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Steam Explosion Pretreatment of Sludge for Pharmaceutical Removal and Heavy Metal Release to Improve Biodegradability and Biogas Production

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Abstract: Steam explosion pretreatment was developed and evaluated to remove pharmaceuticals and heavy metals from wastewater sludge and to improve its biodegradability and methane yield. Effects of pressure (5–15 bar) and duration (1–15 min) during the pretreatment were examined, and the pretreatment efficiency was evaluated based on the solubilization degree, the capillary suction time (CST) test and anaerobic digestion. The removal efficiency of ibuprofen, acetaminophen, and amoxicillin was 65%, 69%, and 66% and 70%, 66%, and 70% in primary sludge (PS) and waste-activated sludge (WAS), respectively. The highest percent release efficiency of heavy metals, i.e., lead, cadmium, and silver, for PS and WAS was 78%, 70%, and 79% and 79%, 80%, and 75%, respectively. The highest methane yield was obtained after pretreatment at 10 bar for 15 min and at 15 bar for 10 min, with respective yields of 380 and 358 mL CH₄/g volatile solids (VS) for the PS and 315 and 334 mL CH₄/g VS for the WAS. The results of methane production indicated that the decreased concentrations of pharmaceuticals and heavy metals resulted in increased biodegradability of PS and WAS.

Keywords: steam explosion pretreatment; heavy metals; pharmaceuticals; sludge; anaerobic digestion; methane yield

1. Introduction

In recent decades, with the growing population and ever-increasing industrialization, the number of wastewater treatment plants has substantially increased globally [1]. A great amount of sludge is produced as a byproduct in wastewater treatment plants all over the world. Of this material, approximately 45 million tons of dry sludge are produced per annum [2]. In addition to water and organic compounds, sludge treatment streams contain considerable amounts of hazardous elements, such as pharmaceuticals, as well as contaminants from industrial sources, such as metal plating facilities, mining operations, fertilizer industries, chloralkali facilities, radiator manufacturing, smelting, alloy industries, tanneries, battery production, paper industries, body care products, detergents, and pesticides; these industrial sites are the initial sources of heavy metals in wastewater treatment plants. Industrial contaminants such as zinc, copper, chromium, nickel, cadmium, and lead are present in sludge and are discharged into the environment at an increasing rate [3].

Waste materials from hospitals, industries, private households, veterinary clinics, and pharmaceutical manufacturing facilities are several sources of pharmaceutical residues in sludge

that eventually find their way to wastewater treatment plants. Pharmaceuticals include different therapeutic groups, e.g., analgesics, antibiotics, diuretics, beta-blockers, hormones, antidepressants, psychiatrics, and lipid regulators, which have toxic effects on the environment and human health [4].

Currently, these toxic components of sludge have attracted much attention due to their adverse environmental effects. Different treatment methods for sludge removal have been proposed to reduce environmental hazards and protect human health before its release into the environment [2]. Conventional treatment methods of sludge disposal include incineration, gasification, pyrolysis, landfilling, and biological treatment methods such as aerobic/anaerobic digestion [5]. Due to its environmental and economic benefits as well as technical advantages, the anaerobic digestion method is suitable for the disposal of sludge in modern wastewater treatment plants [6].

Although anaerobic digestion is a useful technique, its use is limited because this treatment method produces carbon dioxide (CO_2) and hydrogen sulfide (H_2S), as well as the low digestion rate of sludge. Most importantly, the presence of heavy metals and pharmaceuticals has an inhibitory effect on biogas production. The increased concentrations of toxic substances due to their low or nonbiodegradability decreases the activity of microorganisms and the digestibility of the sludge [7,8]. The theoretical methane yields for waste activated sludge and primary sludge can be between 210 and 650 mL CH_4/g volatile solids (VS). However, biogas production is low in anaerobic digestion due to the presence of toxic substances in the sludge [9].

The biomethane potential for waste activated sludge and other wastes to obtain an optimal substrate mix was investigated in [10]. The BMP test showed 247 mL CH_4/g VS methane production from the sludge, while the theoretical methane potential (TMP) was calculated to be 406 (mL CH_4/g VS). Theoretical methane potential was calculated to the optimum co-digestion of municipal solid waste and sludge. TMP for sludge was obtained at 333.9 mL CH_4/g VS, and after 40 days anaerobic digestion, the methane content reached 164.5 mL CH_4/g VS [9]. Enhanced biogas production of waste-activated sludge (WAS) investigated using hydrothermal pretreatment. The theoretical methane obtained for WAS was 290 mL CH_4/g VS after 50 days incubation, while the practical methane yield reached 142.7 mL CH_4/g VS. Hydrothermal pretreatment under the conditions of 210 °C and 30 min resulted in an increase in the methane yield to 344 mL CH_4/g VS [8]. The biochemical methane potential for sewage sludge was evaluated, and hydrothermal pretreatment was used to increase biogas yield [11]. Methane production of sludge without pretreatment was 155 mL CH_4/g VS, while the methane yield after pretreatment under the conditions of 170 °C and 1 h was 275 mL CH_4/g VS. In [12] the effects were examined of several pretreatments on the increased biogas production of WAS. During 30 days of anaerobic digestion, methane production of sludge reached 57.6 mL CH_4/g VS, and after pretreatment, the best result for methane yield was 84.4 mL CH_4/g VS following thermal pretreatment. Therefore, anaerobic digestion is unable to completely digest compounds of sludge. Then, [13] examined the effects of anaerobic digestion at 35, 55 and 60 °C on pharmaceutical removal in the sludge matrix. Generally, during anaerobic digestion, treatment was not seen reduce pharmaceuticals in the sludge matrix. Accordingly, the use of pretreatment is necessary to degrade compounds of sludge such as toxic materials (heavy metals and pharmaceuticals), which is effective in the increasing microorganism activities in order to enhance methane yield [14–16].

Different pretreatment techniques include biological, chemical, thermal, and physical processes, as well as combinations of these methods, and a key step is to improve the breakdown of sludge in order to increase biogas production [6]. However, there are few studies describing pretreatment effects to reduce heavy metals and pharmaceuticals in sludge prior to anaerobic digestion in order to increase methane production. In the present study, steam explosion was used as a new pretreatment method to decrease heavy metals and pharmaceuticals in sludge. Steam explosion pretreatment with high pressure and heat, followed by a sudden pressure drop, causes the breakdown of sludge structure [17]. As a major advantage, steam explosion does not require chemical catalysis and is an environmentally friendly pretreatment.

The main objective of this study was to apply steam explosion with different pressures and retention times as pretreatments for removing pharmaceuticals and heavy metals in sludge prior to anaerobic digestion. The goal was to enhance the digestibility or biodegradability rate of sludge while removing pharmaceuticals and release heavy metals for optimization of anaerobic digestion in order to increase methane yield in the wastewater treatment plant.

2. Materials and Methods

2.1. Sludge and Inoculum

Primary sludge and waste activated sludge were acquired from a municipal wastewater treatment plant (Tehran, Iran) and were stored in a cold room at 4 °C for further experiments. The inoculum and primary sludge were centrifuged to enhance the total solids. Total solids ranged from 9% to 19% and from 7% to 12% for inoculum and primary sludge, respectively. The inoculum was activated at 37 °C for 4 days prior to use.

2.2. Steam Explosion Pretreatment Procedure

The steam explosion reactor was constructed and included a steam generator, pressure vessel, and vacuum tank [18]. The operating pressure and temperature were up to 40 bar and 280 °C, respectively. Pressures of 5–15 bar and times from 1–15 min were investigated during pretreatment. Pressure and heat were produced using a steam generator with a capacity of 20 L. The pressure vessel had a capacity of 3 L, and up to 1 L of primary sludge and WAS were used for each pretreatment. Steam was sent to the pressure vessel via a solenoid valve until the desired pressure was reached. After the desired retention time, the pressure was released through a vacuum tank (200 L), creating a sudden pressure drop. A pressure difference was created between the inside of the fibers and the surrounding environment. Therefore, the structures of primary sludge (PS) and WAS were broken down after the sudden pressure drop.

2.3. Anaerobic Digestion Process

Anaerobic digestion processes were carried out by mesophilic bacteria at 37.5 °C in batch reactors, and the anaerobic condition into the reactors was obtained with the injection of pure nitrogen into the headspace for 2 min. The reactors were glass bottles with 118 mL total volume and closed with butyl rubber seals and aluminum caps [19]. The volatile solids percentage (%VS average) was 7.7% and 10.4% for primary sludge and WAS, respectively. Each reactor was filled based on the $VS_{inoculum}:VS_{substrate}$ ratio. The first substrate was the pretreated WAS, which contained 1.04 gVS inoculum and 0.52 gVS of the pretreated WAS. The second substrate was the pretreated primary sludge, in which each reactor contained 1.04 gVS inoculum and 0.53 gVS of the pretreated primary sludge. The total volume of the reactor was brought to 25 mL with the addition of deionized water. The control samples consisted of mixtures of unpretreated primary sludge and WAS with inoculum. The initial pH was 7.8 and 7.6 for primary sludge and WAS, respectively. All reactors were incubated for 60 days, and each condition of the reactor was carried out in triplicate. During the incubation, the reactors were shaken once a day.

2.4. Analytical Methods

The concentrations of the heavy metals, Cd, Pb, and Ag were determined using a microwave plasma-atomic spectrometer 4200 (Agilent Technologies, Santa Clara, CA, USA). Primary sludge and WAS after steam explosion pretreatment were prepared using a previously described method [20] for analysis with high-performance liquid chromatography 1260 (Agilent Technologies, Santa Clara, CA, USA). HPLC was equipped with a C18 column (100 mm × 2.1 mm and 10 µm particle size). Acetaminophen, ibuprofen, and amoxicillin were investigated in this case, and all the pharmaceutical standards for target compounds were of high purity grade (>90%). Sludge samples were centrifuged at 18,000× g for 15 min. The total solids (TS) and volatile solids (VS), capillary suction time (CST), total

chemical oxygen demand (TCOD), and soluble chemical oxygen demand (SCOD) of the samples were measured by standard methods [21]. The methane produced in the reactor during the incubation was measured using a gas chromatograph (Auto System Perkin Elmer, Waltham, MA). Data analysis was carried out as described by [22]. Theoretical methane yield (TMY) was determined by Equation (1) [23].

$$\text{TMY (mL CH}_4\text{/g VS)} = 22.4 \times 1000 \times [((4_c - h - 2_o - 2_s)/8)/(12_c + h + 16_o + 14_n - 32_s)] \quad (1)$$

Biodegradability of samples was examined based on Equation (2) [24].

$$\text{BD\%} = (\text{experimental methane yield/theoretical methane yield}) (\text{mL CH}_4\text{/g VS}) \times 100 \quad (2)$$

Degree of solubilization COD was measured using Equation (3) [25].

$$\text{SD\%} = [(\text{SCOD}_{\text{pretreated}} - \text{SCOD}_{\text{control}})/(\text{TCOD}_{\text{control}})] \times 100 \quad (3)$$

2.5. Statistical Analysis

A generalized linear model ANOVA was used to compare the effects of parameters of the pretreatment on the methane production. The data were displayed as the means of triplicates \pm the standard deviation. The ANOVA was performed with $p < 0.05$ confidence intervals for the response variable. The significance of each coefficient was determined at a 95% confidence level using the *F*-value test.

3. Results and Discussion

Anaerobic digestion is widely used as treatment for sludge stabilization to promote biogas production at wastewater treatment plants. The hydrolysis of solid matter is the main limiting factor in the digestion. In addition, the increased concentrations of heavy metals and pharmaceutical residuals in sludge decrease digestion and biogas yield. Consequently, enhancement of biogas production is related to the improvement of biodegradability and hydrolysis rate. Accordingly, steam explosion pretreatment at different pressures and durations was used to degrade pharmaceutical residuals and release heavy metals in order to increase biodegradability. Finally, the impacts of the pretreatment on the composition and structure of sludge were investigated by performing anaerobic digestion.

3.1. Effect of Steam Explosion on Heavy Metal Release

The presence of heavy metals in sludge is an environmental challenge, and it has a negative effects on the anaerobic digestion process [26]. Steam explosion pretreatment was used as a new technique for heavy metal release in the primary sludge and WAS. The effects of pressure and retention time on the behavior of heavy metals such as Pb, Cd, and Ag in primary sludge and WAS were examined, and the results are shown in Figure 1.

The results show that steam explosion was effective in the release of heavy metals into liquid phase in PS and WAS (Figure 1). The amount of heavy metals changed in response to different steam explosion pretreatments. High-pressure pretreatments dictated which heavy metals in the ionic state easily leached out into the liquid phase (Figure 1). Both pressure and retention time of the steam explosion had a major impact on the extraction effects of heavy metals in sludge [27]. Therefore, more heavy metals were transferred from sludge into the liquid phase [28]. The content of heavy metals did not a significant change after pretreatment with 5 bar with a low retention time. The highest release efficiency of heavy metals in for primary sludge and WAS were observed at 10 bar for 10 min and 10 bar for 15 min and at 15 bar for 10 min and 15 bar for 15 min, respectively (Figure 1). The cadmium release increased in the liquid phase with the increased pressure and retention time. For silver, the increased release was observed only with high-pressure pretreatment (10 and 15 bar) and high retention time. A

large amount of lead was released in the liquid phase, even at low pressure and a short retention time. There was a linear relationship between treatment time and pressure and heavy metal release.

Heavy metals are surrounded in the sludge by organic matter, residuals, iron, manganese oxides, and carbonates, where high temperature is required to break down the cells and flocs. Steam explosion pretreatment can release heavy metals within the flocs to the liquid phase. This effect is most likely the reason that the increased pressure and temperature resulted in an increased release of heavy metals in the sludge [29,30].

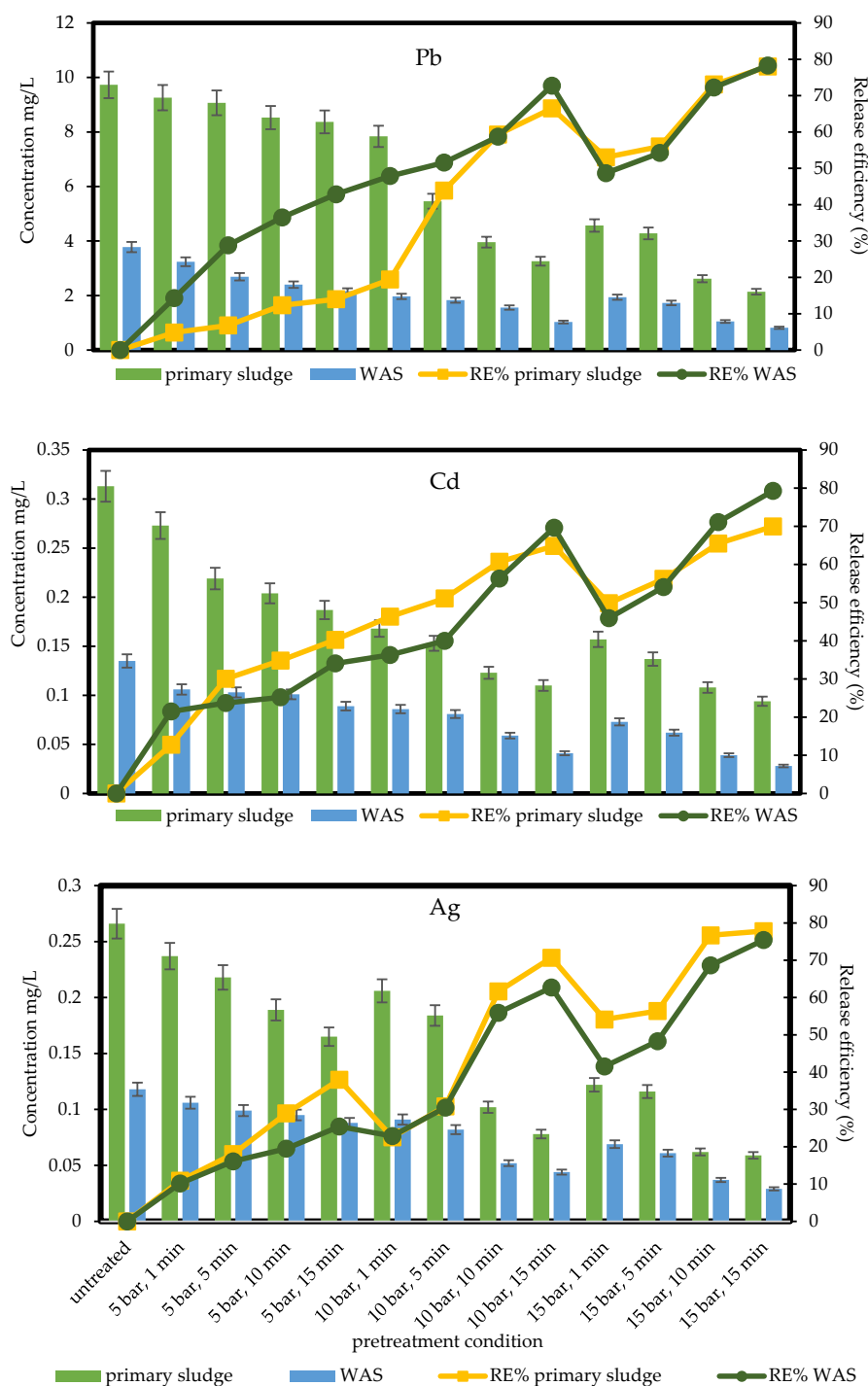


Figure 1. Effect of steam explosion on release efficiency of heavy metals in the primary sludge (PS) and waste-activated sludge (WAS).

3.2. Effect of Steam Explosion on Pharmaceutical Removal

Pharmaceutical residuals are resistant to biodegradation in sludge. The presence of pharmaceutical residuals in the environment at high concentrations can pose potential threats to public health [31,32]. Pharmaceutical residuals are limiting factors of the activity of microorganisms in the anaerobic digestion process that are involved in biogas production [33]. The results of pharmaceutical removal under different conditions of steam explosion are shown in Figure 2.

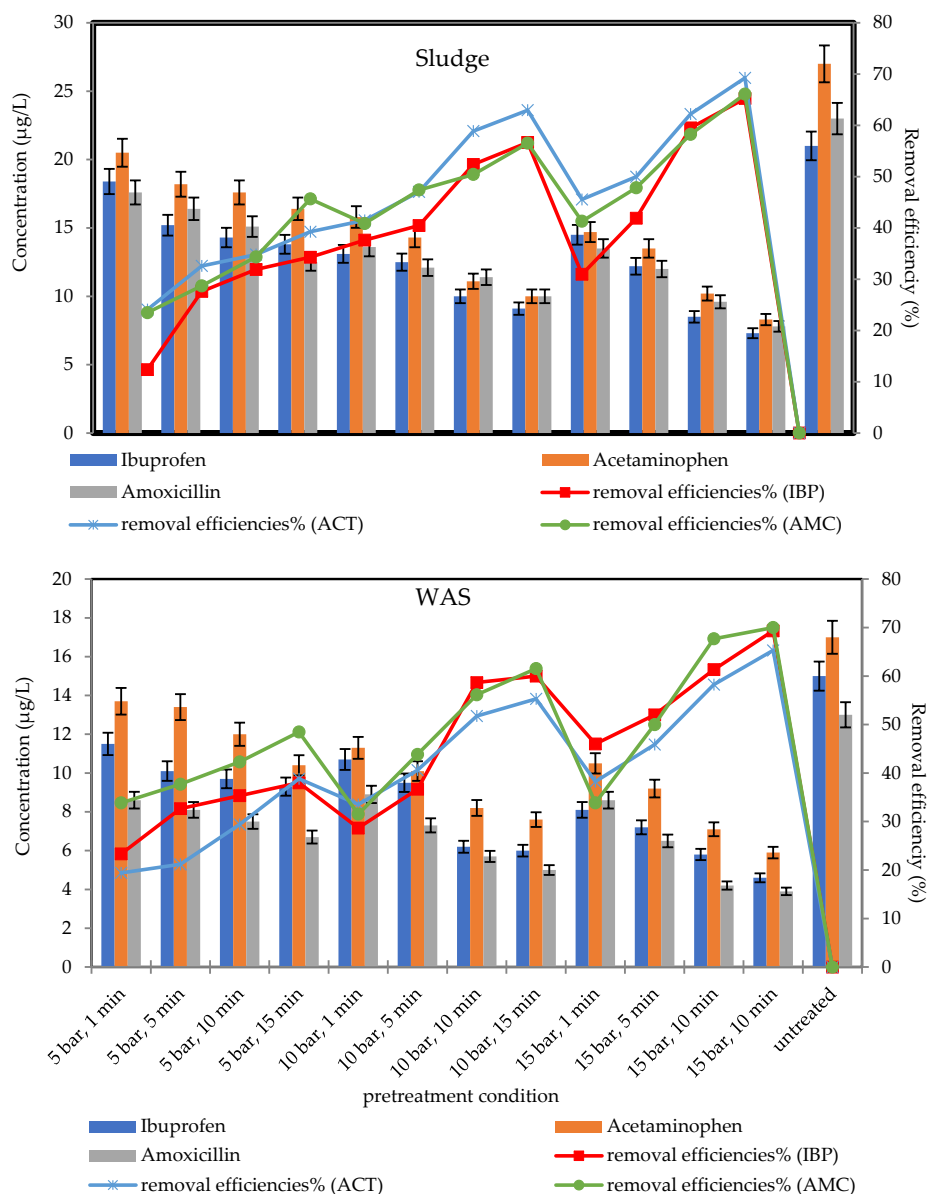


Figure 2. The efficiency of the steam explosion pretreatment in pharmaceutical reduction.

Only pretreatment with a high pressure and long retention time (10 bar for 10 min, 10 bar for 15 min, 15 bar for 10 min, and 15 bar for 15 min) resulted in the degradation of the pharmaceuticals. The highest removal efficiencies for ibuprofen, acetaminophen, and amoxicillin were obtained in the primary sludge at percentage removals of 65%, 69%, and 66% respectively. For WAS, the removal rates were 70%, 66%, and 70% for ibuprofen, acetaminophen, and amoxicillin, respectively. Therefore, pharmaceutical residuals in primary sludge and WAS can be eliminated with a high pressure and long retention time with steam explosion pretreatment [31].

3.3. Effect of Steam Explosion Pretreatment on the Sludge Properties

The effect of pressure and retention time of steam explosion pretreatment on the breakdown of primary sludge and WAS structure were examined in order to improve biodegradation, solubilization, and dewaterability or filterability. The results for the changes in the solubilization of the pretreated inoculum and primary sludge are presented in Table 1.

According to Table 1, the increased pressure and retention time led to improved solubility of COD (Figure 3). The greatest increase in SCOD was obtained at 10 bar for 15 min, 15 bar for 10 min, and 15 bar for 5 min for WAS and primary sludge. The SCOD of primary sludge in these pretreatments was optimized by 53%, 57%, and 49%, respectively. The SCOD of waste activated sludge was improved by 52%, 54%, and 50%, respectively. Therefore, increasing the pressure and the retention time increased the SCOD amount because more organic material was digested in the primary sludge and WAS and more soluble components entered the liquid phase (Figure 3).

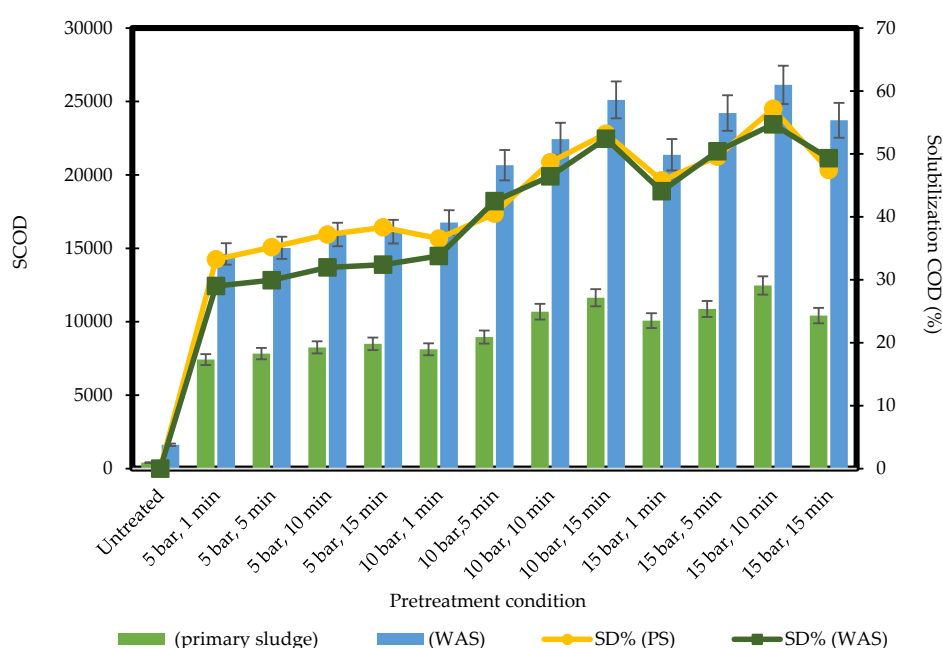


Figure 3. Increase of solubilized COD by steam explosion pretreatment.

The TCOD concentration decreased when the pressure was increased from 5 to 10 and 15 bar, which confirms that high pressure is necessary for degrading organic components and consequently to increase biogas production [12]. The results showed the retention times of 1 min and 5 min were not sufficient to optimize the solubilization of COD (Figure 3 and Table 1). However, the results also indicated that there are limits to the improvements in solubility achieved by increasing the retention time. When the retention time reached 15 min, the amount of solubility was decreased. Hence, the impact of the retention time is lower than that of pressure.

Table 1. Changes in properties of primary sludge (PS) and waste-activated sludge (WAS) by steam explosion pretreatment.

Pretreatment Conditions			SD%		VS/TS		pH	
Pressure (bar)	Time (min)	T (°C)	Primary Sludge	WAS	Primary Sludge	WAS	Primary Sludge	WAS
5	1	160	33 ± 2	29 ± 1	0.64 ± 0.2	0.55 ± 0.1	7.7 ± 0.1	7.6 ± 0.08
5	5	160	35 ± 2	30 ± 1	0.63 ± 0.2	0.54 ± 0.13	7.6 ± 0.1	7.5 ± 0.11
5	10	160	37 ± 1	32 ± 3	0.62 ± 0.1	0.53 ± 0.16	7.4 ± 0.08	7.3 ± 0.12
5	15	160	38 ± 3	32 ± 2	0.61 ± 0.15	0.51 ± 0.1	7.1 ± 0.06	7.3 ± 0.1
10	1	185	36 ± 2	33 ± 1	0.63 ± 0.28	0.51 ± 0.19	7.2 ± 0.1	7.1 ± 0.07
10	5	185	40 ± 3	42 ± 2	0.62 ± 0.2	0.49 ± 0.15	7 ± 0.05	6.8 ± 0.09
10	10	185	48 ± 5	46 ± 4	0.59 ± 0.24	0.48 ± 0.14	6.6 ± 0.07	6.6 ± 0.11
10	15	185	53 ± 4	52 ± 4	0.58 ± 0.3	0.50 ± 0.09	6.1 ± 0.03	6.5 ± 0.15
15	1	205	45 ± 3	44 ± 2	0.62 ± 0.1	0.48 ± 0.12	7.1 ± 0.11	6.7 ± 0.1
15	5	205	49 ± 2	50 ± 3	0.58 ± 0.17	0.47 ± 0.18	6.3 ± 0.05	6.5 ± 0.13
15	10	205	57 ± 4	54 ± 5	0.57 ± 0.22	0.46 ± 0.26	6 ± 0.09	6.1 ± 0.14
15	15	205	47 ± 3	49 ± 2	0.60 ± 0.14	0.47 ± 0.21	6.2 ± 0.14	6.2 ± 0.12
Untreated					0.64 ± 0.1	0.55 ± 0.14	7.8 ± 0.12	7.6 ± 0.09

The VS/TS ratios of untreated primary sludge and inoculum were 0.64 and 0.55, respectively. These results indicated that the increased pressure caused a decrease in VS/TS (Table 1). This factor is a positive indication of the degradation of the organic solids in the pretreated primary sludge and WAS [8]. The VS/TS ratio was reduced during the pretreatment at 10 bar for 15 min, 15 bar for 10 min, 10 bar for 10 min, and 15 bar for 10 min for primary sludge and WAS (Table 1). Protein hydrolysis is limited because the proteins are inside the cells of sludge. Therefore, carbohydrates are more easily hydrolyzed than proteins. Hence, the decrease in pH after the steam explosion of primary sludge and WAS confirms that low-molecular-weight acids are generated due to the hydrolyzation of carbohydrates. When the pressure increased to 10 and 15 bar, the pH was decreased, which enhanced the hydrolysis of the carbohydrates [34].

CST analysis was used to reveal the effects of steam explosion pretreatment on the filterability and dewaterability of primary sludge and WAS. The CST values of primary sludge and WAS were 124 s and 138 s, respectively (Figure 4).

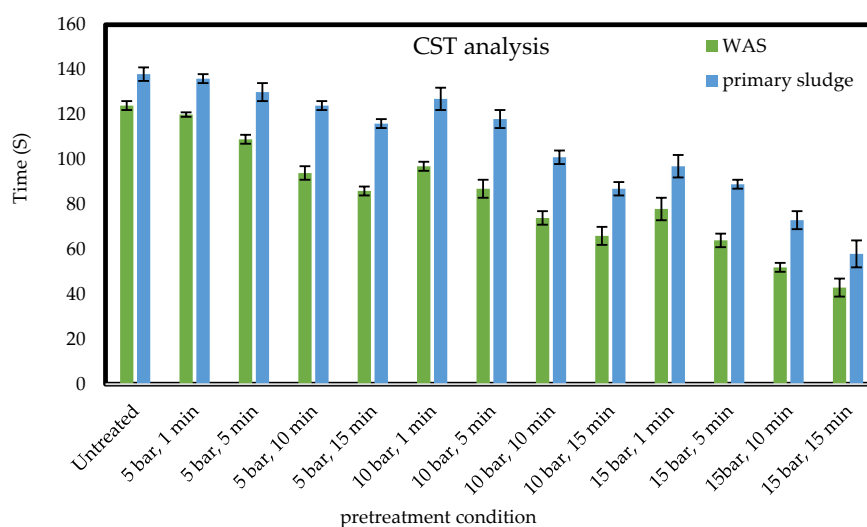


Figure 4. Effects of steam explosion pretreatment on capillary suction time (CST) of PS and WAS.

The best results of the CST test were obtained with the 15 bar for 15 min pretreatment. The amount of CST was decreased with the increasing pressure and retention time. The steam explosion led to an improvement in the specifications of sludge so that the water bonded to the sludge floc was released to become bulk water. Under all the pretreatments, the filterability and dewaterability of sludge and WAS were respectively lower than those in the untreated sludge and inoculum. Accordingly, the decrease of CST shows that the steam explosion was effective in changing the structure of primary sludge and WAS, which is related to the breaking up sludge flocs to increase the solubilization of organic components [35]. As a result, the increased pressure and retention time caused an improvement in the filtrate yield [36].

3.4. Effect of the Steam Explosion on Biogas Production

The results of the influence of the steam explosion on methane production from the primary sludge and WAS are shown in Table 2. Cumulative methane was obtained from pretreated primary sludge and WAS after 60 days of incubation. The average amount of methane produced per day was measured during the first ten days of the anaerobic digestion process as the initial production rates. Time and pressure were investigated as pretreatment variables, and the impacts of the pretreatment were determined using the methane yield as the response variable.

The methane production of the WAS and primary sludge without pretreatment or control samples after 60 days was 117 and 135 mL CH₄/g VS, respectively (Figure 5). Theoretical methane yield based on Equation (1) was estimated at 470 mL CH₄/g VS. Total methane production of the PS and WAS pretreated with all of the steam explosion treatments were higher than those of the primary sludge and WAS without pretreatment. After pretreatment, the best methane yield was obtained after pretreatment with 10 bar for 15 min and 15 bar for 10 min, with respective values of 380 and 358 mL CH₄/g VS for the primary sludge and 315 and 334 mL CH₄/g VS for the WAS (Table 2, Figure 5). Accordingly, the methane yields of primary sludge and WAS increased by 181% and 185%. The highest initial production rate was obtained after pretreatment of sludge at 10 bar for 10 min and 10 bar for 15 min, resulting in 218 and 207 mL CH₄/g VS, a 220% increase versus the values in untreated primary sludge of 68 mL CH₄/g VS. For the WAS, the highest initial production rate was observed at 15 bar for 10 min and 10 bar for 15 min, with increases of 245% to 197 and 192 mL CH₄/g VS, respectively (Table 2, Figure 5).

When the pressure increased from 5 bar to 10 and 15 bar, the methane production increased. The same trend was observed for the treatment time. Improvement of methane production yield showed that the degradation of the primary sludge structure and WAS were achieved by steam explosion pretreatment. The steam explosion led to increased methane production in the first few days of the anaerobic digestion process. The results show that 57% and 59% of total methane were produced during 10 days of incubation. These findings indicate a positive effect of pretreatment on the PS and WAS structures and on the increased digestion of organic matter.

Table 2. Effect of steam explosion pretreatment on methane production.

Pretreatment Conditions			Methane Production			
Pressure (bar)	Time (min)	T (°C)	Waste Activated Sludge		Primary Sludge	
			Production Rate mL CH ₄ /day	Yield mL CH ₄ /g VS	Production Rate mL CH ₄ /day	Yield mL CH ₄ /g VS
5	1	160	166	252 ± 12	178	278 ± 10
5	5	160	158	271 ± 14	185	281 ± 5
5	10	160	168	276 ± 21	192	308 ± 11
5	15	160	173	284 ± 15	172	325 ± 14
10	1	185	162	253 ± 10	193	311 ± 21
10	5	185	163	285 ± 12	180	301 ± 19
10	10	185	182	297 ± 19	207	353 ± 20
10	15	185	192	315 ± 26	218	380 ± 35
15	1	205	163	269 ± 17	178	288 ± 14
15	5	205	170	271 ± 10	197	320 ± 22
15	10	205	197	334 ± 25	196	358 ± 28
15	15	205	178	289 ± 36	189	335 ± 22
Untreated			57	117 ± 7	68	135 ± 9

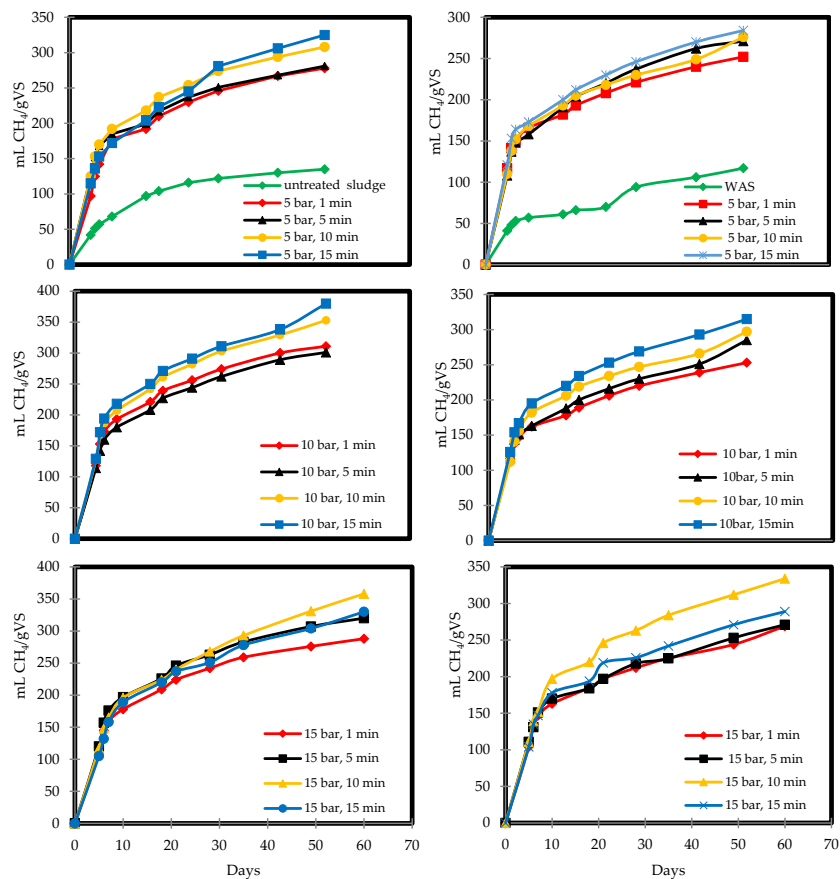


Figure 5. Cumulative methane production during anaerobic digestion from PS and WAS pretreated by steam explosion.

3.4.1. Effect of Solubilization on Biodegradability

The relationship between solubilization and biodegradability after pretreatment with methane production is shown in Figure 6. The figure shows that the increase in the organic solubilization rate and structure degradation are effective in increasing the biodegradability and methane yield [12].

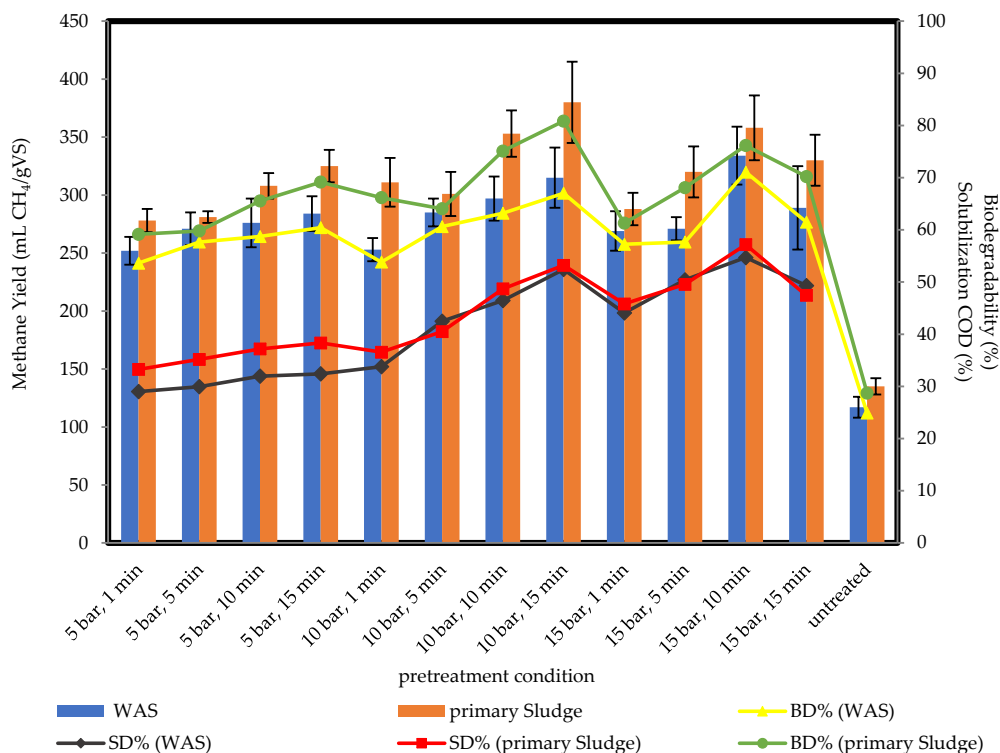


Figure 6. The relation between experimental methane yields, biodegradability, and solubilization of PS and WAS.

The steam explosion pretreatment led to enhanced solubilization followed by biodegradability when high pressures (10 and 15 bar) with long retention times were applied (Figure 6). The best solubilization was observed at 10 bar for 15 min and 15 bar for 10 min pretreatment, with improvements of 57% and 54% for primary sludge and WAS, respectively. However, the 15 bar for 15 min pretreatment resulted in decreasing the solubilization and biodegradability. This decrease was due to the thermal reaction that led to the change in chemical structure and the complete destruction of the biodegradable matter [8]. Additionally, when the retention time was too short (i.e., 1 and 5 min) at all pressures, the pretreatment was not successful in structure breakdown or in changing the chemical structure. The conditions with the pressure and time of greater 5 bar and 5 min, respectively, had the greatest effect on the methane yield of the PS and WAS [37]. The biodegradability of pretreated primary sludge and pretreated WAS was found to increase from 29% and 25% to 80% and 71%, respectively (pretreatment at 10 bar for 15 min for sludge and 15 bar for 10 min for inoculum) (Figure 6). These results indicated the steam explosion hydrolyzes the solids or disrupts their structure; thus, COD organic matter became available to microorganisms and, consequently, the biodegradability was improved.

3.4.2. Effect of Reduction of the Pharmaceuticals and Heavy Metals on Biodegradability

The effects of the reduction of pharmaceuticals and heavy metals on the biodegradation of primary sludge and WAS are shown in Figure 7.

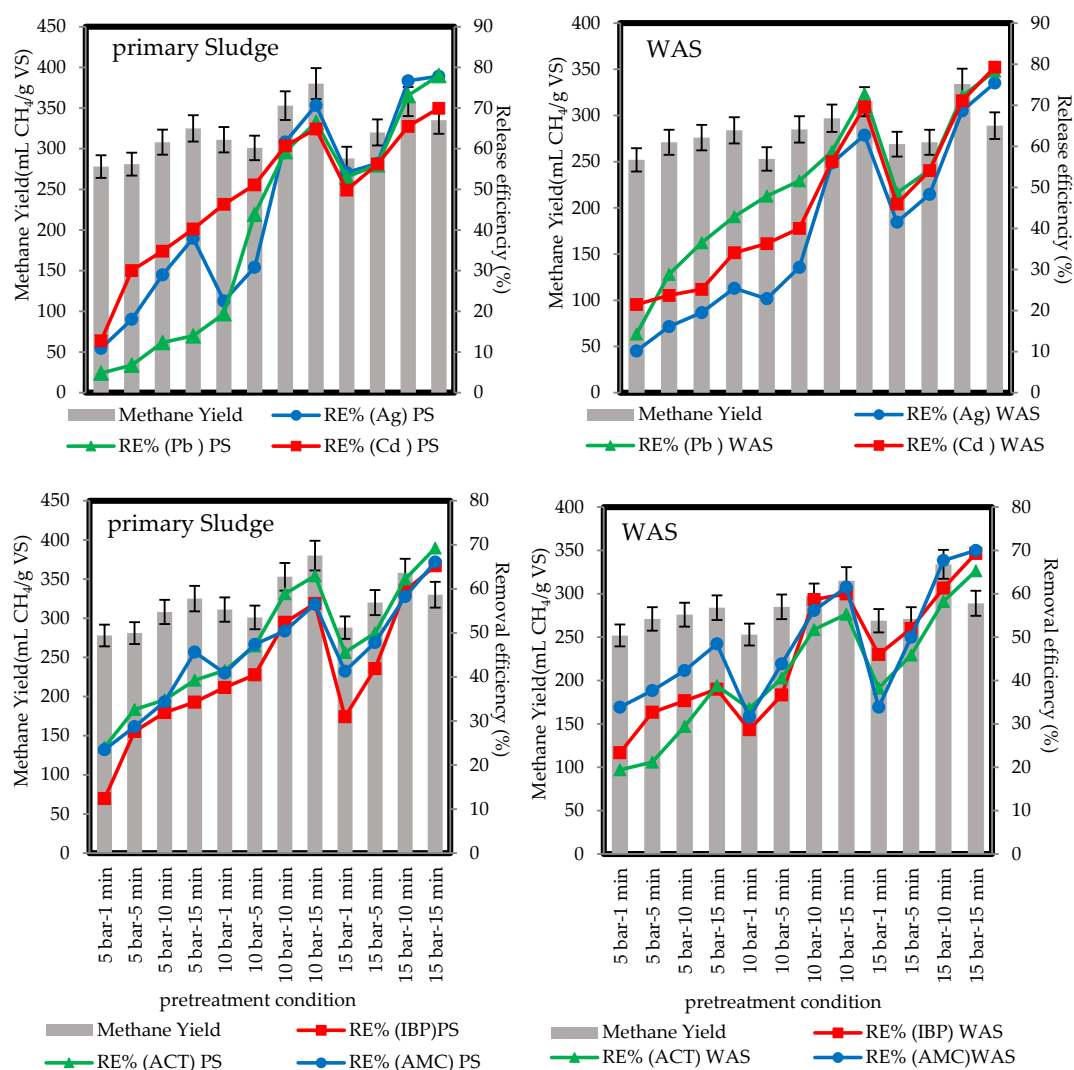


Figure 7. The relation between the removal efficiency of pharmaceuticals and release efficiencies of heavy metals with the methane yield.

Accordingly, it was observed that the reductions in pharmaceuticals and heavy metals had a positive effect on biodegradability, which resulted in increased methane production. The pretreatments with high pressure and long retention time resulted in increased removal efficiency of pharmaceuticals and heavy metals, which led to an increase in biodegradability. Accordingly, the pretreatments at 10 bar for 15 min and 15 bar for 10 min resulted in the highest methane yield. In the first condition (10 bar for 15 min), the release efficiencies of Ag, Cd, and Pb were 71%, 65%, and 67% for primary sludge and 63%, 70%, and 72% for WAS, respectively. In the second condition, the release efficiencies of Ag, Cd and Pb were 77%, 66%, and 73% for primary sludge and 69%, 72%, and 72% for WAS, respectively. The highest removal efficiencies of pharmaceuticals were obtained at 10 bar for 15 min, reaching values of 57%, 63%, and 56% for PS and 60%, 55%, and 62% for WAS for ibuprofen, acetaminophen, and amoxicillin, respectively. The highest removal efficiency of pharmaceuticals for the primary sludge at 15 bar for 10 min was 60%, 63%, and 58% for ibuprofen, acetaminophen, and amoxicillin, respectively, and for WAS, these values were 62%, 58%, and 68% (Figure 7). Therefore, the reduction of pharmaceuticals and heavy metals by steam explosion pretreatment could enhance the biodegradation of primary sludge and WAS [38].

Results of the ANOVA are shown in Table 3, which presents the coefficient for the linear effect of the time and the effects of the pressure on methane yield. The differences are statistically significant

model terms at the 95% confidence level ($p < 0.05$). ANOVA results revealed that the factors pressure and time affected methane production. According to the results, steam explosion pretreatment causes the disintegration and solubilization of solid sludge particles and toxic substances, thereby enhancing the hydrolysis step and, in turn, increasing the biodegradability biogas production.

Table 3. GLM ANOVA to determine the parameter effect of steam explosion on the methane yield.

Analysis of Variance								
Source	DF	Seq SS	Adj SS	Adj MS	F-Value	p-Value	Coef	SE Coef
pressure	1	1384.6	1132.7	1132.7	5.60	0.039	2.1024	0.8883
time	3	3836.7	3836.7	1278.9	6.32	0.011	2.9496	0.9589
Error	10	2022.1	2022.1	202.2				
Total	14	7243.3						

S = 14.2199 R-Sq = 72.08% R-Sq(adj) = 60.92%

4. Conclusions

Steam explosion pretreatment led to a positive change in the structure of PS and WAS, improving their solubilization, filterability, and biodegradability. The steam explosion was effective in pharmaceutical removal and heavy metal release in both PS and WAS before the anaerobic digestion process, thereby increasing biodegradability and methane production. There was a direct correlation between solubilization and biodegradability. When solubilized COD was increased by the pretreatment, the biodegradability of PS and WAS, and consequently methane production, was enhanced. The best methane production yields were obtained after 10 bar for 15 min and 15 bar for 10 min pretreatments, with values of 380 and 358 mL CH₄/g VS for the primary sludge and 315 and 334 mL CH₄/g VS for the WAS, respectively. According to the results, methane yield increased by 181% and 185% for primary sludge and WAS, respectively. Therefore, steam explosion is a suitable technique for removing toxic substances to improve biodegradability and biogas production as a pretreatment prior to anaerobic digestion for PS and WAS in wastewater treatment plants.

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