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ENHANCED NITRIFICATION BY IMMOBILIZED CLINOPTILOLITE IN AN ACTIVATED SLUDGE

Chang Gyun Kim†, Hyung Sool Lee*, and Tai Il Yoon
Division of Environmental & Geosystem Engineering, Inha University
*Regional Research Center for Coastal Environments of Yellow Sea, Inha University,
Inchon 402-751, Korea

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Abstract : Clinoptilolite amended activated sludge (CAAS) was developed to improve nitrification in treating municipal wastewater. Its performance was compared to that of a conventional activated sludge (AS) as a control. In addition, the sludge characteristics were comparatively observed with regard to floc size distribution, settlability and dewaterability. CAAS showed that nitrification was achieved as high as 90% for 0.28 kg total Kjeldahl nitrogen (TKN)/m^3·day at 10 days of solid retention time (SRT). In comparison, nitrification from the AS was accomplished at approximately 20%. For 20 day SRT, there was no significant differences in the degree of nitrification between the two processes. However, a significant sludge bulking was observed from the control, which in turn attributed to deteriorating its sludge characteristics such as initial settling velocity (ISV), sludge volume index (SVI) and specific resistance. Increasing the TKN load to 0.42 kg/m^3·day for 20 day of SRT, the nitrification efficiency of the control was declined as low as 53%. Conversely, the nitrification from the CAAS was unvaryingly achieved at the highest of 90% without any occurrence of filamentous bacteria. Floc size observed from the CAAS was greater by a factor of four than that of the AS. For 10 day of SRT, ISV was 11 m/hr for the CAAS and 5 m/hr for the AS. For 20 day of SRT, it was not varied from the CAAS, but it was considerably declined for the AS showing 0.7 m/hr. Specific resistance of sludge taken from the CAAS was observed at 2.2×10^8 m/kg, that was lower by four order of magnitude than that of the AS. It was thus concluded that, without significant modification, simply amending clinoptilolite into an existing activated sludge could successfully enhance the performances of its nitrification with sludge property being ameliorated.

Key Words : activated sludge, clinoptilolite, nitrification, sludge property

INTRODUCTION

In the past 20 years, activated sludge processes have been significantly improved throughout a number of investigations.[1-3] Powdered activated carbon (PAC) has been applied for the activated sludge process to enhance nitrification and sludge characteristics by providing an increased surface area for microorganisms to grow on.[1] Moreover, PAC addition into the conventional activated sludge process was attempted to remove nonbiodegradable organic matters.[4] For their experiments, their enlarged surface area and adsorption property were only used such that nitrification could only be improved as high as 60%. Rigid polyethylene as biomass carriers was introduced into the activated sludge system to increase mixed liquor suspended solids (MLSS) up to 75%, but filamentous microorganisms were increasingly found in the effluent. Suspended marble particles were used to promote nitrification in the activated sludge as autotrophs-filmed layer formed around

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† Corresponding author
E-mail: cgk@inha.ac.kr
Tel: +82-32-860-7561, Fax: +82-32-865-1425

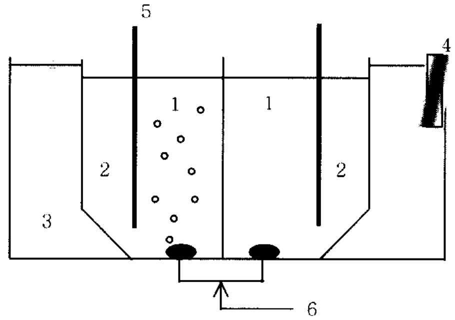
the marble particles can implement nitrification on varying pH and alkalinity.[5] However, its application simply used alkaline property of marble particles while nitrification efficiency was not varied from the conventional one. Bowen and Dempsey[6] found that dosing levels of $Al_2(SO_4)_3$, $FeCl_3$ and SiO_2 could comparatively improve the metabolism of microorganisms relevant to nitrification in the activated sludge. Such investigations simply addressed that expanded surface area of adding inorganic materials was the most important initiative for nitrification being improved.[3,5,7]

For talc addition, Cantet et al.[8] revealed that SVI was lowered by half compared to that of the control, coincidentally same extent of specific resistance being decreased. Moreover, talc addition could have sludge concentrated up to 44,000 mg/L, which equivalent to approximately 40% reduction of SVI rather than that of the control.[7] Alexis and Willy[3] used both talc and polymer to comparatively thicken the sludge volume by a factor of two employing 20 mg/L of polymer and 8.5 g/L of talc. Rasmussen et al.[9] attempted to increase sludge settleability by adding mixtures of talc and chlorite. Moreover, adding clay could increase sludge settleability by a factor of ten compared to that of the control.[10] However, these investigations were solely attempted to improve sludge characteristics.

In this study, clinoptilolite was investigated for a potential fluidized media in an activated sludge because it features a higher cationic exchange capacity on ammonium ion among others, which can consequently improve the degree of nitrification. High degree of cationic exchange capacity can make nitrifiers more readily activated in nitrification.[11] In the following, sludge characteristics were comparatively observed on varying SRT.

MATERIAL AND METHODS

Bench scale of activated sludge equipped with 5 L of aeration tank and 2.5 L of clarifier were either used for a test reactor where clinoptilolite introduced or employed for the control as described in Figure 1. Cationic exchange capacity of clinoptilolite was 1.28 meq/g and its size was ranged from 10 to 100 μm of which effective diameter was 19.75 μm. Synthetic wastewater was prepared for the experiment as shown in Table 1. The reactors were inoculated with sludge taken from a domestic wastewater treatment plant. Nitrification was conducted at 20(±2)°C while dissolved oxygen (DO) was maintained between 3 and 5 mg/L. For the purpose, industrial grade of air in a cylinder was supplied. Bicarbonate buffer was sufficiently introduced at 300 mg/L as $CaCO_3$ to the reactor, thereby pH being ranged from 7.6 to 7.8. During test of period, two experimental parameters (i.e. SRT and TKN load) were investigated under constant



1. aeration tank (5 L)
2. sedimentation tank (2.5 L)
3. water jacket
4. temperature controller
5. baffle
6. air supply

Figure 1. Schematic diagram of biological reactor used in the experiment.

Table 1. Compositions of lab prepared synthetic wastewater used in the test

Components	Concentration (mg/L)
Glucose	50
Glutamate	80
CH_3COONH_4	96
NH_4Cl	50
K_2HPO_4	44
KH_2PO_4	40
$MgSO_4 \cdot 7H_2O$	24
$FeCl_3 \cdot 6H_2O$	0.12
$CaCl_2$	2.4
$NaHCO_3$	500

organic load of 1.0 kg chemical oxygen demand (COD)/m^3·day and 6 hr of hydraulic retention time (HRT). SRT was varied at 10 day for 0.28 kg/m^3·day of TKN and 20 day for 0.42 kg TKN/m^3·day. SRT was correctly controlled as nominal amount of sludge was daily wasted. To get more critical SRT, suspended particles in the effluent were filtered with 0.45 μm of membrane filter and then returned them to the reactor. For assessing any possible inhibition against nitrification efficacy as reported by Barnes and Bliss,[12] 50 mg/L of peptone was introduced to both reactors.

200 mg/L of clinoptilolite (i.e., influent basis) was daily dosed in the reactor at 10 day of SRT until approximately 14,000 mg/L of MLSS was obtained. After that, 4,000 mg/L of the clinoptilolite in the aerator was maintained. Amount of wasted sludge was incinerated at 500°C, which was then added into the reactor.[13] In the mean time, physical properties of sludge taken from both reactors were comparatively observed on sludge settling characteristics and dewaterability.

Analysis

Physical characteristics of clinoptilolite were analyzed by X-ray diffraction (X'pert MPD, Philips) and inductively coupled plasma mass spectroscopy (SPQ 9000, Waters). Microbes grown on clinoptilolite were optically observed by a microscope (Nikkon) at a 600 magnification and scanning electron microscope (Hitach S-4200). Cationic exchange capacity on clinoptilolite was investigated as 20 g of clinoptilolite was contacted with 50 and 100 mg/L of NH_4Cl, respectively, for 24 hr.

Floc size was observed by Coulter Multisizer (Coulter Electronics Limited, U.S.A.) after the sample taken from the reactor was introduced into 1% of NaCl solution. Sludge settling property was determined as ISV was obtained for 5 minutes on 1 L of sludge in a volumetric mass cylinder.[14] The specific resistance of settled sludge was obtained by employing a Toyo 5A filter in the same manner as given by a time-to-filter method.[14]

The activity of nitrifiers was evaluated by nitrification rate (NR) at 20°C, which was observed for 400 mL of mixed liquor taken from reactor followed by placing it into 2 L of beaker, where 20,000 mg/L of NH_4Cl was diluted into 50 mg/L of NH_4^+-N. In the following, diffused air and bicarbonate buffer were added into the beaker so that DO and pH should be maintained at 3 to 4 mg/L and 7.2 to 7.5, respectively. In addition, activity of heterotrophic microbes was determined by endogenous oxygen uptake rate (OUR) as DO decline was monitored at every 30 sec for 300 mL of 4,000 mg/L of MLSS in BOD bottle (YSI 50).

The sample was taken at every 30 min and then various water quality parameters were obtained. TKN and NH_4^+-N were determined by macro-Kjeldahl and titrimetric method, respectively.[14] The concentrations of NO_2^--N and NO_3^--N were observed by using DX-500 System Ion Chromatography (Dionex). For a while, concentrations of COD, MLSS and MLVSS were measured in the same manner as given by Standard Methods.[14]

RESULTS AND DISCUSSION

Physical Properties of Clinoptilolite

XRD investigation demonstrated that zeolite was consisted of $CaNaK_4AlSi_5O_{12} \cdot 24H_2O$ that was one of the Heulandite groups as given in Figure 2. It was dominantly composed of SiO_2 and Al_2O_3 as illustrated in Table 2. The cationic exchange capacity of clinoptilolite was observed

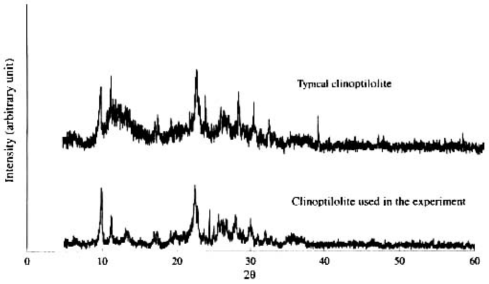


Figure 2. XRD patterns on zeolite employed in the test.

Table 2. Physical characteristics on clinoptilolite employed in the test

Mean diameter (μm)	19.75
C.E.C (meq/L)	8.4
Specific gravity (g/cm^3)	2.42
SiO_2	58.48
Al_2O_3	15.14
Fe_2O_3	3.12
PbO	0.022
MoO_3	0.058
MnO	0.10
MgO	1.96
CaO	3.05
Ig-loss	12.84

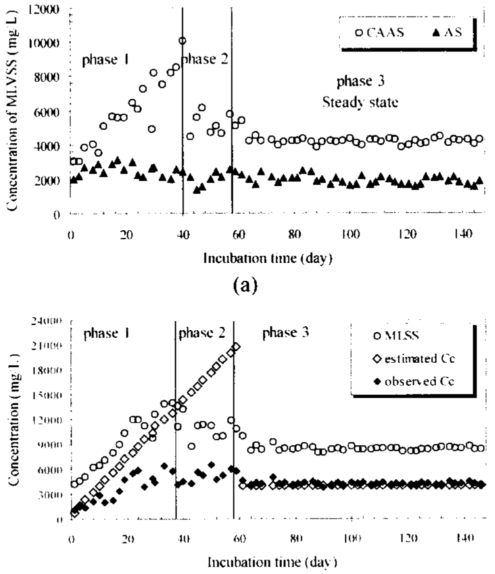
Concentration of elements (wt%), Ig-loss: Ignition loss

at 8.4 meq/L, which was similarly reported in Nitrogen Control Manual.[15]

The Effect of Zeolite on Microbial Growth

Microbial concentration in the CAAS was proportionally increased as clinoptilolite was daily dosed at 200 mg/L until it reached 10,100 mg·MLVSS/L. It was higher by a factor of four than that of the AS as shown in Figure 3(a). At that time, dosing clinoptilolite was terminated. Since then, MLVSS concentration was gradually reduced as low as 4,287 mg/L after 20 day of incubation period, thereafter significant variation of MLVSS concentration was not observed. The decrease of MLVSS concentration may attribute to missing of the role of seeding for bioflocs being intensively agglomerated as the addition of clinoptilolite was interrupted. At the same time, clinoptilolite concentration was peaked at 5,880 mg/L as shown in Figure 3(b) for 40 day of incubation (phase 1). For a while, it was reduced to as low as 4,000 mg/L for 20 day of incubation that was then consistently retained during remaining test of period. To calculate biomass solely filmed on clinoptilolite, it was assumed that biomass observed from the AS would be present in free space in liquid phase, therein differences of MLVSS concentration between the CAAS and the AS was 2,680 mg/L. It can be consequently estimated that biomass attached on clinoptilolite was 670 mg·MLVSS/g·clinoptilolite (phase 3).

As shown in Figure 4, SEM observed dense bio-flocs on clinoptilolite in the CAAS dominantly consisting of *Colurella* and *Monostyla* (optically observed by a microscope (Nikkon) at a 600 magnification), which demonstrated that they were more activated as a predator against carbonaceous utilizing bacteria under low carbonaceous loads. In addition, optical microscope observance revealed that a number of protozoa such as *Aspidisca, Oxytricha, Philodina,*



(a)

(b)

Figure 3. Biomass and clinoptilolite concentration in both units, A (MLVSS between CAAS and AS); B (MLSS and clinoptilolite concentration in the CAAS), phase 1 (200 mg/L of clinoptilolite was daily added; phase 2 (after addition of clinoptilolite was stopped); phase 3 (steady state).

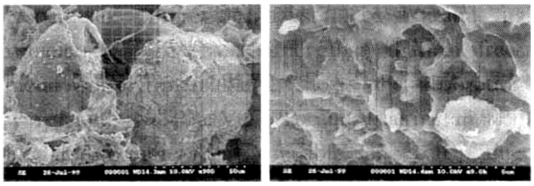


Figure 4. SEM photos on microbes embedded by clinoptilolite.

Colurella, Monostyla, Nais sp. and *Vorticella* were present, indicating the system being reliably operating in attached or crawling type of microcosms showing stable effluent water quality sustained. In comparison, it was found for the AS to a limited diversity of micro-organisms such as *Heterotrichida* and *Vorticella*, especially *Sphaerotillus* and *Beggiatoa* that were the major bulking species found at 20 day of SRT.

Organic Compounds Removal

As shown in Figure 5, the two units showed that soluble chemical oxygen demand (SCOD) was equally decomposed up to approximately 90%, which was consistent with the result obtained by Piirtola et al.[16] It suggested that there were no any competency for attracting sites for carbonaceous utilizing microbes grown on clinoptilolite particle. It thus attributed to the same extent of SCOD utilized in the CAAS compared to that of the AS. It was also demonstrated by the comparison of heterotrophs activity decomposing SCOD between two systems. It was ranged from 2.8 to 12.3 mg·SCOD/g MLVSS/day in the CAAS, while it was slightly highly observed at 4.9 to 15.8 mg·SCOD/g·MLVSS/day in the AS. It also indicated that clinoptilolite itself may not be related with improving metabolism of those heterotrophic bacteria in the CAAS. For a while, total chemical oxygen demand (TCOD) was greatly removed for the CAAS at ranging from 90 to 95%, whereas it was variably degraded for the AS in between 43 to 92%. Such significant variation of removal efficacy observed from the AS was attributed to a poor separation of the sludge at the extended SRT of 20 day. It attributed to predominant bulking colonies of pinned flocs such as *Sphaerotillus* and *Beggiatoa* evidently occurred from the AS.

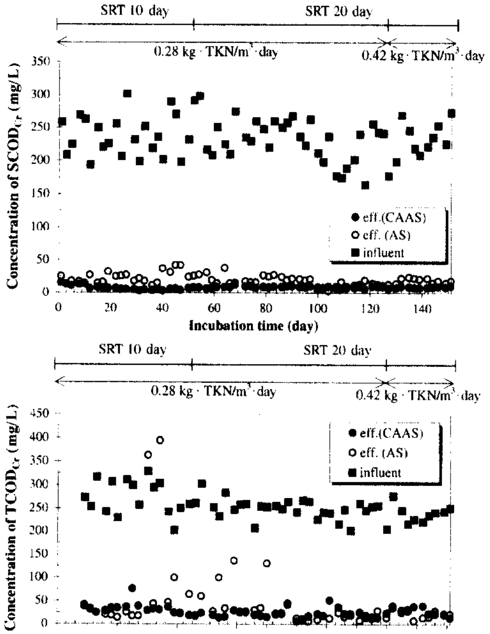


Figure 5. Comparison of COD being removed between the CAAS and the AS according to different SRT of 10 and 20 day.

Nitrification

The nitrification experiment was conducted based on a theory given by Semmens[17,18] and Olah[19]. They suggested; 1) zeolite is activated as a seed forming a dense floc around, 2) nitrification is occurred through the interface between zeolite (Z) and its contacting bio-floc. The nitrification mechanism was thus implied as given below;

$$NH_4^+\text{-N} + Z\cdot Na^+ \Rightarrow Z\cdot NH_4^+\text{-N} + Na^+ \quad (1)$$

$$Z\cdot NH_4^+\text{-N} + Na^+ + 2O_2 \Rightarrow Z\cdot Na^+ + NO_2^-\text{-N} + 2H_2O \quad (2)$$

$$NO_2^-\text{-N} + 0.5O_2 \Rightarrow NO_3^-\text{-N} \quad (3)$$

Overall reaction : $NH_4^+\text{-N} + 2.5O_2 \Rightarrow NO_3^-\text{-N} + 2H_2O$ (4)

As noted by equation (4), it confirmed that nitrification rate was not dependent upon zeolite itself, but immediately depending upon ammonium exchange capacity and DO concentration.[17] It simply means that an ammonium ion can be readily exchanged by sodium ion on clinoptilolite particle, thereby quickly would move through a contacting biofilm of nitrifiers. Figure 6 showed that nitrification was comparatively observed between the CAAS and the AS at 0.28 kg·TKN/m^3·day for 10 day of SRT, while peptone inhibition was given at 50 mg/L. The inhibition implied reduced nitrification to 43% in the CAAS. On the contrary, it was seriously plummeted to 7% in the AS. Barnes and Bliss[12] also found that 10 mg/L of peptone can decrease nitrification less than 60%.

Extending SRT to 20 day, the nitrification in the AS was gradually increased for 100 day of incubation that consequently approaching to the same degree of nitrification as those in the CAAS ranging from 56 to 70%. It indicates that the extended SRT was led to overcoming nitrification restriction caused by inhibitory substances given in the AS.[20] Subsequently, high TKN load of 0.42 kg/m^3·day was simultaneously introduced to both units for 20 day of SRT. The extent of nitrification was unvaryingly sustained for the CAAS showing 77%, but it was decreased for the AS down to 50%. It simply means that the CAAS in high concentration of nitrifying bacteria present around clinoptilolite can come up with higher loading of TKN.[11,21]

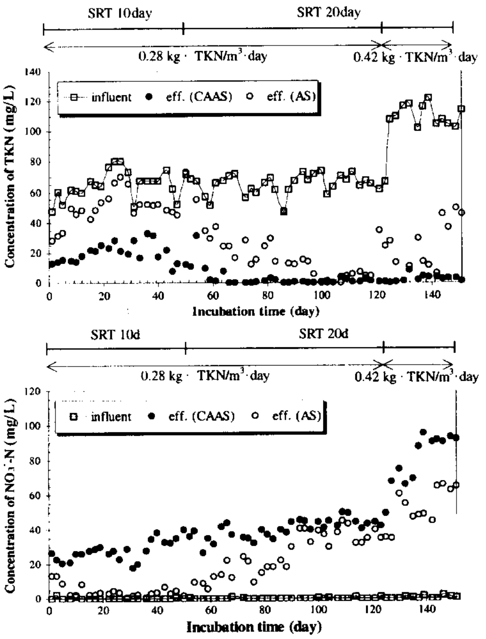


Figure 6. Comparison of nitrification between the CAAS and the AS according to different SRT of 10 and 20 day. 50 mg/L of peptone introduced for SRT 10 day while increased TKN load of 0.42 kg TKN/m^3·day given for SRT 20 day.

Apart from, nitrification rate (NR) was observed for two reactors at different SRT. For 10 day of SRT, NR for the AS was obtained at 0.05 to 1.34 mg·NO_3^--N/g·MLVSS·day. On the contrary, higher NR was observed for the CAAS at 0.28 to 1.75 mg·NO_3^--N/g·MLVSS·day even though 50 mg/L of peptone was introduced as mentioned before. It indicates that microbes attached on clinoptilolite is less inhibited by peptone than those in the solution by the fact that peptone in the solution is hardly adsorbed onto clinoptilolite. Adam et al.[2] also found that dosing of powdered activated carbon in activated sludge can improve nitrification up to 30% compared to that of control, even though 0.7 and 1.4 mg/L of cyanide, non-adsorbable nitrification inhibitor, was introduced in the systems. It was also found that carrier materials with ion exchangeable capacity can resist high concentration of inhibitory compounds being introduced beyond the resisting level against microbes metabolism[22] whose microorganisms were more resistant to antimicrobial agents by hundreds of times than the same cultures grown in suspended solution.[23] Subsequently, NR was observed on increasing TKN load to 0.42 kg/m^3·day for 20 day of SRT. It was gradually increased for the AS up to 4.03 mg·NO_3^--N/g·MLVSS·day which was consequently comparable with that in the CAAS ranging from 3.57 to 6.62 mg·NO_3^--N/g·MLVSS· day. A relative similar degree of NR achieved from the CAAS may be resulted from the less increased nitrate formation rate (oxidized mg·NO_3^--N/day) being divided by higher amount of biomass. Green et al.[24] also suggested that ammonium oxidation rate should be accordingly decreased when microbial concentration is increased. Consequently, it further demonstrated that increased nitrifying biomass grown on activated carbon would escalate NR.[21]

Table 3 summarized the effect of clinop

Table 3. Evaluation of nitrification performances in terms of nitrification efficiency, nitrification rate and nitrification capacity for both reactors with regard to different SRT

Reactors	CAAS		AS	
STR(day)	10	20	10	20
Nitrification efficiencies (%)	29-67 [43±7]	61-91 [77±8]	1-28 [7±5]	37-60 [50±8]
NR(mg·NO_3^--N/ g·MLVSS·day)	0.28-1.75 [0.92±0.28]	2.05-3.98 [3.37±0.53]	0.05-1.37 [0.35±0.26]	3.52-6.62 [5.29±0.95]
NC(mg·NO_3^--N/L·day)	21.6-193 [134±21.6]	237-458 [388±60.9]	3.07-63.8 [20.4±13.0]	169-318 [254±45.6]

AS : conventional activated sludge, CAAS: clinoptilolite amended activated sludge, NR: nitrification rate expressed as mg·NO_3^--N/g·MLVSS·d, NC: nitrification capacity expressed as mg·NO_3^--N/L·d, [ ]:data of fifteen experiments with averaged and standard deviation.

tilolite addition for improving nitrification in terms of nitrification efficiency, rate and capacity.

The nitrification performance could be well described by nitrification capacity expressed as mg·NO_3^--N/L·day reflecting biomass from NR. For SRT 10 day, nitrification capacity in the CAAS was greater by ten times than that of the AS. Likewise, for SRT 20 day, it showed 203 mg·NO_3^--N/L·day in the CAAS, which further increased to 458 mg·NO_3^--N/L·day in response to TKN load being elevated to 0.42 kg/m^3·day. In comparison, it was rather decreased for the AS to be 318 mg·NO_3^--N/L ·day.

Physical Characteristics of Sludge

A number of investigations have reported that sludge dewaterability and settleability were varied depending upon floc size distribution and its mean diameter.[25~30] It was thus assessed such characteristics for sludge taken from two units at 10 and 20 day of SRT, respectively. Figure 7 distinguished the difference of floc size distribution for the samples taken from both units. It showed that the size observed from the CAAS was greater by a factor of four than that of the AS. As SRT being extended to 20 day, floc size was gradually increased from 15.16 to 19.82 μm as shown in Table 4. Likewise, flocs occurring from the AS were escalated from 12.82 to 19.82 μm. It was identically consistent with the result reported by Knocke and Zentkovich,[31] who observed that floc size was proportionally grown on responding to a prolonged SRT.

Aside from, ISV and SVI as given in Table 4 evaluated settling properties of sludge for different SRT. For 10 day of SRT, ISV was observed at as high as 11 m/hr for the CAAS, while SVI was ranged from 50 to 80 mL/g. In contrast, it was reduced for the AS as low as 5 m/hr, whose SVI was ranged from 80 to 100 mL/g. It was consistent with the investigation performed by Rasmuseen et al.,[9] who demonstrated that given seed materials, such as talc, clay and inorganic coagulants, could improve settling velocity by a factor of two as floc density being ameliorated.

For 20 day of SRT, the sludge obtained from the CAAS showed the same settling characteristics as observed for 10 day of SRT. However, it was considerably declined for the AS in terms of ISV to 0.7 m/hr and SVI to 380 mL/g. It was attributed to the occurrence of filamentous bulking due to extended SRT as

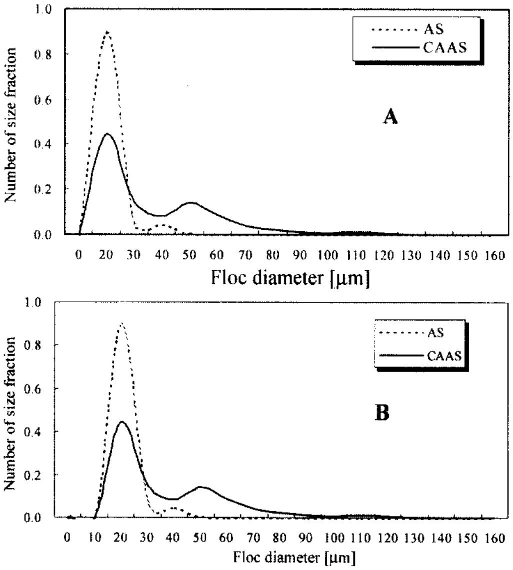


Figure 7. Floc size distribution of sludge taken from both units according to various SRT, A (10 day SRT); B (20 day SRT).

Table 4. Comparison of sludge properties between AS and CAAS according to different SRT

	SRT(day)	10	20
AS	D_{p50}(μm)	12.82	12.82
	Initial velocity (m/hr)	$3.9(\pm 1.01)^a$	$84(\pm 11.7)$
	SVI (mL/g)	$87(\pm 12.4)$	$265(\pm 110)$
	α (m/kg)	3.6×10^{12} $(\pm 3.43\times10^{12})$	8.5×10^{12} $(\pm 5.35\times10^{12})$
CAAS	D_{p50}(μm)	12.82	12.82
	Initial velocity (m/hr)	$10.8(\pm 0.58)$	$10.2(\pm 1.63)$
	SVI (mL/g)	$53(\pm 19.2)$	$61(\pm 28.6)$
	α (m/kg)	8.7×10^{8} $(\pm 5.15\times10^{8})$	2.1×10^{11} $(\pm 3.61\times10^{11})$

AS: conventional activated sludge process, CAAS: clinoptilolite amended activated sludge process, D_{p50}: mean diameter of biofloc, SVI: sludge volume index, Initial velocity: settling velocity observed at the first for five minutes, α: specific resistance, a: standard deviation.

noted previously even though their D_{p50} identically showed at 12.82 μm. The enhancement of settling property for the CAAS may ascribe to seeding of clinoptilolite particles more densely agglomerated.

In the following, sludge dewaterability was estimated for two units at different SRT by determining specific resistance as given in Table 4. For 10 day of SRT, it was observed for the CAAS at 2.2×10^8 m/kg that was lower by four orders of magnitude than that of the AS. The specific resistance obtained from the CAAS was not significantly differed from that observed for the pure zeolite sample showing between 10^7 and 10^8 m/kg. It indicates that a mass of bio-film produced around the clinoptilolite surface made no influence on its intrinsic dewatering property. Further increase of SRT to 20 day, sludge dewaterability was more deteriorated for the CAAS by about three order of magnitude than that of 10 day of SRT. It may ascribe to the increment of biomass in response to SRT being extended. In comparison, it was not significantly varied for the AS depending upon SRT showing approximately 10^{12} m/kg of specific resistance.

CONCLUSIONS

Clinoptilolite addition to conventional AS system can secure a consistent nitrification, regardless of the inhibition of peptone and high load of nitrogen implied. The improved nitrification in the CAAS ascribes to a continuing ammonium ion exchange capacity, which leads to providing the correspondingly increased colonies of nitrifiers. However, clinoptilolite addition does not influence the significant removal of soluble organic compounds.

Sludge produced from the CAAS can be considerably dewatered with low water content after it was separated in a shortened settling time requirement. The increased settling velocity was invariably sustained for an extended SRT of 20 day. It was apparent that simple rearrangement of the system in clinoptilolite will cope with reinforced regulations in the effluent water quality of nitrogen compound and subsequent eutrophication of water resources.

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