Solubilization of Waste Activated Sludge with Alkaline Treatment and Gamma Ray Irradiation

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Abstract: Alkaline pretreatment and gamma ray irradiation were applied to destroy the refractory structure of waste activated sludge (WAS) and to increase its biodegradability. This study was conducted to investigate the effects of alkaline treatment and gamma ray irradiation on the hydrolysis of WAS. The initial total solid (TS) concentration can be insignificantly affected by the solubilization of WAS due to alkaline treatment and gamma ray irradiation. The suspended solids (SS) reduction efficiency was 20.9 % due to alkaline treatment (pH 11) and 14.8 % due to gamma ray irradiation (50 kGy) with a constant TS concentration. The combined alkaline treatment and gamma ray irradiation showed more effective SS reduction and solubilization efficiencies. Both soluble chemical oxygen demand (SCOD) and biochemical oxygen demand (BOD₅) increased with increasing pH of WAS from 9.0 to 11.0 and gamma ray from 1 to 50 kGy. The total chemical oxygen demand (TCOD) remained almost constant for various pH and gamma ray doses. Therefore, the SCOD/TCOD ratio showed similar patterns with changes in the SCOD concentration. No BOD₅ enhancement was observed with gamma ray doses higher than 20 kGy. The experimental results indicated that the combination of alkaline and gamma ray pretreatment was useful for enhancement of biodegradability.

Keywords: gamma ray, biodegradability, waste activated sludge, alkaline treatment, VFAs

Introduction

Sludge originates from wastewater treatment process, and due to the physicochemical processes involved in the treatment, this sludge tends to have concentrated heavy metals and refractory organic compounds as well as potentially pathogenic organisms (viruses, bacteria etc) present in wastewaters. Moreover, from 2012, domestic law will prohibit the ocean dumping of sewage sludge due to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matters (London Convention). Therefore, the disposal of sewage sludge has become a critical problem because of the increased cost of sludge disposal. In order to solve this problem, the recycling of sewage sludge has become necessary.

Recently, at domestic wastewater treatment plants, external carbon sources (ethanol, methanol) are being used, which incurs an extra cost. From an economical perspective, the fermentation of primary sludge or its mixture with WAS has been used to increase the soluble COD and VFAs at the wastewater treatment plants [1-4]. In the denitrification processes, a carbon source (biodegradable COD) has been added for the production of the enzymes necessary for the utilization of the carbon, where volatile fatty acids (VFAs) are required by phosphorus-accumulating organisms to enhance biological phosphorous removal [5,6]. The initial hydrolysis of particulate organic matter into soluble substances is the rate-limiting step of anaerobic digestion [7]. When the particulate organic matters contained in activated sludge are not properly solubilized, only 30–50 % of the total COD (TCOD) or volatile solids (VS) in WAS has been reportedly biodegraded in 30 days [8].

Many sludge treatments (such as thermal, freezing and thawing, thermo-chemical, mechanical and enzymatic treatments) have been used to enhance the rate of
hydrolysis sludge for use as a carbon source [9,10]. Several researchers have shown that an alkaline treatment method was effective for the solubilization of WAS, as shown by increases in the SCOD concentrations and biodegradability [11,12].

Radiation technologies (including gamma ray, electron beam and UV) have mainly been studied for the sterilization or disinfection of sewage sludge and the treatment of complex mixtures of hazardous chemicals such as halogenated solvents and non-halogenated aromatic compounds [13-15]. Electron beam irradiation has been used to reduce SS in sludge [16] and enhance the biodegradability of wastewater, such as textile wastewater and landfill leachate [17-19]. Gamma ray irradiation, as a pre-treatment process, leads to release soluble carbohydrates from activated sludge [20]. However, the effects of gamma ray irradiation on the solubilization of WAS and the production of VFAs have seldom been investigated.

This study was designed to compare the potential of WAS as an external carbon source using alkaline treatment, gamma ray irradiation and both treatments combined. The SCOD/TCOD ratio and BOD₅ concentration have been used as indicators to evaluate the enhancements of solubilization and biodegradability [21,22].

**Experimental**

**Source of WAS and Irradiation**

The WAS used in this study was obtained from the secondary sedimentation tank of a municipal wastewater treatment plant located in Jeongeup, Korea. The sludge was concentrated by settling at 4 °C for 2 h. All experiments were completed within 10 days of sampling to minimize the physicochemical changes of the sludge. The characteristics of the sludge used in this study are presented in Table 1.

For the alkaline treatment, the settled WAS was equally divided into 4 beakers (1 L volume). The pH was set at 9.0, 10.0 and 11.0 by the addition of 10 N sodium hydroxide (NaOH). Each beaker was mechanically stirred at 250 rpm for 2 h. Gamma irradiation was conducted at room temperature (22 ± 2 °C) using a high-level Cobalt-60 source (MDS Nordion Inc., Canada) at the Korea Atomic Energy Research Institute (Jeongeup, Korea). The absorbed doses were measured using the alanine-EPR dosimetry system (ISO/ASTM 51607:2004) [23].

**Analysis**

WAS samples from the beakers after alkaline treatment and irradiation were centrifuged at 4000 rpm for 20 min and filtered through a glass microfiber filter (1.2 µm pore size, Whatmann GF/C). The filtrate was analyzed for SCOD, TOC, VFAs, total nitrogen (T-N), ammonia nitrogen (NH₄⁺-N), organic-N, nitrite nitrogen (NO₂⁻-N) and nitrate nitrogen (NO₃⁻-N). The pH was measured using a pH meter (Orion Ross ultra pH, Thermo Electron Corporation). The TS and VS were measured by drying and ashing at 105 and 550 °C, respectively. The TSS and VSS were analyzed using Standard Method [24]. The SCOD and TCOD concentrations were measured using a closed reflux-colorimetric method (colorimeter: Hach DR/4000). The NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N were analyzed by ion-chromatography equipped with an AS-18 4 mm column (model ICS-2000, Dionex Corp.). VFAs (acetate, propionate, butyrate, iso-butyrate, and valerate) were analyzed using high performance liquid chromatography (HPLC Agilent 1200) equipped with an UV absorbance detector operated at 210 nm. Separation of acids was conducted using a Rezex ROA organic acid column (300 × 7.80 mm), with 0.005 N H₂SO₄ as eluent, at a flow rate of 0.5 mL/min; the column temperature of 60 °C.

**Results and Discussion**

**Effect of Different TS Concentrations on Solubilization**

Figure 1 shows the effects of different TS concentrations on the solubilization and biodegradability. The TS concentrations of the WAS produced from real wastewater treatment plants will vary each day. Therefore, the hydrolysis of WAS has to be considered for various TS concentrations. In this study, TS concentrations of 3830, 5960, 9410, 12960 and 16220 mg/L were examined at pH 10, with a gamma ray dose of 10 kGy. As shown in Figure 1, the SCOD concentration increased from 270 to 1900 mg/L with increasing of TS concentration; however, the SCOD/TCOD ratios only increased slightly from 8 to about 12 %. Although the TS concentration increased, no significant enhancement of the solubilization was observed, indicating the rate of solubilization was not significantly affected by an increase in the TS concentration when pH and gamma ray conditions remain uncertain.
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Figure 1. Effect of alkaline treatment (pH 10) and gamma ray irradiation (10 kGy) on the SCOD and SCOD/TCOD at different TS concentration.

constant. Therefore, the initial TS concentration was not considered, with the undiluted WAS used directly in this study.

Reduction of WAS

In order to investigate the effects of sludge alkaline treatment, gamma ray irradiation and the combination of both on the reduction of sludge, the TS and SS concentrations were measured. The TS concentrations were between 16110 and 17350 mg/L in relation to different pH and gamma ray doses are shown in Figure 2. The SS removal efficiencies were 20.9 and 14.8 % with alkaline hydrolysis (pH 11) and 20 kGy gamma irradiation, respectively; whereas, the combined treatment showed 28.3 % SS removal efficiency at pH 11 and 20 kGy gamma irradiation (Figure 2(c)). As shown in Figure 2(a), the SS concentration continuously decreased with increasing pH from 9 to 11. With gamma irradiation, the SS concentration decreased from 0 to 20 kGy (Figure 2(b)). However, no further significant reduction of the SS concentration was observed after 20 kGy, indicating no further SS conversion to dissolved solids. The decrease of SS concentration in this study was most likely the results of the breaking down of the molecular structure of the WAS by the gamma irradiation [20], with disintegration of the cells due to alkaline hydrolysis [26].

Solubilization and Biodegradability

The production of SCOD from WAS by alkaline treatment and gamma ray irradiation has potential to provide a good carbon source for denitrification, leading to substantial cost savings for wastewater treatments. Figure 3 shows the changes in the SCOD concentration for each of the pre-treatment methods. For the alkaline pretreatment, the SCOD concentration and SCOD/TCOD ratio gradually increased with increasing pH (Figure 3(a)), as a result of alkaline hydrolysis; consistent with the finding of Chen and coworkers [27].

For gamma ray irradiation between 0 and 50 kGy, the SCOD concentration increased from 140 to 1,740 mg/L (Figure 3(b)). Water radiolysis due to gamma ray irradiation forms electronically excited and ionized molecules such as \( \text{OH} \cdot \), \( \text{e}_{\text{aq}}^{-} \) and \( \text{H} \cdot \) as very reactive primary species, and \( \text{H}_2 \) and \( \text{H}_2\text{O}_2 \) as molecular products [28]. The reducing species H-atoms and the “solvated electrons” (\( \text{e}_{\text{aq}}^{-} \)) are converted to oxidizing species (\( \text{HO}_2 \cdot \), \( \text{O}_2 \cdot \)) in the presence of oxygen and water. These oxidizing radicals with the OH-radicals can enhance the production of SCOD from WAS. However, the SCOD concentration slightly increased after 20 kGy.

The application of the combined treatment showed an increase in the SCOD concentration from 2850 to 4340 mg/L at pH 11 (Figure 3(c)). The maximum SCOD concentration (4340 mg/L) at pH 11 and 50 kGy gamma ray irradiation was almost twice that at pH 11 and 0 kGy. To increase the SCOD concentration from WAS, the combined treatment showed better efficiencies than either of the single pretreatments alone.

Figure 3 also shows SCOD/TCOD ratios for the three different treatments. The TCOD concentration remained almost constant at different pH and gamma ray doses. Therefore, the SCOD/TCOD ratio showed a similar pattern to the change in the SCOD concentration. As show in Figure 3, SCOD/TCOD ratios increased from

Figure 2. TS and SS reduction by alkaline treatment and gamma ray irradiation: (a) alkaline treatment, (b) gamma ray irradiation and (c) alkaline treatment (at pH 11) and gamma ray irradiation.
1.1 to 21.8 and 1.1 to 13.0 % for alkaline hydrolysis and gamma irradiation from 0 to 50 kGy, respectively. The maximum SCOD/TCOD ratio of 31.4 % was observed at pH 11 and 50 kGy. The SCOD/TCOD ratio increased with an increasing gamma ray dose. Apparently, the rate of WAS hydrolysis was enhanced by alkaline treatment as well as gamma ray irradiation, which has also been reported by other researchers [12,27].

Not only the SCOD but also the BOD$_5$ also can be used as an indicator of the enhancement of biodegradability [21]. Figure 4 shows the changes in the BOD$_5$ and BOD$_5$/SCOD ratio after the alkaline pre-treatment (at pH 11) at different gamma ray doses from 0 to 50 kGy. The BOD$_5$ concentration increased from 1000 to 1440 mg/L until 20 kGy, as gamma irradiation converts nonbiodegradable organics to biodegradable compounds [17]. However, no enhancement of the BOD$_5$ was observed after 20 kGy. The BOD$_5$/SCOD ratio indicates the change in the amount of biodegradable compounds in the WAS. In Figure 4, the BOD$_5$/SCOD ratio decreased from 65 to 45 %, which has two possible explanations. Firstly, alkaline and gamma ray irradiation treatment accelerate the mineralization of biodegradable compounds. The second is the potential for the greater production of non-biodegradable SCOD from TS than conversion of non-biodegradable compound into biodegradable in SCOD.

**VFAs Production**

The VFAs concentrations were analyzed immediately after the alkaline treatment and gamma ray irradiation. Figure 5 shows the effects of alkaline treatment and gamma ray irradiation on the production of VFAs. In Figures 5(a) and (b), the total VFAs and TOC concentrations can be seen to be increased by alkaline treatment and gamma ray irradiation. The production of VFAs by alkaline treatment was higher than by gamma ray irradiation. The production of VFAs under alkaline
conditions increased the rate of WAS hydrolysis to produce more soluble substrates [29]. Short chain fatty acids such as acetate, propionate, butyrate and valerate are important products for the hydrolysis of sludge [27]. Chen and coworkers [27], showed that the individual VFAs concentrations increased in the order acetic > propionic > iso-valeric acids for the hydrolysis of WAS at different pHs. In this study, three VFAs including acetic, propionic, iso-butyric acids were predominantly detected after both alkaline treatment and gamma ray irradiation. The VFAs concentrations were analyzed, and found to be in order: iso-butyric > acetic > propionic and iso-butyric > propionic > acetic acid by gamma ray irradiation and alkaline treatment, respectively.

Conclusion

The hydrolysis of WAS for the recovery of a carbon source was enhanced by both alkaline treatment and gamma ray irradiation, but the alkaline treatment was more effective than gamma ray irradiation for the reduction of SS in WAS. The combined process of alkaline treatment and gamma ray irradiation resulted in higher rate of SS reduction and more solubilization than either of the single pretreatments. Alkaline treatment and gamma ray irradiation effectively disrupted the sludge floc and degraded biological cells, which increased the SCOD concentration. The production of VFAs during the hydrolysis of sludge was enhanced by both alkaline treatment and gamma ray irradiation. The optimal conditions for the recovery of a carbon source in this study were at pH 11 and 20 kGy. Under these conditions, 26.2 % COD solubilization was obtained. This combined process can be used for the recovery of carbon source from WAS.

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References