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QUALITY OF WASTEWATER FROM CREAMING PROCESS OF SKIM NATURAL RUBBER LATEX USING HYDROXYPROPYL METHYLCELLULOSE

คุณภาพน้ำทิ้งจากกระบวนการครีมหางน้ำยางธรรมชาติโดยใช้ไฮดรอกซีโพรพิลเมทธิลเซลลูโลส

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Abstract

In this study, hydroxypropyl methylcellulose (HPMC) was used instead of concentrated sulfuric acid in the creaming process of skim natural rubber latex. In comparison to the process using concentrated sulfuric acid, the effluent acidity and sulfate ion were significantly lower but biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were slightly higher. In overall, the pollution of the effluent from creaming process was reduced using recovered HPMC process. In the effect of hydraulic retention time, acidity and sulfate ion of the effluent from recovered HPMC process were decreased as increasing the hydraulic retention time. In contrast, BOD and COD were increased. However, the high value of BOD and COD was valuable for wastewater treatment by anaerobic process.

Keywords+: creaming process, hydroxypropyl methylcellulose, hydraulic retention time, skim natural rubber latex

บทคัดย่อ

งานวิจัยนี้ได้ศึกษาการใช้ hydroxypropyl methylcellulose (HPMC) แทนกรดซัลฟิวริกเข้มข้นใน

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กระบวนการครีมหางน้ำยางธรรมชาติ น้ำทิ้งจากกระบวนการเมื่อเปรียบเทียบกับการใช้กรดซัลฟิวริกเข้มข้น มีค่าความเป็นกรดและปริมาณซัลเฟตน้อยกว่ามาก แต่บีโอดี (BOD) และซีโอดี (COD) มีค่ามากกว่าเล็กน้อย โดยสรุป การใช้ HPMC ในกระบวนการครีมหางน้ำยางและมีการนำกลับ HPMC ได้น้ำทิ้งที่มีความเป็นมลพิษลดลง สำหรับผลของระยะเวลากักพักน้ำทิ้งความเป็นกรดและปริมาณซัลเฟตในน้ำทิ้งจากการใช้ HPMC ในกระบวนการครีมหางน้ำยางและมีการนำกลับ HPMC มีค่าลดลงเมื่อระยะเวลากักพักน้ำทิ้งเพิ่มขึ้น ในทางตรงกันข้าม บีโอดีและซีโอดีมีค่าเพิ่มขึ้น อย่างไรก็ดี ค่าบีโอดีและค่าซีโอดีที่เพิ่มขึ้นมีประโยชน์ในระบบบำบัดน้ำทิ้งแบบไร้อากาศ

คำสำคัญ : กระบวนการครีม, ไฮดรอกซีโพรพิลเมทิลเซลลูโลส, ระยะเวลากักพักน้ำ, หางน้ำยางธรรมชาติ

Introduction

Thailand has been one of the main producers of natural rubber latex in the world. About 40% of the total natural rubber is produced in Thailand. The rubber industry has continuously provided a high income for Thailand both the value of production and export. The samples used in this financial evaluation were involved with producing and selling preserved latex, rubber smoked sheet, crumb rubber, crepe rubber and concentrated latex. In concentrated latex industries which nowadays increasing in production and consumption, centrifugation process is the most used in production. This process produces a large volume of skim latex as a by product which still contains about 3-10% DRC (dry rubber content). Nevertheless, it should be economically attractive and environmentally desirable to recover this significant fraction of rubber from skim latex. The usual method to recover rubber from skim latex is acid coagulation with concentrated sulfuric acid (conc H_2So_4). However, this method result a low quality of skim rubber and the remaining acid leading to the generation of highly acidic effluent which is one of the major sources of environmental pollution.

Alternatively, polymer had been reported in creaming of skim natural rubber latex[1]. Creaming of skim latex using hydroxyl propyl methylcellulose (HPMC) result a cream phase which is a concentrated skim latex and a serum phase as an effluent. The efficiency of skim rubber was similar to the use of concentrated sulfuric acid. Advantageously, skim rubber using HPMC in creaming process reported better quality as protein content in skim rubber was reduced. Moreover, HPMC is soluble in water. The lower critical solution temperature (LCST) is low (60-70°C) and reversible from gelling to solving at different temperature[2-3]. Therefore, HPMC is retained in serum phase and can recover by heating the serum phase.

The use of HPMC in creaming process of skim natural rubber latex was very interesting as a production of good quality of skim rubber as well as easy recoverability of this agent for reuse. However, there is only the report of quality of the skim rubber. Therefore, the effluent from creaming process using HPMC was studied in this article and compared to that using

concentrated sulfuric acid. Furthermore, hydraulic retention times of the effluent were studied. The effluent from the process was evaluated with the intention of the list of wastewater discharge regulation.

Materials and Methods

Creaming process of skim natural rubber latex

In sulfuric acid process, conc H_2So_4 (commercial grade) was added into skim natural rubber latex until the pH is about 4.5. A cream phase and a serum phase were separated by allowing the mixture to stand at room temperature for a few hours. Serum phase was collected as an effluent from the process.

In HPMC process, HPMC solution was first prepared by dissolved HPMC in 50 mL of deionized water to result 0.6% of HPMC in final mixture. Adding HPMC solution into 200 g skim natural rubber latex and stirred for 1 hr. The mixture was allowed for phase separation at room temperature for 1 day. Serum phase was collected as an effluent from the HPMC process.

Recovery of hydroxypropyl methylcellulose (HPMC)

The serum from creaming process using HPMC was heated at 90 °C. The precipitate of HPMC was formed and collected by filtration. The serum after recovered HPMC was collected as an effluent from the recovered HPMC process.

Effect of hydraulic retention time

The effluent from recovered HPMC process was allowed to stand at room temperature in open system for 1 y, 3 and 5 days.

The quality of the effluent from sulfuric acid, HPMC and recovered HPMC processes

The quality of the effluent from all processes was examined[4] for the parameters listed on Table 1 using AOAC standard method.

Table 1 Parameters and analytical methods for determining the quality of the effluent.

Parameters	Methods
pH	Electrometric Method
Conductivity	Electrometric Method
Total Dissolved Solids (TDS)	Total Dissolved Solids Dried at 103-105 °C
Suspended Solids (SS)	Suspended Solid Dried at 103-105 °C
Sulfide as H_2S	Methylene Blue Method
Sulfate	Turbidimetric Method
Dissolved Oxygen (DO)	DO meter
Biochemical Oxygen Demand (BOD)	5-Day BOD Test
Chemical Oxygen Demand (COD)	Closed Reflux Method
Total Kjedahl Nitrogen (TKN)	Kjeldahl and Titration Method
Ammonia Nitrogen	Titration Method
Nitrite Nitrogen	Colorimetric Method
Nitrate Nitrogen	Brucine Method

The quality of the effluent at various hydraulic retention times were evaluated for the parameters listed on Table 1 except the nitrogen parameters.

All values were compared based on ANOVA statistical.

Results and Discussion

Quality of the effluent from creaming process

The quality of effluent from creaming process using conc H_2So_4, HPMC and recovered HPMC was summarized in Table 2.

pH value

The recovery of skim rubber using HPMC is by depletion mechanism of coagulation. Therefore, the pH of solution before and after coagulation were unchanged[5]. As shown in Table 2, sulfuric acid process produced an acidic effluent while HPMC and recovered HPMC result in a basic effluent which is similar to the pH of skim natural rubber latex. The pH of the effluents from HPMC and recovered HPMC processes was not significantly different (P=0.05) but significantly distinctive from the sulfuric acid process (P=0.05). In addition, the effluent pH of recovered HPMC process was slightly lower than that of HPMC process since ammonia that still in the effluent can evaporate out during the recovery of HPMC[6]. The pH of the effluent (pH=9.12) was close to the wastewater regulated value (pH=5.0-9.0)[1]. As a result, recovered HPMC process facilitated the pH of the effluent and required a few treatments before discharge.

Table 2 Quality of effluent from creaming process using concentrated sulfuric acid and 0.6% HPMC.

Parameters regulation[1]	Wastewater HPMC	Sulfuric acid	HPMC	Recovered
pH	5.5-9.0	4.59[a]	9.24	9.12
Conductivity (μs/m)	not regulated	17.40[a]	10.73[b]	11.93[c]
TDS (mg/L)	< 3000	28287	33521[a]	28090
SS (mg/L)	< 50	554	506	181[a]
Sulfate (mg/L)	not regulated	11367[a]	377	410
Sulfide (mg/L)	< 1.0	0.15[a]	0.45	0.49
DO (mg/L)	not regulated	1.19	1.03	0.65[a]
BOD (mg/L)	< 20	11430[a]	17767	16527
COD (mg/L)	< 120	22917[a]	35747	32827
TKN (mg/L)	< 100	5000[a]	1733	1567
Ammonia (mg/L)	not regulated	993[a]	323	242
Nitrite (mg/L)	not regulated	0.004	0.006	0.011
Nitrate (mg/L)	not regulated	0.205	0.133	0.116

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[a,b] and [c] significantly different (P=0.05)

Conductivity

Conductivity of the effluent in sulfuric acid process was higher than that of HPMC process. This was caused by the content of sulfate ion from sulfuric acid and a nonionic polymer type of HPMC. Conductivity value is not in the list of wastewater regulation but the information is helpful and supportive to the understanding of sulfuric acid and HPMC in creaming processes.

Total dissolved solids (TDS) and suspended solids (SS)

TDS in the effluent of sulfuric acid process and recovered HPMC process were not significantly different (P=0.05) but considerably lower and differed (P=0.05) from HPMC process. This proved that after creaming process, HPMC which is water-soluble remained in the effluent and can be recovered. In the case of SS, the effluents from sulfuric acid process and HPMC process were not significantly different (P=0.05) but notably higher than that of recovered HPMC process. As a result, creaming of skim natural rubber latex by recovered HPMC process did not have an effect on TDS of the effluent but can reduce SS of the discharge wastewater.

Sulfate and sulfide

Sulfate and Sulfide concentrations in of the effluents from HPMC process and recovered HPMC process were not significantly different (P=0.05) but differed from sulfuric acid process. The effluent of sulfuric acid process contained lower sulfide content but greatly higher in sulfate content comparing to that of HPMC processes. Nevertheless, sulfide content from all processes was lower than the regulated value. On the other hand, sulfate is not regulated but it can produce hydrogen sulfide naturally[7]. Therefore, a large amount of sulfate in the effluent could lead to pollution problem in the environment after discharge. The use of HPMC in creaming process resulted in small amount of sulfate and was advantageous than using sulfuric acid.

Dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD)

DO in the effluents from sulfuric acid and HPMC processes were not significantly different (P=0.05) but differed from recovered HPMC process. Recovery of HPMC lowered the DO concentration in the effluent because oxygen gas in the effluent could be taken out during heating process.

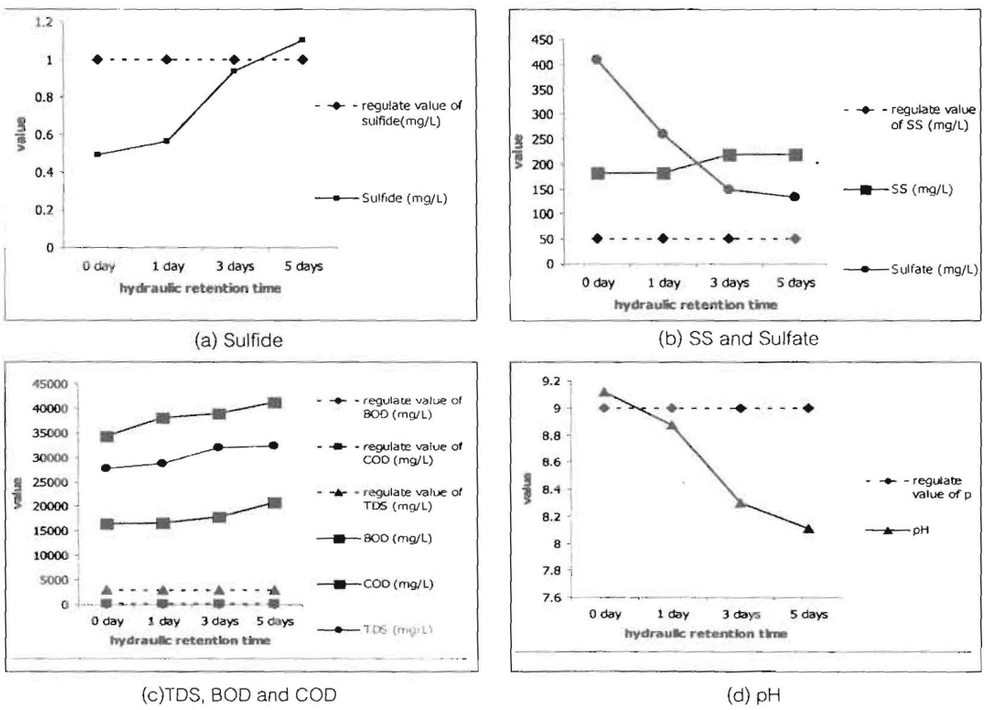
BOD and COD of the effluents from HPMC and recovered HPMC processes were not significantly different (P=0.05) but considerably higher than that of sulfuric acid process. This might be caused from the elimination of impurity in skim rubber during creaming process using HPMC. In other words, protein was washed out from the skim rubber and remained in the serum phase causing the increment of BOD and COD values[8]. However, the high amount of BOD and COD would benefit the nutrient requirement for anaerobic treatment of wastewater which produced a byproduct of methane-rich biogas. This can be used to supplement or release natural gas for energy systems.

Total kjedahl nitrogen concentrations (TKN), ammonia nitrogen, nitrite nitrogen and nitrate nitrogen

TKN and ammonia concentrations in the effluents from HPMC and recovered HPMC processes were not significantly different (P=0.05) but differed from sulfuric acid process. However, nitrite and nitrate concentrations in the effluents from all processes were not significantly different (P=0.05). Therefore, creaming a skim natural rubber latex using HPMC did not influence the nitrite and nitrate contents. A lower TKN in the effluents from HPMC and recovered HPMC processes resulted from a decrease of ammonia concentration from these processes. Therefore, creaming a skim natural rubber latex using HPMC can improve the quality of the wastewater from the process.

Effect of hydraulic retention time on quality of the effluent from recovered HPMC process

In Figure 1, the quality of effluent from recovered HPMC processes with hydraulic retention times of 0, 1, 3 and 5 days was summarized.



(a) Sulfide

(b) SS and Sulfate

(c)TDS, BOD and COD

(d) pH

Figure 1 Effect of hydraulic retention time on the quality of the effluent from recovered HPMC process

pH and Sulfate values decreased when hydraulic retention time increased. The decrease of pH value was caused from oxidation of ammonia during nitrification process, by aerobic bacteria[9] and evaporation of ammonia into the air. This leaded to the reduction of pH value which is significantly useful for effluent treatment, especially during an extended hydraulic retention. For sulfate, it is generally broken down into hydrogen sulfide by bacteria leading to the decrease of sulfate quantity during the hydraulic retention time. The reduction of sulfate in the effluent will help reduce expenses of effluent treatment in industrial factory.

The concentrations of SS, TDS, sulfide, BOD and COD were increased when hydraulic retention time increased. For TDS and SS, a slightly increase of these values could be from particles in the environment falling into the effluent because the effluent was in an open system. The raise of sulfide was related and supported the decrease of sulfate amount. Moreover, the

increase of sulfide content produced an unpleasant smell in the effluent. The growth of BOD and COD values were caused from the use of HPMC polymer. In rubber production procedure, less dirty rubber will be received which drives the effluent more dirty. The dirty substance contains nutrients suitable for the growth of bacteria. It helps increase the number of bacteria rapidly and high amount of oxygen needed for the digestion of food substances. However, the increase of BOD and COD values may help boost the production of biological gas in anaerobic treatment. Naturally, organic nitrogen will be oxidized into ammonia and nitrate by aerobic bacteria under nitrification process causing the reduction of organic nitrogen while the ammonia and nitrate concentrations intensify.

Conclusions

The pollution of effluents from creaming skim natural rubber latex was improved by using recovered HPMC process. Most of the regulated parameters were lower than that of sulfuric acid process, especially the acidity and sulfate content. The improvement of acidity and sulfate content were enhanced by hydraulic retention time. Besides, BOD and COD from recovered HPMC process were considerably higher than that of sulfuric acid process and increased after a period of hydraulic retention time. However, the high values of these parameters were useful for biogas production in anaerobic treatment of wastewater.

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