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Enhanced aerobic sludge granulation with layered double hydroxide

Jizhi Zhou[1], Haoyuan Sun[1], Xiangling Li[1], Guangren Qian[1], Jianyong Liu[1,*]

[1] School of Environmental and Chemical Engineering, Shanghai University, 333 Nanchen Road, Shanghai 200444, P. R. China

*corresponding author e-mail address:***liujianyong@shu.edu.cn***

ABSTRACT

Aerobic granular sludge technology has been developed for the biochemical treatment of wastewater in the present study. A fast cultivation of aerobic granular sludge was realized in Sequencing Batch Reactor (SBR), where Mg-Al layered double hydroxide (LDH) was used as a carrier for granules growth. In comparison, the sludge particle size with LDH addition was bigger than those without LDH, with more than 50% of compact granular sludge >1.4 mm in size. This indicatestheLDH improved the growth ofthegranular sludge. The frequency of LDH addition had little effect on the granule growth. Moreover, the formation of granules led to the low sludge volume index (SVI) and high mixed liquid suspended solids (MLSS) in SBR reactor. With the formation of granular sludge, more than 80% of COD was removed in SBR reactor. The high COD removal efficiency of wastewater was observed regardless of various COD loading strength. The results suggest that the growth of granular sludge with LDH as a carrier enhanced the treatment efficiency. Therefore, our results have provided a promising way to prepare the granular sludge for wastewater treatment.

Keywords: *Aerobic sludge, Granulation, Mg-Al LDH, SBR.*

1. INTRODUCTION

In comparison to conventionally activated sludge, aerobic granular sludge has a denser and stronger microbial aggregate structure, a higher biomass concentration, and a more excellent settling capacity [1,2]. As a result, the development of granular sludge has attracted much attention in effective biological wastewater treatment [3]. To date, aerobic granular sludge has been widely cultivated in sequencing batch reactors (SBRs). Nevertheless, aerobic granular sludge technology still faces challenges in its cultivation and application process, such as the acceleration, microbial fast growth and activity of sludge granules.

To overcome the challenge, inorganic carriers, including zeolite powder [4,5], struvite [6,7], and granular activated carbon [8,9,10,11] have been introduced into the granular sludge. With these carriers, the characteristics of biofilm formation and sludge granulation are enhanced as the inert nuclei or polymer-bonding process [12]. Because of the fact that negative charges of microorganism is not beneficial to the microbial aggregation, the addition of carriers with positive surface charge in SBR system leads to the attachment of microorganisms on the inert carrier surfaces to form initial biofilms. This results in the further development of mature granules. However, inorganic carriers are non-degradable in the rapid formation of aerobic granular sludge process, which is considered to decrease the effective volume of the reactor and increase the proportion of granular sludge. In addition, the organic polymer carriers reduced the microbial growth and activity. Therefore, it is necessary to develop a new carrier that not only improves the granular sludge growth but enhances the activity of microbial sludge.

Layered Double Hydroxides (LDH), as a group of clay, have been widely used in industrial application [13,14]. LDHs are represented by the chemical formula $M(II)_{1-x}M(III)_x\ (OH)_2\ (An)_{x/n\bullet m}\ H_2O$, where M(II) or M(III) is bivalent or trivalent metal cation, respectively, An is anion. In comparison to conventional carriers, LDH has some special advantages. Firstly, LDH has a stable inorganic structure, which can act as the nuclei for the formation of granular sludge. Secondly, the positively charged surface of LDH attracts negatively charged microbes for initiating the aggregation of granular sludge [15, 16]. Finally, LDH has little toxic influence on the microbes. Consequently, adding LDH to the reactor can achieve the synergistic effect of accelerating theaerobic granular sludge granulation and stimulating microbial growth.

Hence, the objective of the present study was to investigate the effect of Mg-Al LDH on the formation of aerobic granular sludge. For this purpose, the size of sludge was determined in SBR reactor after 50 days of treatment. The characteristics of sludge activity in terms of SVI and MLSS were determined. In addition, the performance of granular sludge was evaluated based on the COD removal efficiency. The present results have suggested a promising way to develop the granular sludge for wastewater treatment.

2. EXPERIMENTAL SECTION

2.1. Reactor setup

Sequencing Batch Reactor was used in the study (Figure 1). The reactor had a working volume of 1.8 L with an internal diameter and working height of 6.0 and 90.0 cm, respectively. The reactor was operated at a volumetric exchange ratio of 50 %. Air was introduced through a fine bubble air diffuser in the bottom of the reactor and its volume was controlled by a gas flowmeter, with the aeration rate maintained at 0.1 m^3/h. Three sampling ports were located at 5, 25, and 40 cm above the bottom of the reactor, respectively.

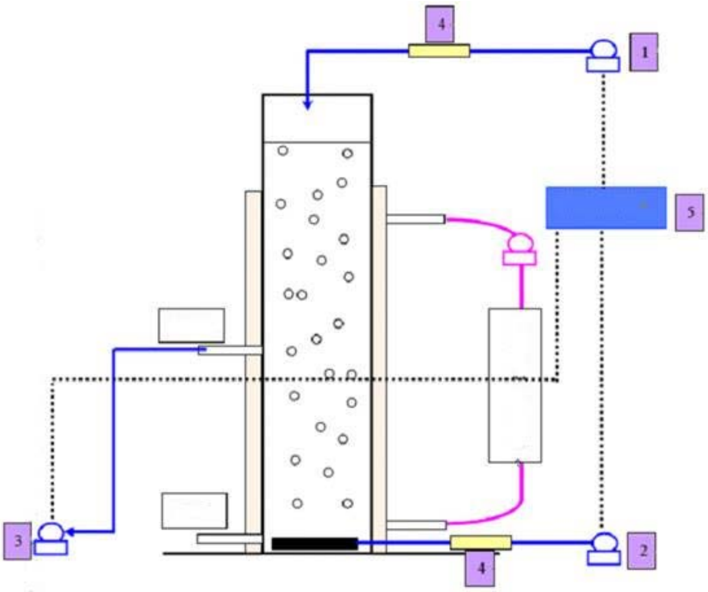

Figure1. Schematic representation of the SBR in thisstudy: 1 influent pump 2 air compressor 3 solenoid valve 4 flowmeter 5 time controller.

The SBR was operated automatically through a timer controller. The temperature of the SBR was maintained at 20–30 °C.

2.2. Seeding sludge

The reactor was directly inoculated with fresh activated sludge which was sampled from Shanghai Quyang Sewage Treatment Plant. The initial mixed liquor suspended solid (MLSS) concentration and sludge volume index (SVI) of the seeding sludge in SBR were 4.05 g/L and 56.72 mL/g, respectively.

2.3. Synthesis of Mg-Al LDH

Mg-Al LDH (Mg/Al molar ratio 2:1) was synthesized by using co-precipitation method [17]. Briefly, The samples were obtained by simultaneously drop wise adding one solution containing 1.0 mol $Mg(NO_3)_2{\bullet}6H_2O$ and 0.5 mol $Al(NO_3)_3{\bullet}9H_2O$ in 50 ml of distilled water, into 100 mL NaOH solution (0.5 M) in a beaker. The suspension obtained was magnetically stirred for 24h at room temperature for the production of precipitates, which was collected by filtration and washed several times with distilled water to remove excess soluble ions. The precipitates were dried in an oven at 60 °C for 12 h to obtain Mg-Al LDH.

2.4. Characteristics of wastewater and dosing method

All of the operational conditions were similar to those described above, except for LDH addition. The synthetic wastewater contained (mg/L): COD (as sodium acetate), 600-1,000; NH_4^+-N (as ammonium chloride), 50-100; K_2HPO_4, 5; $CaCl_2$, 60; $FeSO_4$, 15; EDTA, 30; $MnCl_2{\bullet}2H_2O$, 0.12; $CoCl_2{\bullet}6H_2O$, 0.15; $(NH_4)_6MoO_{24}$, 0.18; KI, 0.06; H_3BO_3, 0.15; $CuSO_4{\bullet}5H_2O$, 0.03. Particle size of LDH was between 150 and 300 μm, the reactor was supplied with LDH during sludge inoculation. LDH was added to R2 and R3 by the following two ways:

(1) One-time dosing: once-off addition of 2000 mg/L;

(2) Regular supplement dosing: an aliquot of 100 mg/L, was added in every six cycles.

2.5. Operating conditions

The reactor was operated in three phases. The first phase was from day 1 to day 7, consisting of cycles of operation (480 min for one cycle with 5 min influent filling, 455-460 min aeration, 10-15 min settlement). The superficial gas velocity was 1.47 cm/s. The influent COD concentration and the initial organic loading rate of the reactor were 600 mg/L and 0.9 $kg/m^3{\bullet}d$, respectively. The second phase was from day 8 to day 15, consisting of cycles of operation (360 min for one cycle with 5 min influent filling, 340-345 min aeration, 5-10 min settlement. The superficial gas velocity was 1.56 cm/s. The influent COD concentration and the initial organic loading rate in the reactor were 800 mg/L and 1.2 $kg/m^3{\bullet}d$, respectively. The third phase was from day 16 to day 50, consisting of cycles of operation (240 min for one cycle with 5 min influent filling, 225 min aeration, 2-5 min settlement. The superficial gas velocity was 1.76 cm/s. The influent COD concentration and the initial organic loading rate of the reactor were 1000 mg/L and 1.5 $kg/m^3{\bullet}d$, respectively. The volumetric exchange of water of the three phases was 900 mL.

2.6. Analytical methods

The effluent samples from the reactor were analyzed for COD, and sludge samples were analyzed for MLSS, SV and SVI values using the standard methods. The sludge particle size was measured by the wet sieving method and extracellular polymeric substance (EPS) was extracted by the heating method. The granule morphology of the sludge was observed by a scanning electron microscope.

3. RESULTS SECTION

3.1. Size of granular sludge after LDH introduction

The experiments demonstrated that the size of granular sludge in SBR reactor was the function of reaction time (Figure 2). Without LDH particle, the size of most granular sludge in R1 was < 0.18 mm in culture for 15 d. The granular formation was observed in 30 d. About 35% (w/w) of the sludge was 0.18-0.43 mm in size and < 10% sludge had a size of 0.43-1.4 mm. The particle size in R1 was further increased during 50 days cultivation, with more than 80% sludge appeared in the size group of 0.18-1.4 mm and 10% sludge in > 1.4 mm. In comparison, the size of granular sludge at one-time dosage of LDH in R2 was increased faster and the proportion of size group of 0.18-0.43 mm increased from 13% to 45% and 35% in the 0.43-1.4 mm group in 15-30 d culture. Increasing the culture time to 50 days, resulted in > 50% sludge in size >1.4 mm. This evolution of granule size in R2 indicated that the addition of LDH improved the formation of granule with large size (d>1.4 mm). Similar situation was observed in R3 where LDH was added repeatedly at regular dosing mode. This suggests that the addition frequency of LDH had little effect on the granule growth. In addition, the big granular sludge in cases of R2 and R3 is under the form of macroaggregates, compared to fine granular sludge in R1.

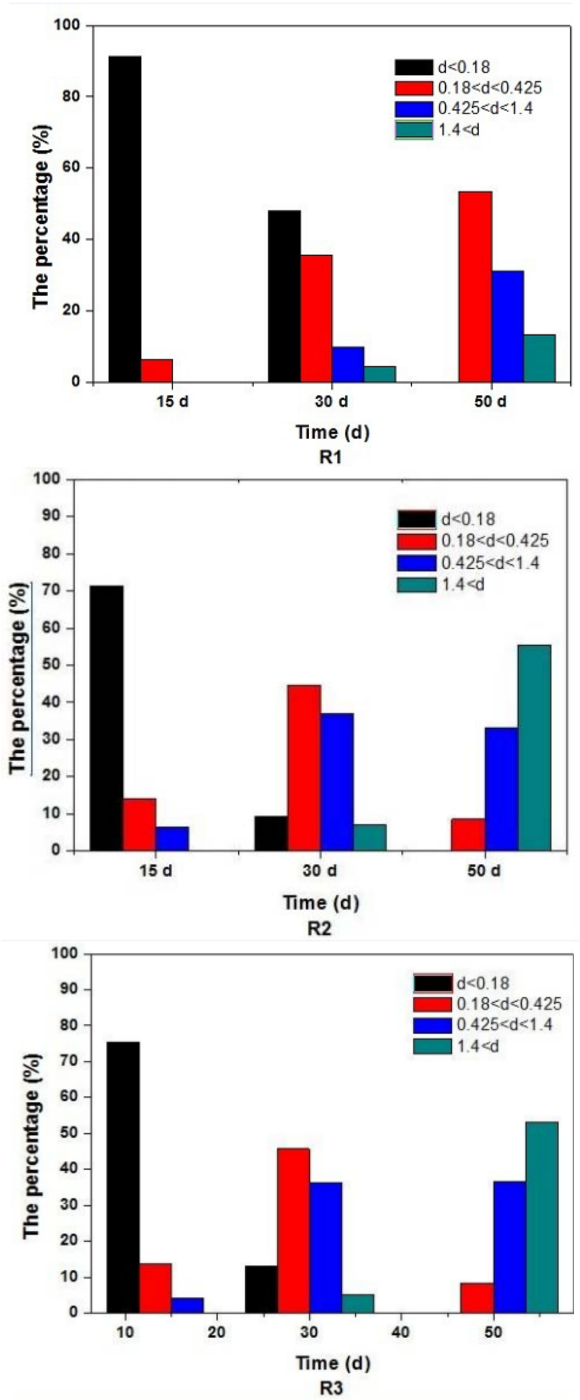

Figure 2. Size distribution of granules in reactors

This is also supported by the photograph of granular sludge in 50 d (Figure 3). Moreover, the surface structure of three granules was characterized by scanning electron microscopy (SEM) after 30 d culture. As shown in Figure 4A, the relatively irregular spherical or ellipsoidal morphology was observed in the granular sludge in R1. In contrast, the granule images in R2 and R3 showed that the granules had complete compact structure (Figure 4B and 4C) through the aggregation of fine sludge floc (Figure 4D). Therefore, it is proposed that LDH is an effective core for the adsorption of sludge floc in the sludge granulation process.

Figure 3. Photographs of the sludge after 50 days in three SBRs

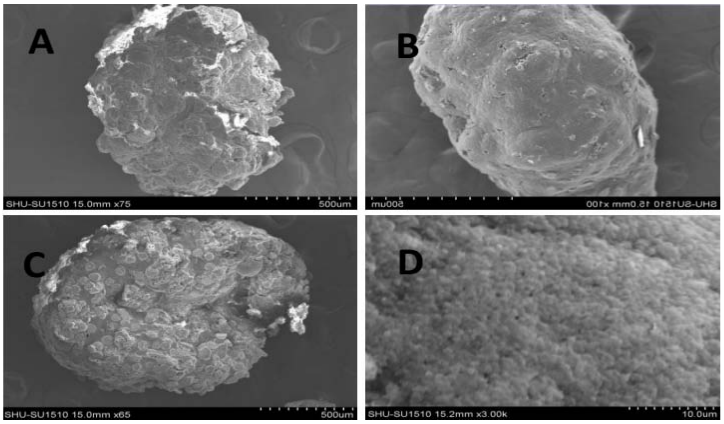

Figure 4. SEM photos of aerobic granular sludge

3.2. Granular sludge settling properties

The sludge settling property is commonly evaluated by the sludge volume index (SVI) that refers to the ratio of sludge volume to weight after 30 min settling (SVI_{30}). In comparison, the value of SVI after 5 min settling (SVI_5) was also used to estimate the early growth of granular sludge. The SVI value of granular sludge in SBR reactor changed with reaction time in the reactor (Figure 5). Without adding LDH in R1, the SVI value of granular sludge was increased sharply in the first five days, followed by the slow decreasing of the SVI value in 25 days. At the end of the experiment, the SVI value of R1 was 43.13 mg/L (Figure 5a). The change of the SVI value of R2 was similar to R1 in the first five days. With the gradual formation of granular sludge, the SVI value declined sharply acnd tended to be stabilized at 33.55 mg/L in 25 days (Figure 5b). The results indicate that the addition of LDH improved the sludge settling property in the reactor as the sludge granulation progressed. Similar situation was observed in R3 (Figure 5c). The results were also supported by the ratio of (SVI_5-SVI_{30})/SVI_5 (Figure 5d). In general, the complete granular sludge process was achieved when the ratio of (SVI_5-SVI_{30})/SVI_5< 10% [18]. As shown in Figure 5d, in 8 days, the ratios of R2 and R3 began to decline sharply to 8 and 9.15, respectively, by day 12. In R1 the ratio was 11.5 by day 12, and then declined to 9.3 by day 21. This indicates that most of flocs sludge in R2 and R3 became granular sludge with LDH addition. Therefore, the results suggest that the addition of LDH could have an apparent effect to decrease the granulation time, which was almost halved in the present experiment (from 21 to 12 days).

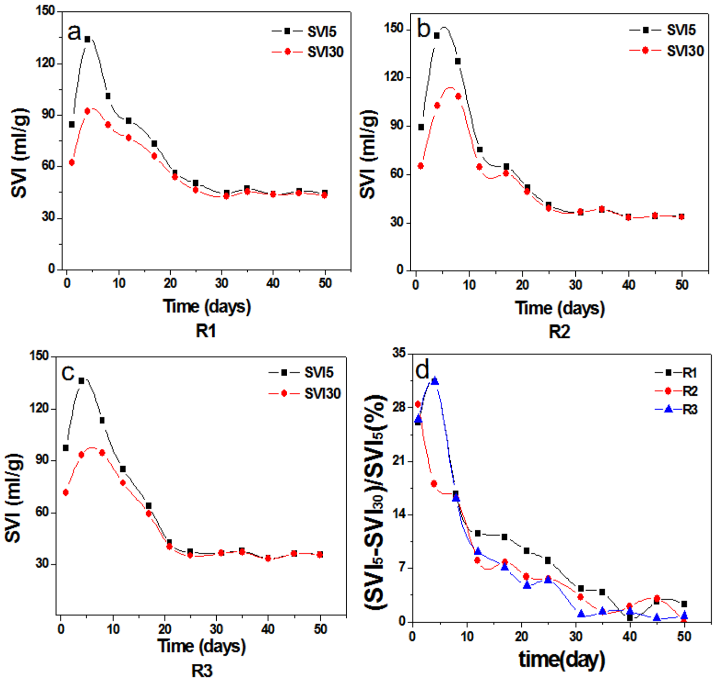

Figure 5. Changes of SVI_5, $SVI_{30}$and the ratio of (SVI_5-SVI_{30})/SVI_5during the process of study.

3.3. Performance of three column-type SBRs

In the reaction, COD concentration in the influent gradually increased from 600 mg/L to about 1000 mg/L, eventually reached around 1000 mg/L in 25 days. The COD removal efficiencies of three column-type SBRs began to improve with increasing COD concentration during the experiment (Figure 6a). At the beginning of the reaction, COD removal efficiency of three SBRs increased to 80%, along with the operation, which eventually could reach more than 90 %. But the COD removal efficiency in R1 appeared unstable when the OLR was changed. In contrast, COD removal efficiency in R2 and R3 remained stable during the experiment. The results indicated that the addition of LDH could achieve granular sludge to improve the stability of the reactor. At the same time, when COD removal efficiencies increased, granular sludge began to appear and grow, MLSS concentration increased rapidly in reactors (Figure 6b). In 30 days, the MLSS concentration of R1 increased to 8.0 g/L, which was lower than those (10.0 g/L) in R2 and R3. As was shown in Figure 5, granular sludge showed a good settling property so that MLSS concentrations in R2 and R3 were higher than that in R1.

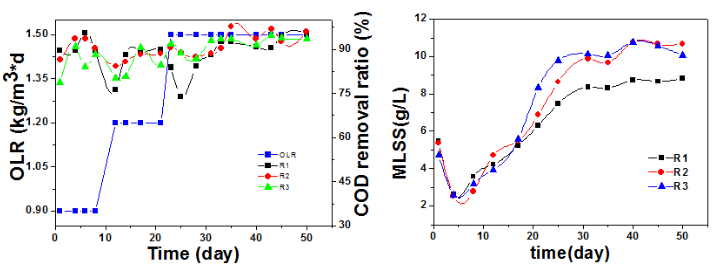

Figure 6. Performance of the three SBRs: a COD removal efficiencies, b MLSS changes

Overall speaking, granular sludge in R2 and R3 had better settling property, a higher biomass concentration and a higher treatment capacity than those of the flocs sludge in R1.

3.4. Mechanism of aerobic granulation by the addition of LDH in SBR

It has been known that the sludge granulation process was dependenton the formation of nuclei through which microorganisms gradually accumulate to form granular sludge. Adding LDH to the reactor could promote the 'nucleation' process of microorganisms. Typically, the microorganisms were adsorbed to the mineral surface, which could be summarized as four steps. Firstly, the adsorption process between microorganisms and LDH occurred through non-specific and reversible interactions, such as static electricity and hydrophobic interactions (Figure 7a); Secondly, the microorganisms produced polysaccharides, proteins and large amounts of pili, through the specific interactions in which the microorganisms were adhered to the surface of LDH (Figure 7b). Thirdly, after adaptation to the environment the microorganisms started to reproduce themselves to form colonies (Figure 7c). Lastly, the microorganisms and LDH formed stable and compact granular sludge (Figure 7d).

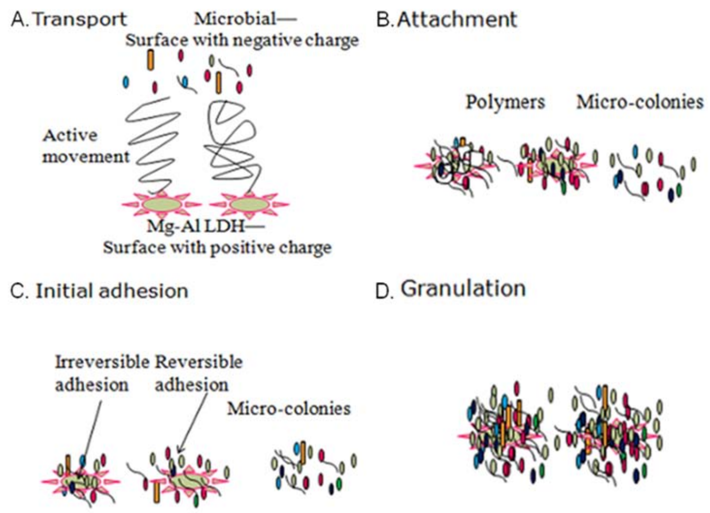

Figure 7. Diagram of Mg-Al LDH acceleration the aerobic sludge granulation

In addition, EPS played an important role in aerobic sludge granulation and the growth of granular sludge. From day 0 to day 50, the content of proteins and polysaccharides in reactors were analyzed once every 10 days.

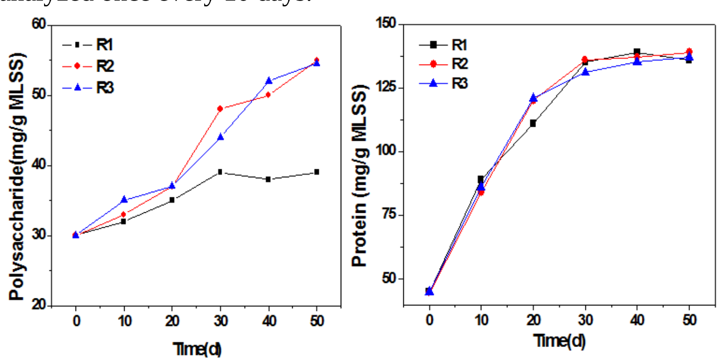

Figure 8. Changes in the concentrations ofpolysaccharides and proteins

It was found that the content of polysaccharides in R2 and R3 were twice as much as that in R1, which had changed little, but the content of polysaccharides in R2 and R3 had increased a great deal

(Figure 8). However, the contents of protein in three reactors were not different. According to the results, it is supposed that the microorganisms produced EPS in the growth process, which would have had an important physiological significance [19]. EPS could have also changed the physical properties of the microorganism surface and granular sludge and enhanced bacterial aggregation [20,21]. Moreover, EPS could help cells to absorb soluble nutrients and increase the ability of microorganisms to resist adverse environmental toxic substances [22]. In the meantime, aerobic sludge granulation process was influenced by divalent cationic [23], especially Mg^{2+} [24] and Ca^{2+} [25,26,27] could significantly promote the sludge granulation process, Mg^{2+} or Ca^{2+} could adhere to EPS of the microorganisms, Which could form Mg^{2+}-EPS-Mg^{2+} or Ca^{2+}-EPS-Ca^{2+} structures to influence the aerobic sludge granulation.

4. CONCLUSIONS

In the present research, the granulation of sludge in SBR system was performed with the addition of Mg-Al LDH as a carrier. The addition of Mg-Al LDH, resulted in improved physical properties exhibited as granule size, in comparison with those without Mg-Al LDH. Moreover, the time of granulation was almost halved. The corresponding COD removal efficiency was improved with lower SVI and higher MLSS, compared to the situation without Mg-Al LDH. This indicates that theLDH promoted the growth of granular sludge. The process involved in the granulation process may involve cations released from LDH, which acted as a bridge linking the microorganisms and stimulate the production of EPS. In such way, LDH was employed as the inert carriers to accelerate the nucleation process.

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6. ACKNOWLEDGEMENTS

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