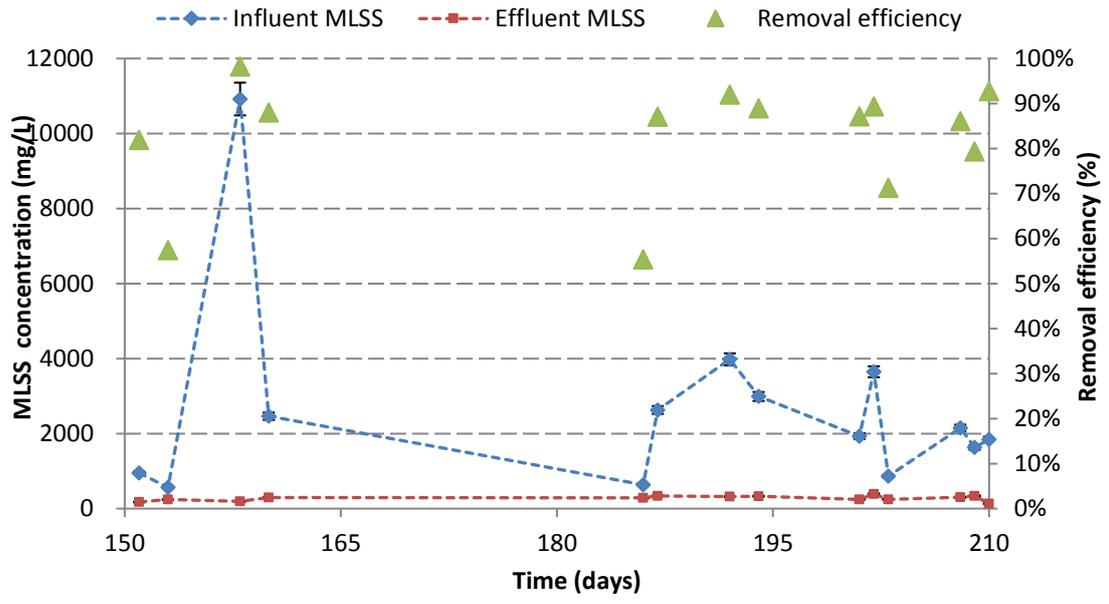
3.3. Effect of Fe^{3+} dosage

Raw data of MLSS, TCOD and SCOD from tests 7 to 10 with coagulant dosage are shown in Figure 4. The sorption column provided intimate contact between Fe^{3+} , influent MLSS and SCOD to investigate any benefit of Fe^{3+} dosing using real industrial wastewaters. DO was maintained at 0.4 (except for test 10 at 0.7 mg DO/L) as it was observed that higher DO were detrimental for SCOD removals. The TCOD removals were in the range 40-76%.

However, TCOD and MLSS removals greater than 90% were observed on certain days in this study which is not achievable by conventional PST. It has been reported that under optimal conditions TCOD removal in laboratory scale A-stage can be 70–80% (30% of it is SCOD), while MLSS removals can be as high as 80 to 95% (Zhao et al. 2000). Diamantis et al. (2013) reported 80% COD removal in a bench scale A-stage treating municipal wastewater with a

lower COD content (400–700 mg/L) than this study. However, previous studies in laboratories sometimes report only the best conditions and should therefore be interpreted with caution. Wett et al. (2014) reported 40–85% COD removal from a full scale A-stage unit which is similar to the pilot scale data in this study. Despite some occasional high removals, it seems therefore that the A-stage suffers from greater variability at larger scale in particular when treating industrial wastewater containing oils and grease. SCOD removals obtained by other researchers at laboratory scale could not be replicated in this pilot-scale study with real municipal-industrial wastewaters.

The large variability obtained in this study may be due to the high oil and grease content from industrial and municipal wastewater in South East Asia, but also from the sludge recycle from the A-stage clarifier to the sorption column. Oil and grease can inhibit the adsorption of SCOD and colloids even when Fe^{3+} was added because it will adsorb onto bioflocs preferentially due to hydrophobicity. This is consistent with several literature reports suggesting a poor settling performance of primary sludge and hence limiting application of the AB process (Jenkins et al. 2003; Frijns & Uijterlinde 2010). Better results could be obtained with an oil and grease trap placed in front of the sorption column.



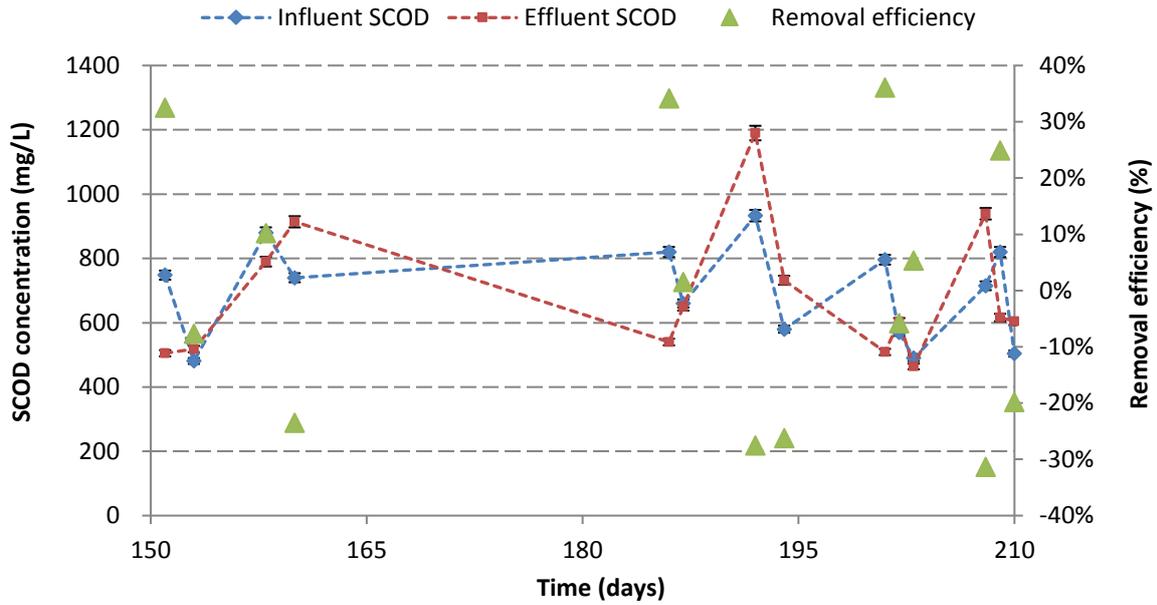


Figure 4. Evolution of MLSS (top), TCOD (middle) and SCOD (bottom) and the respective removal efficiency during continuous operation of the A-stage process with Fe^{3+} dosage (tests 7 to 10). Error bars indicate standard deviation. The error bars were omitted when smaller than the marker.

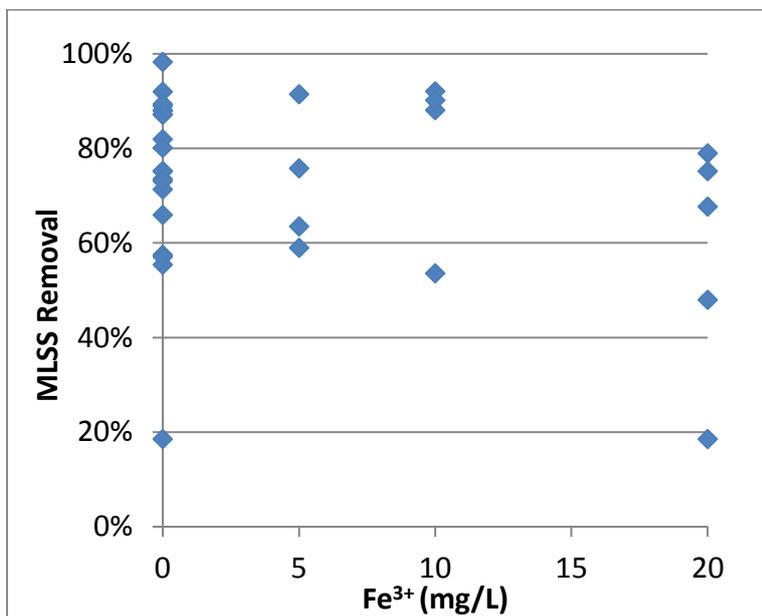


Figure 5. Effect of Fe^{3+} dosage on MLSS removal (Tests 1 to 10).

Figure 5 revealed that Fe^{3+} dosage did not result in better removal. Increasing DO to 0.7 mg/L in Test 10 did not have any significant effect. SCOD removal efficiencies highly fluctuated

from negative values to maximum of 50% regardless of presence of coagulant or not. This may be due to the particular nature of industrial wastewaters used in this study. **The high inorganic content of the spent sludge (VS/TS was in the range 24%-61%) can explain why it was not effective for SCOD adsorption.** Alternatively, SCOD could not be removed by biosorption due to the nature of the organics, or due to the short SRT used in this study.

Since the hydraulic retention time was maintained constant, the organic loading rate (OLR) varied according to the influent COD concentration. As shown in Figure 6, the OLR to the process had an impact on the MLSS removal. This is similar to Diamantis et al. (2013) results where the COD removal increased at OLRs in the range 5-20 kg COD/m³.day with municipal wastewater. It appeared from this study with industrial wastewater that high OLR (25-60 kg COD/m³.day) were favorable to remove MLSS. Up to 90% MLSS and 83% TCOD could be removed at an OLR of 36 kg COD/ m³.day. This represents a significant advance compared to the conventional **PST** that can only achieve 50-55% MLSS removals and 30-40% BOD removals at 2-4 hours HRT (Metcalf & Eddy, 2014).

When the OLR was below 20 kg/m³.day the MLSS was generally greater than 60% which makes the A-stage an interesting competing technology for the treatment of industrial wastewater compared to conventional primary clarifiers. At low OLR the activated sludge is prone to fragmentation due to an increase in water soluble EPS, while organic matter is desorbed from the floc and effluent quality is deteriorated (Guellil et al., 2001). Another reason is the lower strength wastewater (potentially diluted with rainfall). This is attributed to the ionic strength and divalent cation concentration of the raw wastewater.

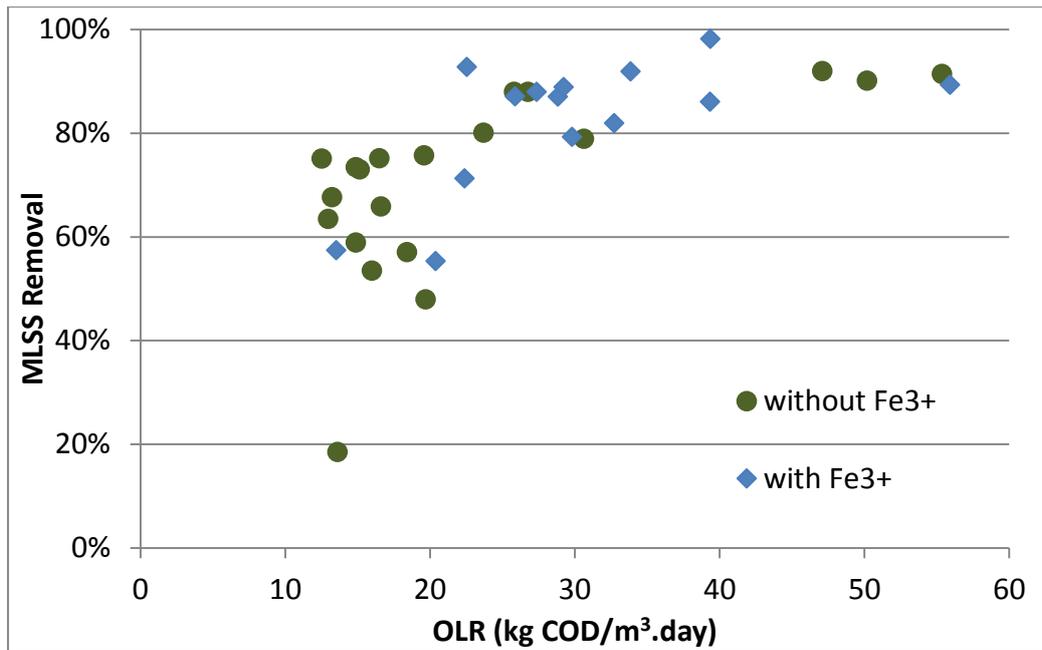


Figure 6. Effect of the Organic Loading Rate (OLR) on the MLSS removal with and without Fe³⁺ dosage (all data point in tests 1 to 10).

Considering the low HRT (2 hrs) and high OLR, it is evident that the removal mechanism is not biological degradation, but physical adsorption followed by settling. Indeed, biological degradation in high-rate activated sludge systems normally takes place at 2-3 kg COD.m⁻³d⁻¹ (Tchobanoglous et al., 2003) which was not the case in this study. Furthermore, it was demonstrated that the pre-treatment of industrial wastewater can take place in a very compact A-stage system, and can therefore be applied where land space is a constraint.

3.4. Spent sludge anaerobic methane potential and calorific value

In conventional wastewater treatment plants, anaerobic digestion is generally applied to mixture of primary and secondary (waste activated) sludge. But waste activated sludge is known to be more difficult to digest than primary sludge (Bougrier et al., 2007). For example, Kepp and Solheim (2000) reported a production of methane of 306 mL CH₄/g VS for primary sludge against 146-217 mL CH₄/g VS for secondary sludge. The proposed A-stage process configuration in this study considered the possibility of introducing sorption ahead of the aerobic process (B-stage) to concentrate organics from combined municipal-industrial wastewater and transfer carbon-rich biomass to the anaerobic digester, where high calorific value biomass can be recovered as methane. It is therefore important to confirm that the resulting sludge has a high calorific value and is indeed biodegradable and that the tested parameters such as DO did not affect methane production rate in a negative way. It is also important to monitor its methane potential for designing future full scale digester. During all phases of experimentation, the spent sludge (56 samples over 210 days) from the clarifier was analyzed for its methane potential (Figure 7) and calorific energy value (Supplementary material A1). The methane yield was in the range 70-340 mL CH₄/g VS with an average of 205 ± 56 mL CH₄/g VS. Based on a COD balance, a biodegradability of 30 ± 10% was found for this type of industrial sludge, which is not significantly different than that of the sludge (23.7%) taken from the full scale PST on the same site.

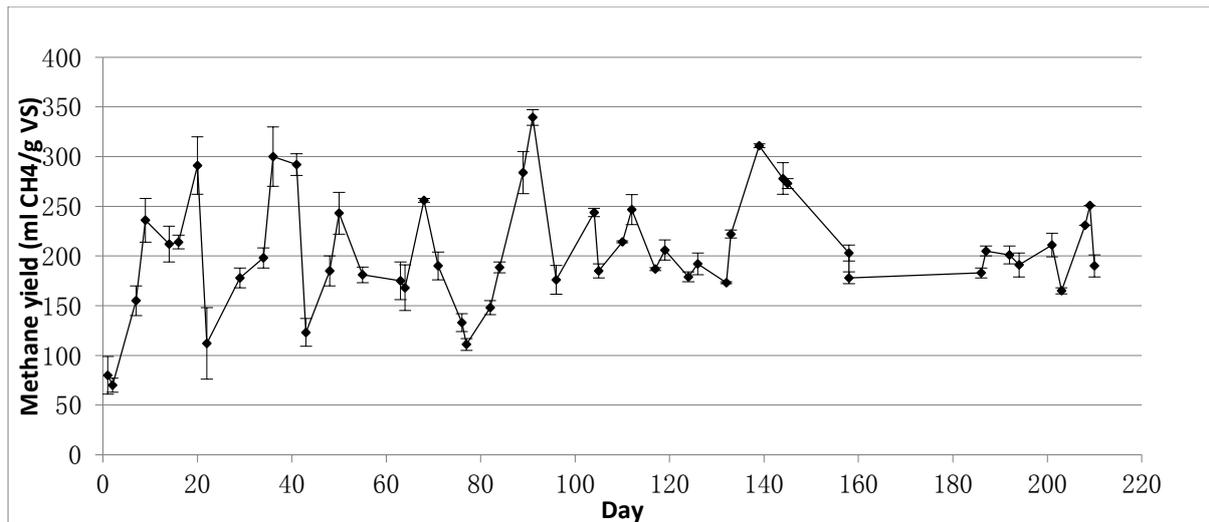


Figure 7. Methane yield of spent sludge. Error bars indicate the standard deviation.

Interestingly, in all the BMP tests methane production was completed in less than 2 weeks, which means that anaerobic digestion of this type of sludge could be carried out in much smaller digester than conventional digesters treating thickened waste activated sludge at 30 days HRT. The process has therefore the potential to channel more carbon to the anaerobic digester due to better MLSS and TCOD removal than conventional PST and results in a faster conversion to methane gas. At the end of the BMP test, the supernatant of digested sludge was analyzed for SCOD, ammonia and phosphate (supplementary material A2). The average SCOD, NH₃-N and PO₄³⁻-P were 210 mg/L, 530 mg N/L and 25 mg P/L. High ammonia and phosphorus concentrations in the centrate were expected due to their release under anaerobic conditions.

3.5 Electricity consumption

The details of electrical equipment used on the pilot plant are listed in Table 4. The average power consumption was 42.8 kWh/day and the average power consumption per treated water

volume was 1.82 kWh/m³. Despite satisfactory solids removal, in this study the methane gas from the A-stage sludge could cover at best 16% of the electricity requirements (assuming an electricity yield of 2.2 kWh_e/m³ CH₄ found in Foladori et al. 2010).

Table 4. List of electrical equipment used on the pilot plant and their specification.

Equipment	Specifications
Blower	Roots type blower 0.81 kW x 2, 10 Nm ³ /hr
Diffuser	Fine bubble diffuser (Ethylene Propylene Diene Monomer), D 250 mm
Mixer	Submersible mixing pump 0.55 kW x 1, 50 L/min
Influent pump	Submersible pump 0.37 kW x 2 with strainer
Sludge pump	Magnetic drive pump 0.18 kW x 1, 0.75 m ³ /hr
Chemical injection pump	Pulsing pump 0.02 kW x 2, Ferric chloride

4. Conclusions

After 6-months operation of an A-stage pilot plant treating combined municipal-industrial wastewater, it was found that more than 60% MLSS removal could be achieved in spite of high fluctuation in influent MLSS and COD concentrations which is remarkable considering the high strength wastewater. The process is operating at an overall HRT of 2 hours and is therefore very compact in size, suitable for land scarce countries or for decentralized applications. Typically 60 to 95% MLSS could be removed in the process at DO levels in the range 0.4-0.7 mg/L and when the influent MLSS was greater than 2,000 mg/L. TCOD removals greater than 60% were demonstrated by the process making it a promising alternative to conventional sedimentation tanks for the pre-treatment of industrial wastewaters. The spent sludge methane potential was on average 205± 56 mL CH₄/g VS.

5. Acknowledgments

The authors would like to thank the Public Utilities Board (PUB) of Singapore for financial support of this research.

6. References

- APHA 2012. *Standard Methods for the Examination of Water and Wastewater*, Washington D.C, American Public Health Association.
- Bougrier, C., Delgenès, J.P., Carrère, H. 2007. Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge. *Biochemical Engineering Journal*, **34**(1), 20-27.
- DIAMANTIS, V., EFTAXIAS, A., BUNDERVOET, B. & VERSTRAETE, W. 2013. Performance of the biosorptive activated sludge (BAS) as pre-treatment to UF for decentralized wastewater reuse. *Bioresource Technology*.
- Foladori, P. Andreottola, G. and Zigli, G. 2010. *Sludge reduction technologies in wastewater treatment plants*. London IWA Publishing.
- Frijns, J., Uijterlinde, C. 2010. Energy efficiency in the European water industry. A compendium of best practices and case studies. KWR and STOWA.
- GUELLIL, A., THOMAS, F., BLOCK, J. C., BERSILLON, J. L. & GINESTET, P. 2001. Transfer of organic matter between wastewater and activated sludge flocs. *Water Research*, **35**, 143-150.

- HAIDER, S., SVARDAL, K., VANROLLEGHEM, P. A. & KROISS, H. 2003. The effect of low sludge age on wastewater fractionation (S-S,S-I). *Water Science and Technology*, 47, 203-209.
- HERNÁNDEZ LEAL, L., TEMMINK, H., ZEEMAN, G. & BUISMAN, C. J. N. 2010. Bioflocculation of grey water for improved energy recovery within decentralized sanitation concepts. *Bioresource Technology*, 101, 9065-9070.
- Jenkins, D., Richard, M.G., Daigger, G.T. 2003. *Manual on the Causes and Control of Activated Sludge Bulking, Foaming, and other solids separation problems. 3rd ed ed. London IWA Publishing.*
- KEIDING, K. & NIELSEN, P. H. 1997. Desorption of organic macromolecules from activated sludge: Effect of ionic composition. *Water Research*, 31, 1665-1672.
- Kepp, U., Solheim, O.E. 2000. Thermo dynamical assessment of the digestion process. *5th European Biosolids and Organic Residuals Conference*, Wakefield, UK.
- LI, A.-J., ZHANG, T. & LI, X.-Y. 2010. Fate of aerobic bacterial granules with fungal contamination under different organic loading conditions. *Chemosphere* 78, 500-509.
- LIAO, B., DROPPA, I., LEPPARD, G. & LISS, S. 2006. Effect of solids retention time on structure and characteristics of sludge flocs in sequencing batch reactors. *Water Res.*, 40, 2583-2591.
- LIM, C.-P., ZHANG, S., ZHOU, Y. & NG, W. J. 2015. Enhanced carbon capture biosorption through process manipulation. *Biochemical Engineering Journal*, 93, 128-136.
- OWENS, W. F., STUCKEY, D. C., HEALY, J. B., YOUNG, L., Y & MCCARTY, P. L. 1979. Bioassay for Monitoring Biochemical Methane Potential and Anaerobic Toxicity. *Water Research*, 13, 485-492.
- Metcalf & Eddy, AECOM 2014. *Wastewater engineering: treatment and resource recovery*, page 392. Fifth Edition. McGraw-Hill. New York.

- TCHOBANOGLIOUS, G., BURTON, F. L. & STENSEL, H. D. 2003. *Wastewater engineering: treatment and reuse*, McGraw-Hill.
- TIAN, X., TRZCINSKI, A., CHONG, W., LIN, L. & NG, W. J. 2014. Insights on the solubilization products after combined alkaline and ultrasonic pre-treatment of sewage sludge. *Journal of Environmental Sciences*, DOI : 10.1016/j.jes.2014.07.024.
- Trzcinski, A., Ganda, L., Kunacheva, C., Zhang, D. Q., Lin, L. L., Tao, G., Lee, Y. and Ng, W. J. 2016. Characterization and biodegradability of sludge from a high rate A-stage contact tank and B-stage membrane bioreactor of pilot-scale AB system treating municipal wastewaters. *Water Science & Technology*, DOI: 10.2166/wst.2016.346.
- VOGELAAR, J. C. T., DE KEIZER, A., SPIJKER, S. & LETTINGA, G. 2005. Bioflocculation of mesophilic and thermophilic activated sludge. *Water Research*, 39, 37-46.
- WANG, Z., LIU, L., YAO, J. & CAI, W. 2006. Effects of extracellular polymeric substances on aerobic granulation in sequencing batch reactors. *Chemosphere*, 63, 1728-1735.
- WETT, B., HELL, M., JIMENEZ, J., TAKACS, I., BOTT, C. & MURTHY, S. 2014. Control measures for improved high-rate carbon removal (A-stage). *Singapore International Water Week*. Singapore: IWA.
- YU, J., LAN, X., SREERAMA, S., WIKRAMANAYAKE, R., KNUAF, R., LIU, W., JORDAN, E. & HU, J. 2014. An Energy Saving Solution for Water Reclamation - A Hybrid Process Combining Bio-Sorption and Anaerobic Digestion- Process Concept and Bio-sorption Using Anaerobic/Aerobic Sludge Mixtures. In: CONFERENCES, I. (ed.) *Singapore International Water Week*. Singapore.
- ZHANG, Z.-B., ZHAO, J.-F., XIA, S.-Q., LIU, C.-Q. & KANG, X.-S. 2007. Particle size distribution and removal by a chemical-biological flocculation process. *Journal of Environmental Sciences-China*, 19, 559-563.

ZHAO, W., TING, Y. P., CHEN, J. P., XING, C. H. & SHI, S. Q. 2000. Advanced primary treatment of waste water using a bio-flocculation-adsorption sedimentation process. *Acta Biotechnologica*, 20, 53-64.