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Contributed Paper

Comparison of Sludge Granule and UASB Performance by Adding Chitosan in Different Forms

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ABSTRACT

This study prepared chitosan with the same properties, i.e. molecular weight and degree of deacetylation in different forms, i.e. solution, bead and powder, and compared their effectiveness in enhancing granulation and UASB performance. A natural polymer chitosan in the form of freely moving polymeric chains was found to enhance sludge granulation and the efficiency of UASB system. The UASB with chitosan addition had a 9-59% lower effluent COD, 5-7% higher COD removal, up to 25% higher biogas production rate, 21-39% lower biomass washout, 37% larger particle size and 4 day longer sludge retention time. The differences are significant ($P<0.05$). However, chitosan in the form of bead and powder did not help enhance granulation process and UASB performances significantly. It was concluded that the size of the particles serving as inert nuclei and the chance of contact between the inert nuclei and biomass were very important. Surprisingly, even though chitosan powders had the net positive charges, their role in reducing electrostatic interaction between negatively charged bacteria was not prominent.

Keywords: Anaerobic Granulation, Chitosan, Granule, UASB.

1. INTRODUCTION

The upflow anaerobic sludge blanket (UASB) process is one of the most commonly used wastewater treatment system, with over 500 installations treating a wide range of industrial wastewaters [1]. The key feature of the UASB process that allows the treatment of high-strength organic wastewater is the development of dense granulated sludge. The UASB system is therefore highly dependent on its granulation process. There have been many proposed models for anaerobic granulation in the literature. The inert nuclei model, initially presented by Lettinga *et al.* [2], proposed that in the presence of inert microparticles in an UASB reactor, anaerobic bacteria could attach to the particle surfaces to form embryonic granules. The mature granules can be further developed through the growth of these attached bacteria. The inert particles that have been studied include zeolite

[3,4], sand [5] and water absorbing polymer [6]. Zeolite particles with 100 μm size were found to enhance granulation, while no difference in granulation process was observed between with and without added sand. It was explained that because the specific gravity of sand is greater than biomass, the chance of contact between sand and biomass may be significantly reduced. Water absorbing polymer employed by Imai *et al.* [6] is a pulverulent resin, which swells in water and exhibits a complex network structure. The results of lab-scale experiments showed that water absorbing polymer with 100-200 μm size and a wet density of 1.0 g/ml could significantly accelerate granulation. The water absorbing polymer has lower density than the other inert materials and the chance of contact between the particles and biomass increases. The recommended dosage was about 750 mg/l of reactor volume. Another model for anaerobic granulation is the polymer or filament bonding model. Freely moving polymeric chains may form a bridge between cells, facilitating the first step towards granulation [7]. It appears that both synthetic [8] and natural polymers, e.g. water extract of *Moringa oleifera* seeds [9] and chitosan [8] can assist anaerobic bacteria to aggregate together.

Chitosan is a natural polymer that has a growing potential due to its biodegradability, less adverse effects on human health, and renewable sources [10]. Chitosan is a polysaccharide comprising copolymers of glucosamine and N-acetyl-glucosamine and is mainly produced by alkaline deacetylation of chitin. Chitosan in the form of freely moving polymeric chains was found to enhance sludge granulation and shorten the start-up period of UASB systems [8,11]. This study prepared chitosan in different forms, i.e. solution, bead and powder, and compared their effectiveness in enhancing granulation. The comparison of anaerobic granulation mechanism using chitosan with the same properties, i.e. molecular weight and degree of deacetylation, but in different forms was discussed.

2. MATERIALS AND METHODS

2.1 Chitosan

Chitosan was provided by Taming Enterprises Co., Ltd., Thailand. The chitosan had the following characteristics: %DD = 84.3; MW = 3.5×10^5 dalton; moisture content = 12.2 %; ash content = 1.16%; protein content = 2.79%; viscosity = 33.20 cps.

2.2 Preparation of Chitosan Solution

Chitosan solution (1% w/v) was prepared by dissolving 1 g of chitosan in 100 ml of 1% acetic acid and shaking the solution at 200 rpm, at room temperature for 24 h.

2.3 Preparation of Chitosan Bead

Chitosan stock solution (4% w/v) was prepared by dissolving 4 g of chitosan in 100 ml of 2% acetic acid and shaking the solution at 200 rpm, at room temperature for 24 h. The chitosan solution was pumped into a syringe connected with a 24 G1 needle, dropped into the solution of KOH and ethanol (KOH/Ethanol ratio of 1:1 mol/mol), and left in the solution for 12 h. The chitosan bead products were washed with deionized water until the pH of the washing water was around 7.

2.4 Preparation of Chitosan Powder

Dry powders were obtained by spray-drying chitosan solution (1% w/v) using a laboratory-scale spray dryer (Mini Spray Dryer B-191, BUCHI Laboratory-Techniques Ltd., Switzerland). The spray-drying conditions were: feed rate of 4 ml/min, inlet temperature of 150°C, outlet temperature of 100°C. The air flowrate and the aspirator were constant at 400 l/h and 100%, respectively.

2.5 Chitosan Product Characterization

True density, pore volume and porosity of chitosan beads were determined according to equations (1), (2) and (3), respectively [12]. The chitosan powders were characterized for average density, surface area and pore volume by a surface area analyzer, Autosorb-1 (Quantachrom, USA), zeta potential by Zetasizer 3000 HS_A (Malvern Instruments Ltd., United Kingdom) and morphology by Scanning Electron Microscope, Ibaraki 305-0047 (Tsukuba-shi, Japan).

$$\rho_g = \frac{w_d}{V - \left[(w_w - w_d)/\rho_{H_2O}\right]} \tag{1}$$

$$V_p = \frac{V - (w_d/\rho_g)}{w_d} \tag{2}$$

$$P_r = \frac{V_p}{V_p + (1/\rho_g)} \tag{3}$$

where ρ_g is true density of dry chitosan bead (g/cm^3), ρ_{H_2O} is water density (g/cm^3), w_d is the average weight of dry chitosan bead (g),w_w is the average weight of wet chitosan bead (g), V_p is the pore volume of chitosan bead (cm^3/g), V is the average volume of wet chitosan bead (cm^3) and P_r is the porosity of chitosan bead.

2.6 Reactor System

Two identical reactors, made of clear acrylic with a working volume of 5.3 liters, were running in parallel (Figure 1). Each reactor was a cylindrical shape, 32 cm in height and 14 cm in diameter.

1 Influent wastewater tank; 2 Chitosan solution tank; 3,4 Influents; 5, 6 Sampling ports; 7 UASB-R1; 8 UASB-R2; 9,10 Effluents; 11,12 Biogas out; 13,14 Gasometers.

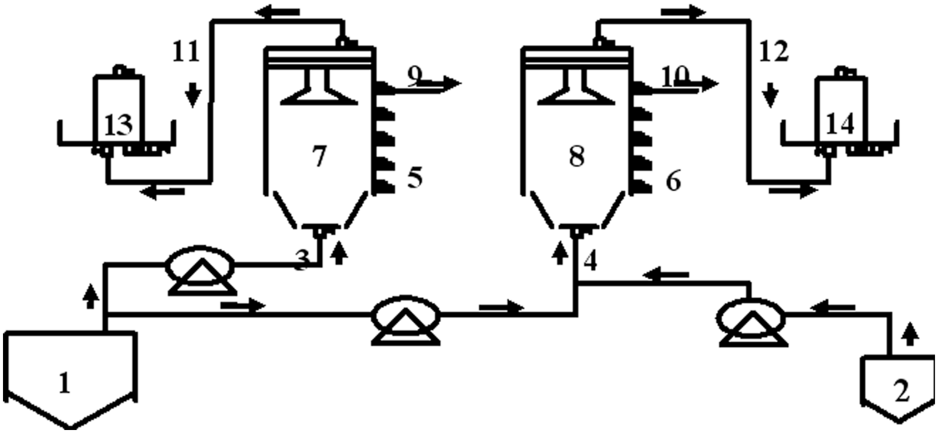

Figure 1. Schematic diagram of the UASB reactor system with two reactors running in parallel.

2.7 Sludge Suspension

Anaerobic sludge was obtained from the Huaw-Kwang Domestic Wastewater Treatment Plant, Bangkok, Thailand. The sludge characteristics, i.e. zeta potential at pH 7 and ionic strength 0.1 M, volume weighted mean of diameter, and water contact angle, were -12.5 ± 1.0 mV, 28.75 μm and 73.74 ± 2.54°, respectively.

2.8 Wastewater

The composition of the wastewater and trace metal solution is presented in Table 1.

2.9 Acclimation, Start-up, and Operation

A sludge suspension with an initial volatile suspended solid (VSS) concentration of 12 kg VSS m^{-3} was inoculated into the reactors. The acclimation of the sludge was carried out in each reactor until the COD removal was approximately 80%. The wastewater was then recirculated to the reactor everyday for a week and the start-up period was followed by gradually flowing wastewater at a hydraulic retention time (HRT) of 1.5 day corresponding to an organic loading rate (OLR) of 1.45 kg COD m^{-3}d^{-1}.

Table 1. Composition of synthetic wastewater and trace metal solution.

Components	Concentration (mg/l)
Glucose	8000
$NaHCO_3$	4000
NH_4HCO_3	400
$(NH_4)_2SO_4$	200
K_2HPO_4	200
$CaCl_2$	200
Yeast	100

Components	Concentration (mg/l)
$MgCl_2.6H_2O$	4.0
$FeCl_3.6H_2O$	5.0
$MnCl_2.4H_2O$	2.0
$Al_2(SO_4)_3.14\text{-}16H_2O$	4.0
$Ca(OH)_2$	3.0
$CoCl_2.6H_2O$	0.40
$ZnCl_2$	0.20
$NiCl_2$	0.40
$CuCl_2.2H_2O$	0.25

2.10 Analytical Methods

Samples from the reactor influent, sampling ports and effluent were collected periodically for analyses of COD, volatile fatty acid (VFA), total alkalinity, suspended solids (SS), VSS and pH according to the standard methods [13]. The subsamples for each test were taken from the same samples. The size of sludge particles were analyzed by a laser particle size analysis system (Mastersizer 2000, Malvern Instruments Ltd., United Kingdom) and the amount of generated biogas was recorded using liquid displacement gasometers.

The solids retention time (SRT) was defined as solids in the reactor divided by the mass of solids removed per unit time [1]. SRT was calculated according to a method described by Caixeta *et al.* [14]. The samples were taken from the five sampling ports and the effluents. The SRT was obtained by dividing the total mass of solids in the reactor by the concentration of solids removed in a unit of time, according to equations (4) and (5).

$$M_r = \sum C_i V_i \tag{4}$$

$$SRT = \frac{M_r}{Q_e X_e} \tag{5}$$

where M_r is the total mass of volatile solids in the reactor; C_i is the VSS at the sampling points along the reactor height; V_i is the volume of each sampling section; Q_e is the effluent flow rate and X_e is the VSS in the reactor effluent.

3. RESULTS AND DISCUSSION

3.1 Properties of Chitosan Bead and Chitosan Powder

The physical appearance of the chitosan beads is shown in Figure 2. The chitosan beads had spherical shape, white color and looked like glutinous pellets. The average diameter was 1.670 mm, average true density 1.039 g/cm^3, pore volume and porosity of 0.559 cm^3/g and 0.367, respectively. The chitosan powders had the average diameter of 6.8 μm, average density of 0.531 g/cm^3, surface area of 4.16 m^2/g, pore volume of 0.0076 cm^3/g and zeta potential at pH 7.35 of +44.5 mA. SEM micrograph of chitosan powders is presented in Figure 3, showing that the powders had round shape with size ranging from 1-7 μm.

3.2 Adding Chitosan Solution Compared with No Addition

Chitosan in the solution form was implemented on the second operating day during a start-up at the dose rate of 2 mg chitosan/g suspended solids. After 30 days of operation, small granules became visible at each reactor bottom. In comparison with the UASB without chitosan addition, the UASB with chitosan addition had a 9-59% lower effluent COD (Figure 4), 5-7% higher COD removal (Figure 5), up to 25% higher biogas production rate (Figure 6), 21-39% lower biomass washout (Figure 7), 37% larger particle size and 4 day longer sludge retention time. The differences are significant ($P<0.05$).

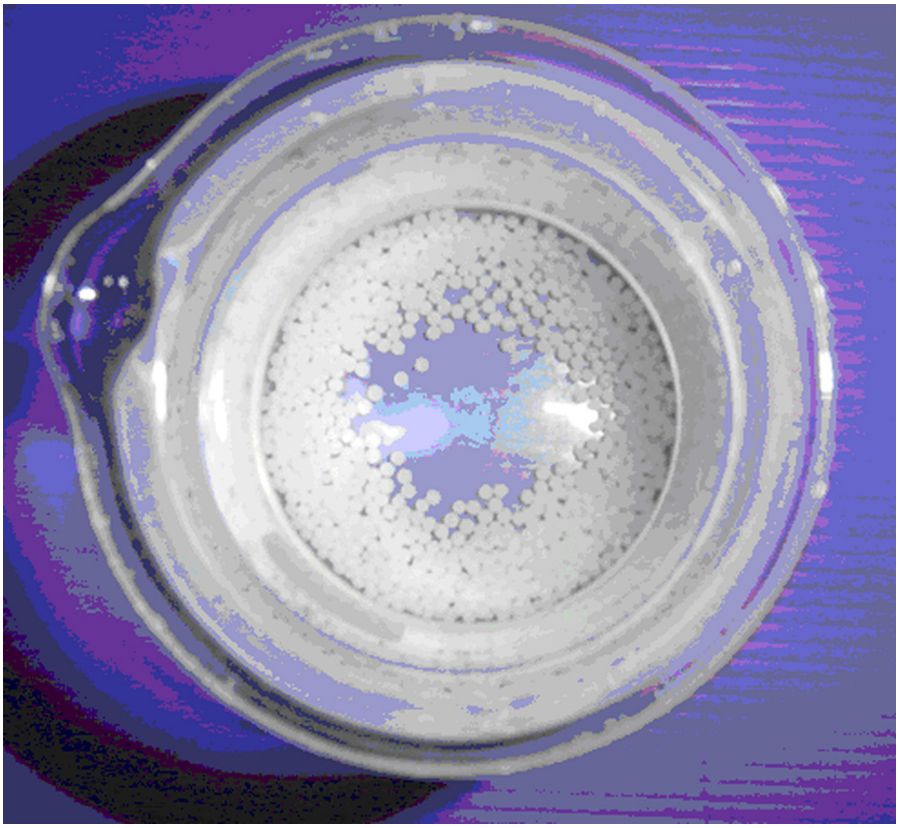

Figure 2. Chitosan beads in the KOH/Ethanol solution.

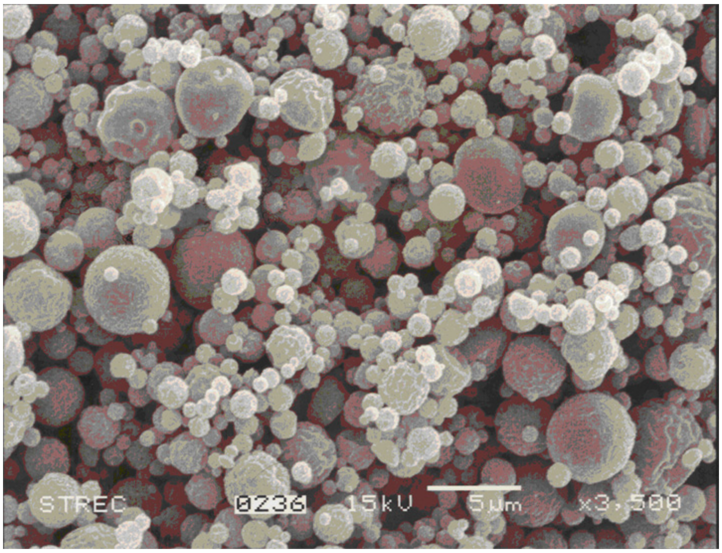

Figure 3. SEM micrograph with 3500x of chitosan powders.

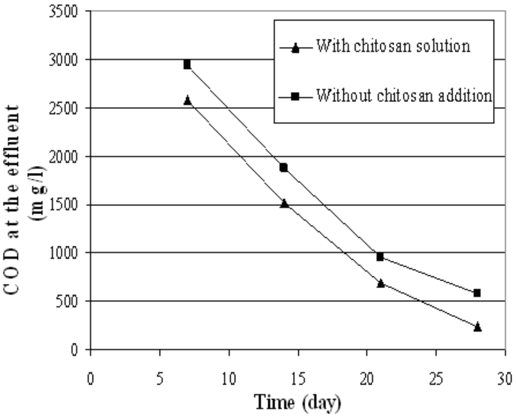

Figure 4. COD effluent against time.

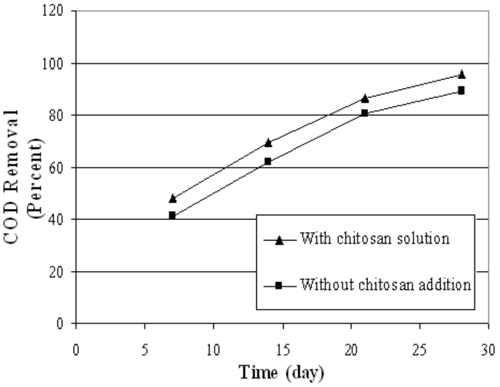

Figure 6. Biogas production against time.

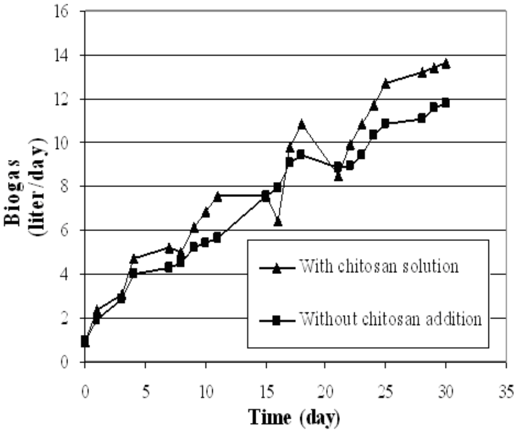

Figure 5. COD removal against time

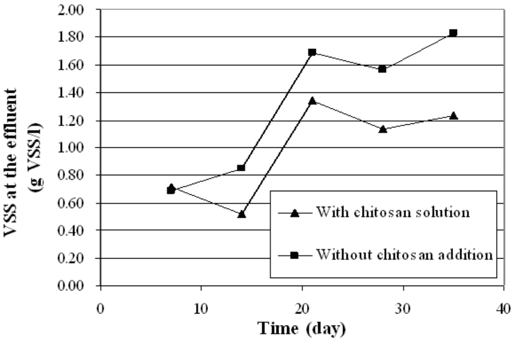

Figure 7. Washout of biomass represented by VSS at the effluent against time.

3.3 Adding Chitsosan Bead Compared with Adding Chitosan Solution

Chitosan in the bead form was implemented on the second operating day during a start-up at the dose rate of 2 mg chitosan/g suspended solids. After 30 days of operation, both reactors showed good performances in treating synthetic wastewater. Based on the effluent data of both reactors, the UASB with chitosan solution showed better performances than that with chitosan beads, i.e. 5-17% lower effluent COD, 16-45% higher COD percent removal, 7-20% lower biomass washout and 3-17% higher biogas production.

3.4 Adding Chitsoan Powder Compared with No Addition

Chitosan in the powder form was implemented on the second operating day during a start-up at the dose rate of 2 mg chitosan/g suspended solids. For 30 days of operation, the average COD removal of the UASB with chitosan addition was 80.84% and that without chitosan was 81.23%. The biogas production rate was 9.85 l/d and 10.23 l/d for the UASB with and without chitosan addition, respectively. The difference is non-significant (P>0.05). Both UASB reactors had the biomass washout in the range of 0.6-1.5 g VSS/l.

4. CONCLUSION

Chitosan in the solution form significantly enhanced granulation process and UASB performances. By adding the same amount of chitosan, UASB with chitosan in the solution form had better performances than that with chitosan in the bead form. Chitosan in the bead form might be a poorer accelerator due to the process of forming bead. Another aspect was that the amount of chitosan in the bead form might be limited, and there was not enough contact between chitosan beads and biomass. Chitosan powders did not help enhance granulation process and UASB performances even though they should have enough contacts with biomass. It was concluded that the size of the particles serving as inert nuclei is very important. Furthermore, even though chitosan powders had the net positive charges, their role in reducing electrostatic interaction between negatively charged bacteria was not prominent.

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