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Effect of suspended solids removal methods on methane production from tapioca starch wastewater

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Abstract

This study aims to evaluate methods for removing suspended solids (SS) from tapioca starch wastewater to increase methane producing activity (MPA) and biochemical methane potential (BMP). Three methods for SS removal, filtration, centrifugation, and settling, were compared using raw wastewater that had a high SS concentration of over 3,000 mg/L. Filtration was found to be the best method and it increased the MPA by 44% while removing 100% of the SS. Centrifugation and gravity settling had substantial effects, increasing BMP by 7.7% and 6.1% and removing 98.4% and 15.5% of SS, respectively. While the SS concentration is the main factor for determining the success of an up-flow anaerobic sludge bed (UASB) system, this study showed that the carbohydrate to protein ratio signifies that the biochemical component of the wastewater is a key factor causing increases in MPA and BMP. The SS removal methods used in this study also led to higher carbohydrate/COD and protein/COD ratios, which can increase MPA and BMP values relative to conditions where SS removal is not performed.

Keywords: Tapioca starch wastewater, Suspended solids removal method, Methane producing activity, Biochemical methane potential

1. Introduction

The tapioca starch industry plays an important role in Thailand's economy. The country is the world's largest exporter of tapioca starch [1], an important material for many industries, from food and animal feed to non-food industries [2]. The production process for tapioca starch requires large volumes of water, which in turn produces great amounts of wastewater. Tapioca starch industries generate an average of 19-20 m^3 of wastewater per tonne of tapioca starch production [1]. This wastewater has high levels of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids (SS) [3-4]. Therefore, an anaerobic biological treatment system is suitable for processing tapioca starch wastewater.

For the most part, treatment systems for tapioca starch wastewater in Thailand are anaerobic covered lagoon (ACL) systems. Such systems are considered to be require little care with low investment and operational costs. They require only technology that is fully commercialized in Thailand and large land area, which Thai factories tend to have in abundance [1, 4-5]. The disadvantages of ACL systems are their high hydraulic retention time and for some factories, investment for a large land area can be prohibitive. High-rate wastewater treatment systems offer an alternative for the tapioca starch industry.

Up-flow Anaerobic Sludge Bed (UASB) systems are commonly employed for wastewater treatment in a variety of industries, especially the food industries [6]. They require a smaller land area than ACLs and achieve a high organic loading rate of around 10 kg COD/m^3-d, as well as a high COD removal of more than 95% [1, 3-4, 6]. However, continuous operation of a UASB system for processing tapioca starch wastewater may lead to system failure, generally caused by the phenomenon of sludge washout. This occurs when wastewater contains large quantities of SS [3], resulting from SS attaching to the granular sludge and biogas bubble surfaces. Blockage of biogas in the sludge bed occurs in the UASB system resulting in the granule sludge rising to the liquid surface. This causes a reduction in the anaerobic active zone, lowers the methane production rate, and decreases the methane production potential [7-8]. A pretreatment system for SS removal, followed by feeding influent wastewater into the UASB system at SS levels below 1,000 mg/L, has been recommended for UASB system operation [3]. However, there remains a lack of information on how SS removal methods in the pretreatment of tapioca starch wastewater affect the methane production rate and potential [3].

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Table 1 SS removal conditions applied to tested wastewater

Test wastewater category	SS removal conditions
Raw wastewater (RW)	Non-SS removal
Filtered wastewater (FW)	Filtration through a 0.45 µm glass fiber filter
Centrifuged wastewater (CW)	Centrifugation at 5,000 rpm, 25 °C for 10 minutes
Gravity settling wastewater (SW)	Settling in an Imhoff cone for 1 hour

Table 2 Medium composition of serum vials

Chemical	Concentration (mg/L)	Chemicals	Concentration (mg/L)
$FeCl_2 \cdot 4H_2O$	2.0	$CuCl_2 \cdot 2H_2O$	0.027
$CoCl_2 \cdot 6H_2O$	0.17	$Na_2MoO_4 \cdot 2H_2O$	0.025
$ZnCl_2$	0.07	EDTA(2Na)	5.0
H_3BO_3	0.06	$MgCl_2 \cdot 6H_2O$	400
$MnCl_2 \cdot 2H_2O$	0.50	$CaCl_2$	113
$NiCl_2 \cdot 6H_2O$	0.04	NH_4Cl	500

Three different SS removal methods were studied to provide data on methane producing activity (MPA) and biochemical methane potential (BMP), filtration, centrifugation, and simple gravity settling. These pretreatment methods were studied to measure the methane production rate and methane production potential.

2. Materials and methods

2.1 Tapioca starch wastewater samples

The tapioca starch wastewater used in this study was collected from a factory based in Khon Kaen, Thailand. The factory has a process capacity of 200 tonnes/day and generated wastewater at approximately 12 m^3/tonne of production. The tapioca starch wastewater samples were collected from a starch extraction process with no SS removal. During experimentation, each raw wastewater (RW) sample was pretreated using one of three different SS removal methods, filtration, centrifugation, or gravity settling. The removal conditions are shown in Table 1. In these experiments, the wastewater tested was separated into four categories, 1) RW, 2) filtered wastewater (FW), 3) centrifuged wastewater (CW), and 4) gravity settling wastewater (SW).

The four types of test wastewater were analyzed for COD, BOD, SS, and volatile suspended solids (VSS) levels according to standard methods [9]. Carbohydrate and protein contents were also analyzed using a phenol sulfuric acid method [10] and Lowry's method [11], respectively. These latter two variables were used to characterize the biochemical components of the tested wastewaters.

2.2 Source of sludge

Sludge was collected from an ACL located at a tapioca starch factory in Khon Kaen, Thailand. The mixed liquor volatile suspended solid (MLVSS) ratio of the sludge was 19,800 mg/L. After preliminary sampling, the sludge was kept at 4 °C for a month. Prior to starting the experiment, the sludge was washed with a 25 mM potassium phosphate buffer under anaerobic conditions at room temperature and then kept at 35 ± 2 °C in a temperature controlled water bath overnight.

2.3 Experimental setup and analytical methods

In this study, MPA refers to the determined capability of an anaerobic digester to convert sludge in the test wastewater to methane. To determine levels of bio-methane that were obtainable from the wastewater of interest, an anaerobic biodegradability test, or BMP, was conducted. In sludge activity assessment, or specific methanogenic activity (SMA), acetate and H_2/CO_2 were used as test substrates. MPA, BMP, and SMA were analyzed in serum vials [12-13] under mesophilic conditions (35±2°C). Table 2 summarizes the concentrations of the mediums in the serum vials. The mediums consisted of 25 mM potassium phosphate buffer, 250 mg/L $Na_2S \cdot 9H_2O$, 1,000 mg/L $NaHCO_3$, the test sludge, and the test substrate or test wastewater. The test substrate or test wastewater and test sludge were initially set at a total COD of 2,000 mgCOD/L and 5,000 mgVSS/L, respectively, or at a food/microorganism (F/M) ratio of 0.4 mgCOD/mgVSS. The experiments were carried out in triplicate, followed by tests on control vials (blanks), in which the serum vials only contained the test sludge and no additional test wastewater. The serum vials were capped with butyl rubber stoppers and aluminum caps, and anaerobic conditions were reached by purging the vials with pure N_2 gas. The serum vials were neutralized to pH 7.0 using a 0.1 N H_2SO_4 or 0.1 N NaOH solution. At the starting point of the experiment, the test wastewater was added and the liquid phase in the serum vial was sampled for analysis of the input COD concentration (COD_{start}). Then, the serum vials were placed in a shaking water bath set at 35 °C and 120 rpm. During the experiment, biogas production was measured and analyzed periodically until it was no longer detected. Biogas production volume was measured using a wetted syringe technique. The methane content in the produced biogas was analyzed using gas chromatography (Shimadzu GC-8A) with a thermal conductivity detector. The net volume of methane produced from the test wastewater was calculated relative to methane production from a control vial to avoid errors in determining the volume of methane produced from the test sludge. This was done according to the following equation:

$$V_{net} = V_{ww} - V_{control}$$

V_{net}: net volume of methane produced from the test wastewater (mL)

V_{ww}: total volume of methane produced from the test wastewater vial (mL)

$V_{control}$: total volume of methane produced from the control vial (mL)

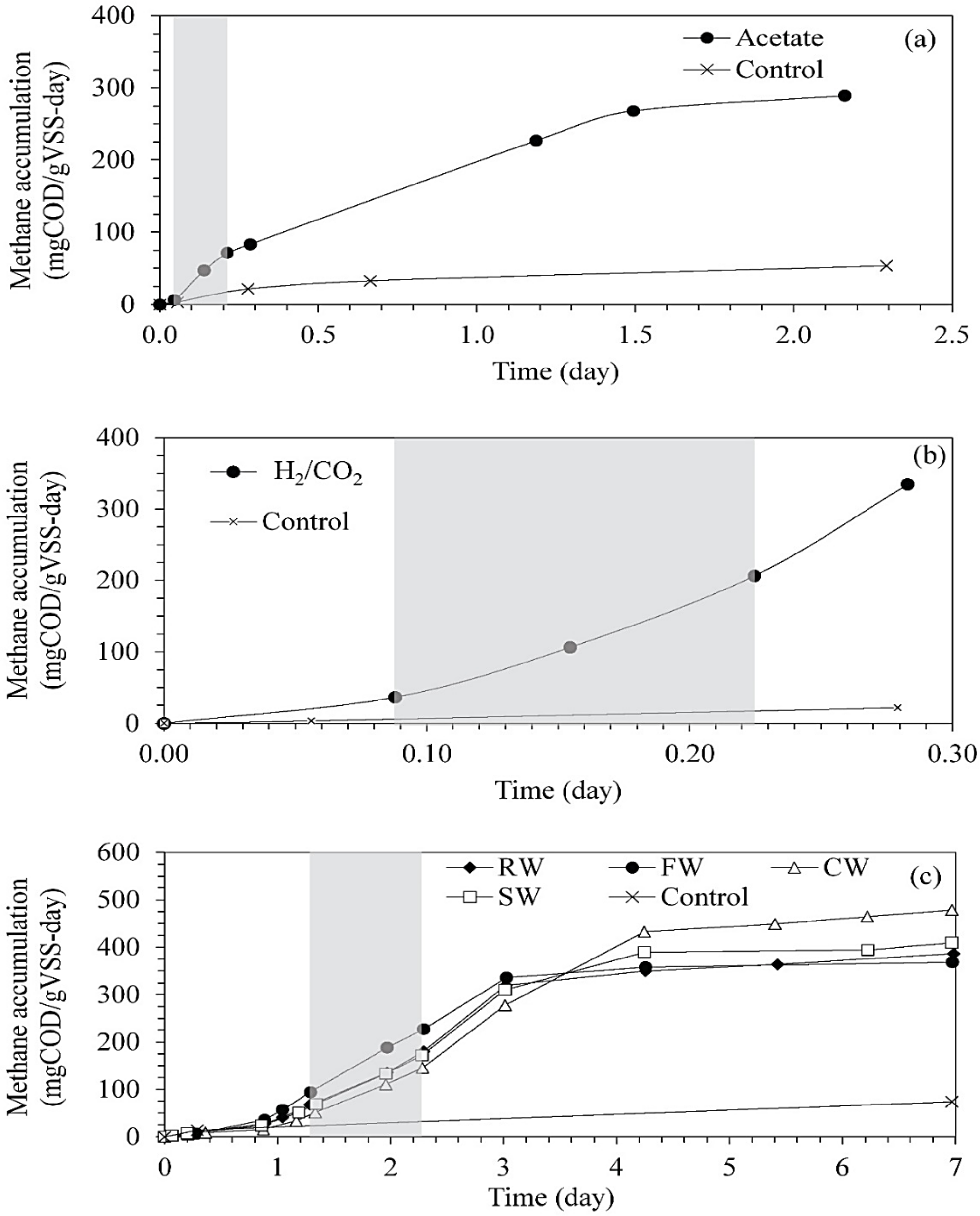

Figure 1 Accumulation of methane over time from (a) acetate, (b) H_2/CO_2, and (c) the various test wastewater types

Measurements of methane production volume at 35 °C were converted from mL to mgCOD/L using a methane COD equivalent value of 0.395 mL/mgCOD.

3. Results and discussion

3.1 Comparison of MPA and BMP

Accumulation of methane produced over time from acetate, H_2/CO_2, and the tested wastewater are shown in Figure 1. Examination of the various test wastewater samples was carried out for seven days until methane accumulation was stable.

The SMA, MPA, and BMP values were calculated from analysis of the graphs in Figure 1. The SMA values of acetate and H_2/CO_2 and the MPA of the test wastewater were calculated from the slopes of the relationships in this figure, using the time with the highest methane accumulation (highlighted area) from Figure 1 (a), (b) and (c), respectively. The BMP values were calculated from V_{net} (mgCOD/L) as a percentage of COD_{start} for each test wastewater sample (mgCOD/L).

As shown in Figure 1 (a) and (b), the SMA values of acetate and H_2/CO_2 were 282 and 816 mgCOD/gVSS-day, respectively. The test wastewater in the present study showed two times the level of acetoclastic methanogenesis activity than previous research [14] on the SMA of ACL sludge treatment for tapioca starch wastewater.

Figure 2 shows that FW had the highest MPA value at 129.6 mgCOD/VSS, 44.0% higher than that of RW. However, the MPA values of CW and SW were lower than that of RW, by 14.1% and 9.0%, respectively. MPA values ranked in descending order were: FW > RW > SW > CW. Conversely, CW and SW achieved the highest BMP values. These were 7.7% and 6.1% higher than RW, respectively. BMP values ranked in descending order were:

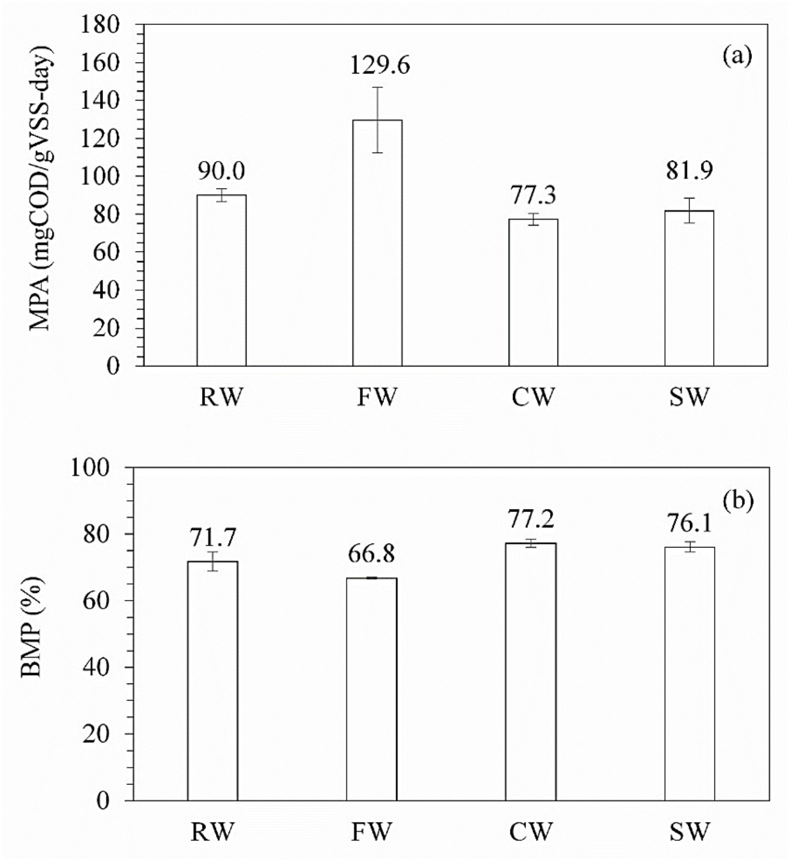

Figure 2 Comparison of (a) MPA and (b) BMP values among the four different wastewater types

CW > SW > RW > FW. These results demonstrate that SS removal methods affect MPA and BMP values.

3.2 Effect of SS removal method on MPA and BMP

The physicochemical and biochemical characteristics of the RW and the wastewaters that underwent various SS removal methods are displayed in Table 3. The findings show that the major differences after application of the various methods of SS removal were changes in total COD, total BOD, SS, VSS, carbohydrate, and protein concentrations.

Table 3 shows that based on the SS measured in the RW, 100%, 98.4%, and 15.5% of SS was removed from the FW, CW, and SW samples, respectively. The filtration method was able to lower the SS and VSS concentration, decreasing carbohydrate and protein content by 14.1% and 43.7%, respectively. This indicates that most of the solid particles consisted of protein, whereas most of the soluble components are carbohydrates in tapioca starch wastewater. The centrifugation method was able to decrease carbohydrate and protein contents by 56.5% and 33.2%, respectively. In the tapioca starch production, centrifugal force is used to separate starch [1, 15]. The results of this study indicate that centrifugation has the ability to remove heavy and light solid particles, including those with diameters less than 0.45 µm. However, a little amount of solid residue is rendered. Additionally, the COD and BOD of the tapioca starch wastewater decreased after pretreatment using filtration and centrifugation methods, indicating that they are both capable of lowering COD and BOD of the SS content in this wastewater.

A significant difference in the characteristics of the various types of test wastewater affected the MPA and BMP values [16-17]. Therefore, to identify the key factors responsible for the MPA and BMP values of the test wastewater, the test wastewater's characteristics (summarized in Table 1) were considered in terms of component ratios, as shown in Figure 3. This data was then compared with the MPA and BMP values shown in Figure 2.

The BOD/COD ratio is an indication of organic matter biodegradability. It can help in the selection of a suitable wastewater treatment system. A higher BOD/COD ratio indicates that degradation will progress more easily during biological treatment. The test wastewater contained a BOD/COD ratio greater than 0.50. This indicates that a biological treatment system would be suitable. The BOD/COD ratios ranked in descending order were: RW > SW > CW > FW. This ranking is not in agreement with the MPA and BMP rankings presented earlier. For anaerobic wastewater treatment, therefore, the biodegradability of the wastewater should be evaluated using the BMP value rather than than BOD/COD ratio.

The findings regrading MPA and BMP (Figure 2) and SS/COD (Figure 3 (a)) show that the sample with the lowest SS/COD ratio (FW) had the highest MPA. CW had a lower SS/COD ratio relative to RW and SW, but had a lower MPA value compared to these samples. FW had a lower SS/COD ratio than RW and SW and had a lower BMP than the other types of test wastewater. Therefore, SS/COD did not have a direct effect on MPA and BMP in this study. However, a UASB system is ideal for treating wastewater with an SS concentration below 1,000 mg/L. Therefore, filtration or centrifugation is suggested as a pretreatment in a UASB system [3].

Table 3 Characteristics of the test wastewaters after application of SS removal methods

Parameters	RW	FW	CW	SW
pH	4.15	4.19	4.13	4.11
Total COD (mg/L)	13,500	11,100*	10,400	12,500
Total BOD (mg/L)	9,000	5,700*	5,600	7,600
SS (mg/L)	3,650	0	58	3,085
VSS (mg/L)	3,025	0	6	2,710
Carbohydrate (mg/L)	1,770	1,520	770	1,300
Protein (mg/L)	1,625	915	1,085	1,540

* Remark: As FW is the test wastewater that underwent filtration, total COD and total BOD are equivalent to soluble COD and soluble BOD, respectively.

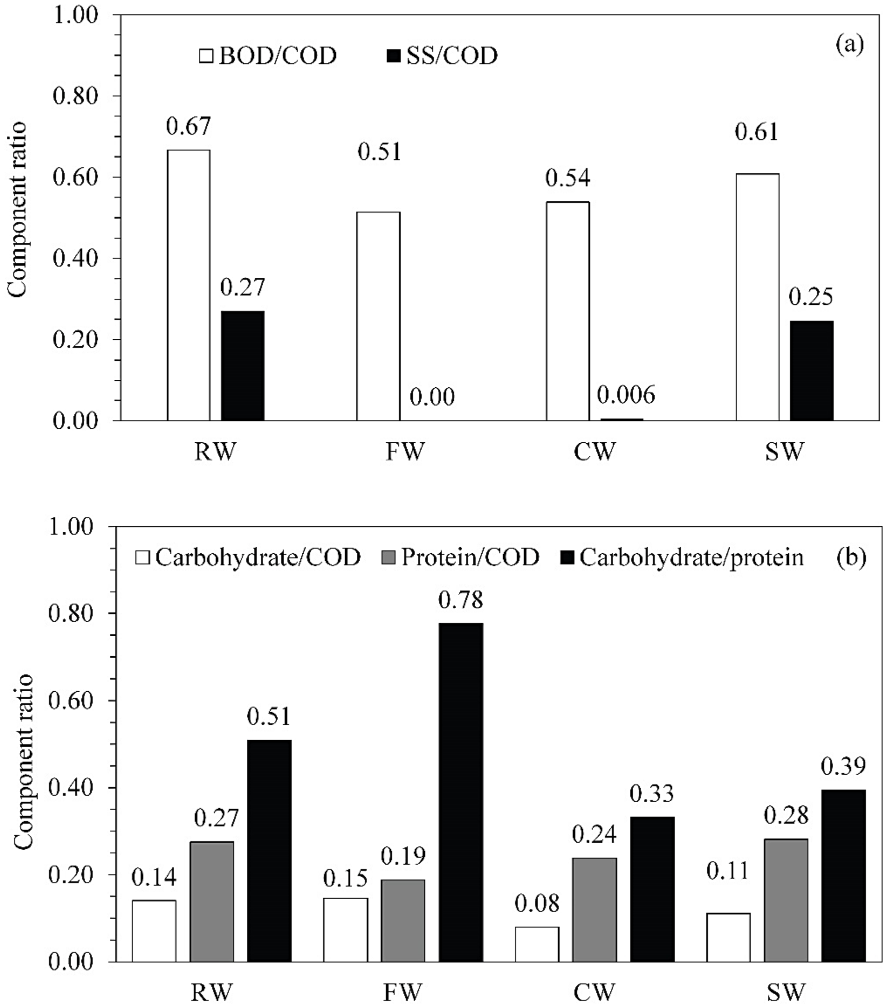

Figure 3 A comparison of the component ratios of the test wastewater types.
(a) BOD/COD and SS/COD, (b) carbohydrate/COD, protein/COD and carbohydrate/protein.
(Remark: carbohydrate and protein were converted to COD equivalent concentrations before dividing by COD concentration)

The descending order of the ranked MPA values were in line with the descending order of the ranked carbohydrate/COD and carbohydrate/protein ratios. This indicates that the FW and RW samples had high MPA values due to their high carbohydrate contents. MPA increased with a carbohydrate/protein ratio higher than 0.5. These results support the theory that the difference in MPA values was due to higher hydrolysis rate of the organic component in the wastewater. Hydrolysis of carbohydrate occurs at a higher rate than for proteins [18].

Alternatively, the descending order of the ranked BMP values correlated with the ascending order of the ranked MPA values and carbohydrate/protein ratios. The methane yield of protein is 1.2 times higher than that of carbohydrate [17]. Therefore, a lower carbohydrate/protein ratio resulted in higher BMP values. These results indicate that a higher protein ratio in tapioca starch wastewater results in an increased BMP value.

The findings from this study suggest that a SS removal method with a carbohydrate/protein ratio above 0.5 is most favorable for increasing MPA values. An anaerobic treatment system fed with wastewater that has higher MPA values that facilitates a higher organic loading rate and shorter hydraulic retention time in a UASB system. This helps to lower the investment costs for contructing a UASB system. Moreover, when applying a pretreatment to a UASB system, the SS removal method must be one capable of decreasing the SS concentration in the influent to less than 1,000 mg/L [3] to achieve optimal treatment. Accordingly, among the SS removal methods tested in this study, filtration and centrifugation are recommended. Their application in the pretreatment process of a UASB system would reduce sludge washout. When considered in terms of real-world applications, the available filtration technology favors sand filtration followed by microfiltration. While these technologies have the capacity to remove 100% of SS from wastewater at industrial scale, they require high investment and maintenance. Alternatively, real-world applications of industrial centrifugation, or decanters, can both remove SS from the wastewater and recover the SS to increase starch production. It should be noted, however, that the MPA of CW was half that of FW, and 58 mg/L SS remained in the tested CW. Thus, before a user makes their final decision on which pretreatment process is best for their situation, each SS removal method should be evaluated in detail, considering its advantages and drawbacks.

4. Conclusions

The tested SS removal methods (filtration, centrifugation, and settling) affect the physico-chemical and biochemical characteristics of tapioca starch wastewater. Filtration is the optimal pretreatment method for the purpose of UASB system treatment, which requires that the SS concentration in the influent be kept lower than 1,000 mg/L and where a high treatment rate is expected.

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