

Rubber and Methane Recovery from Deproteinized Natural Rubber Wastewater by Coagulation Pre-treatment and Anaerobic Treatment

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ABSTRACT: A newly developed natural rubber deproteinization process produces deproteinized natural rubber (DPNR) wastewater as an intermediate product containing a high concentration of sodium dodecyl sulfate (SDS) and rubber. In this study, a novel process to recover the residual rubber and energy as methane from DPNR wastewater was developed. As a pretreatment, SDS and residual rubber in DPNR wastewater were coagulated and recovered by addition of CaCl_2 at $\text{Ca}^{2+}/\text{SDS}$ and $\text{Ca}^{2+}/\text{rubber}$ mass ratios of 0.070 and 0.055, respectively. The remaining organic matter in the pre-treated DPNR wastewater was converted to methane by using a mesophilic up-flow anaerobic sludge bed (UASB) reactor. The UASB reactor with the diluted pre-treated DPNR wastewater showed a total chemical oxygen demand (COD) removal efficiency of $92 \pm 2\%$ at a maximum loading rate of $6.8 \pm 1.8 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ at a hydraulic retention time (HRT) of 12 h. Under the condition of effluent recirculation with raw pre-treated DPNR wastewater, the UASB reactor showed a total COD removal efficiency of $84 \pm 8\%$ at the maximum loading rate of $6.4 \pm 1.7 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ at HRT of 39 h. The results suggest that the newly developed resource recovery process for DPNR wastewater could be a promising treatment system.

Key words: Anaerobic treatment, Latex wastewater, Natural rubber, Rubber recovery, Sodium dodecyl sulfate (SDS)

INTRODUCTION

Natural rubber is used for the manufacture of a wide range of items such as gloves, adhesives, and tires. Several proteins present in natural rubber latex cause latex-allergy and, in some cases, provoke anaphylactic reactions (Bousquet *et al.*, 2006; Turjanmaa *et al.*, 1996). Thus, removal of protein from natural rubber latex is quite important. Recently, an effective deproteinization method for natural rubber that uses urea and sodium dodecyl sulfate (SDS) was developed (Kawahara *et al.*, 2004; Yamamoto *et al.*, 2008). The newly developed process produces

deproteinized natural rubber (DPNR) wastewater as an intermediate product containing a high concentration of SDS and rubber.

At present, natural rubber latex wastewater discharged from a conventional natural rubber manufacturing process is usually treated by stabilization pond methods such as anaerobic, facultative, and aerobic ponds following a residual rubber recovery by addition of sulfuric acid (Tekasakul and Tekasakul, 2006; Chaiprapat and Sdoodee, 2007). The stabilization pond systems require a huge installation area; further, anaerobic ponds emit the

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greenhouse gas methane (Akbarpour Toloti and Mehrdadi, 2011; Arshad *et al.*, 2011; Amani *et al.*, 2011). These are grave problems in countries producing natural rubber. For DPNR wastewater, the usual rubber recovery process of addition of sulfuric acid is not applicable, owing to the high concentration of SDS. Therefore we have been developing a rubber recovery and treatment process for DPNR wastewater since no previous studies have addressed the treatment of DPNR wastewater till date. The several our preliminary studies so far have revealed that the high concentration of SDS in the DPNR wastewater inhibits the conventional rubber recovery method of coagulation using sulfuric acid. Furthermore, the surfactant of SDS inhibits microorganisms (Shcherbakova *et al.*, 1999; Van Hamme *et al.*, 2006); thus, SDS removal from DPNR wastewater is necessary for rubber recovery and anaerobic treatment. There are several methods for surfactant removal from wastewater (Schouten *et al.*, 2007), but we have been focusing on the chemical precipitation of anionic surfactant using a divalent or trivalent cation (Aboulhassan *et al.*, 2006; Talens-Alession *et al.*, 2002) and developing a pre-treatment method for DPNR wastewater. In this study, we developed a CaCl_2 addition method to remove SDS and recover the residual rubber in DPNR wastewater. Then, the rubber recovered pre-treated DPNR (P-DPNR) wastewater from which rubber was recovered was treated using an up-flow anaerobic sludge bed (UASB) reactor.

MATERIALS & METHODS

To determine the CaCl_2 dosage for coagulation of SDS, CaCl_2 solution was added to SDS solution (10,000 mg/L) at concentrations of 0–819 mg/L. After mixing for a few minutes, the coagulated SDS was removed by filtration using a 0.45 μm membrane filter and the chemical oxygen demand (COD) concentration of the filtrate was measured. The SDS removal ratio was determined using a COD equivalent of 2.0 (g/g) for SDS. For determination of CaCl_2 dosage for natural rubber recovery, CaCl_2 solution was added to 36,000 mgVS/L of natural rubber latex at concentrations of 0–3,930 mg/L. After stirring for few minutes, the volatile solid (VS) concentration was measured to determine the coagulated rubber quantities.

The DPNR wastewater (Table 1) was collected from a pilot-scale plant for protein removal at Nagaoka University of Technology. An optimum dosage of CaCl_2 for pre-treatment of DPNR wastewater was experimentally determined by a coagulation study. CaCl_2 solution was added to the DPNR wastewater at concentrations of 0–7,710 mg/L and mixed for 1 min. After agitation, the samples were kept quiescent for 1 h. The SDS and VS concentrations of the supernatant

liquid were measured to determine the SDS and rubber recovery ratios. The pH was adjusted to 4.8 and 7.0, and kept constant at 10.3. The coagulation experiments were conducted at least three times. The process of rubber recovery from DPNR wastewater and the preparation of P-DPNR wastewater used for anaerobic treatment are shown in Fig. 1. First, pH of the DPNR wastewater was adjusted to 7 and a suitable amount of CaCl_2 according to SDS and VS concentrations in the DPNR wastewater was added. After curing for several hours, coagulated rubber was collected. The clear residual liquid was P-DPNR wastewater, which was used for the anaerobic treatment.

A methanogenic degradation test of P-DPNR wastewater was conducted by a previously described method using 3,000 mgVS/L of anaerobic digested sewage sludge (Syutsubo *et al.*, 2001). The lab-scale UASB reactor, which has a working volume of 2.8 L with height of 1.1 m, was used for the P-DPNR wastewater treatment. The reactor was maintained at 35 °C. A mesophilic anaerobic digested sludge taken from a sewage treatment plant and anaerobic granular sludge collected from a mesophilic lab-scale UASB reactor treating artificial wastewater mainly composed of sucrose, acetate, and propionate were used as seed sludge. A mixture of the two types of anaerobic sludge (11.6 g-VSS) was inoculated to the UASB reactor. Mineral solutions and 1,000 or 3,000 mg/L of NaHCO_3 were added to the P-DPNR wastewater and fed to the reactor (Table 2). The compositions of mineral solutions were as described in a previous report (Tamura *et al.*, 2007). The influent pH of P-DPNR wastewater was adjusted to 7.5 by addition of NaOH.

COD_{Cr} was analyzed using a HACH water quality analyzer (HACH DR2000). The biochemical oxygen demand (BOD), suspended solids (SS), and volatile suspended solids (VSS) were determined according to the standard method (APHA-AWWA-WEF, 1998). Concentrations of ammonium, nitrate, nitrite, calcium ions, and sulfate were analyzed by high-performance liquid chromatography (HPLC; Shimadzu LC-20). Biogas composition was analyzed using a gas chromatography equipped with thermal conductivity detector (GC-TCD; Shimadzu GC-8A). SDS was extracted using methanol (Campbell *et al.*, 2004) and the concentration was measured using a gas chromatography equipped with flame ionization detector (GC-FID; Shimadzu GC-14B) with a 30 m DB-5 capillary column (Agilent Technology). The volatile fatty acid (VFA) concentration was determined using a GC-FID (Shimadzu GC-1700; Stabilwax-DA 30 m).

RESULTS & DISCUSSION

The DPNR wastewater has COD, VS, and SDS in very high concentrations (Table 1). The main

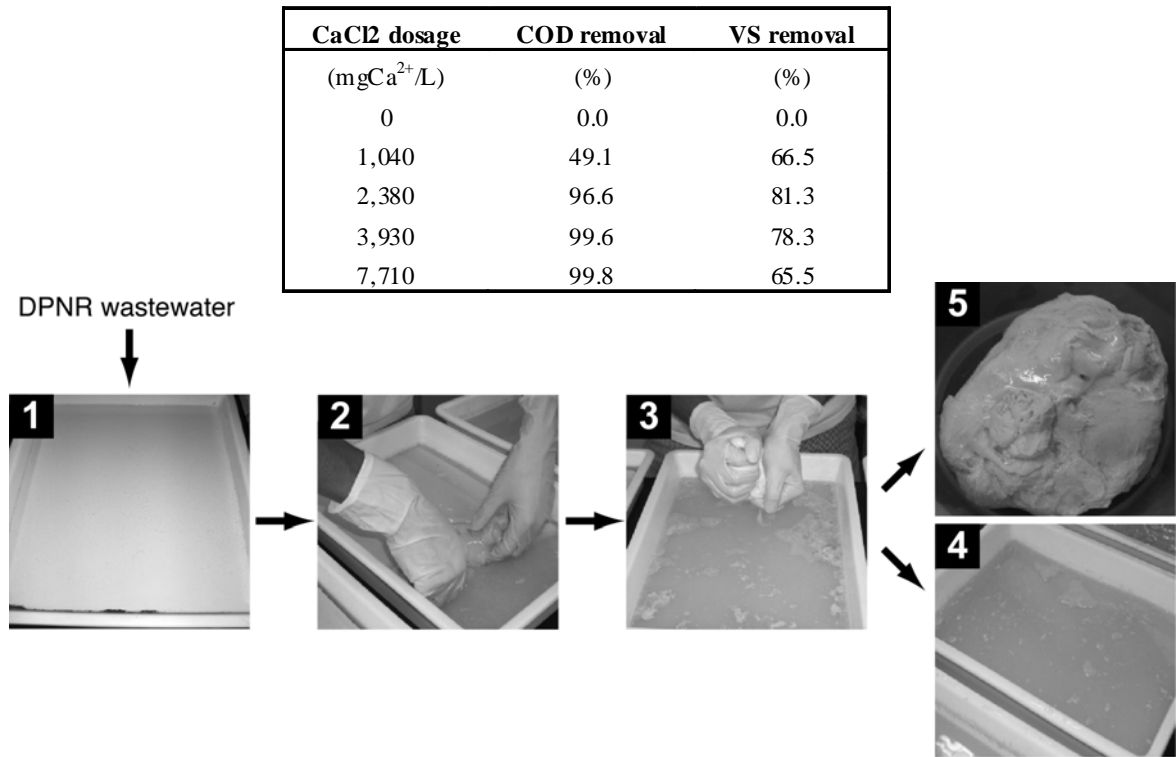


Fig. 1. Process of rubber recovery from DPNR wastewater. The pH of the DPNR wastewater was adjusted to 7 using HCl and an appropriate amount of CaCl₂ was added and mixed (1). After curing for several hours, coagulated rubber was collected (2). The recovered rubber was squeezed to remove the water (3). The clear residual liquid was P-DPNR wastewater, which was used as the UASB influent (4). A block of recovered rubber (5)

Table 1. Compositions of DPNR and P-DPNR wastewater

	Unit	DPNR	P-DPNR
pH		10.3 (0.1)	6.5 (0.1)
Total COOcr	mg/L	131,700 (31,700)	9,690 (380)
Total BOD	mg/L	19,700 (1,800)	6,280 (1,060)
TKN	mg/L	3,620 (840)	2,600 (250)
NH ₄ ⁺	mgN/L	1,710 (410)	1,750 (340)
TS	mg/L	49,900 (8,880)	33,200 (5,340)
VS	mg/L	46,300 (9,240)	17,200 (5,320)
SDS	mg/L	6,570 (3,280)	0
Ca ₂ ⁺	mg/L	0	3,460 (970)
SO ₄ ²⁻	mgs/L	-*	30 (10)

The numbers in parentheses represent the standard deviation.

*Not determined.

Table 2. Operational parameters and process performance of the P-DPNR treating UASB reactor

	Unit	Phase (days)				
		A (0–25)	B (26–38)	C (39–58)	D (59–116)	E (117–219)
HRT	h	22.3 (4.8)	13.2 (1.8)	11.9 (1.2)	12.2 (1.9)	38.6 (10.1)
OLR	kgCOD/m ³ /d	1.06 (0.33)	1.78 (0.27)	4.15 (1.53)	6.83 (1.76)	6.43 (1.71)
Influent pH		7.51 (0.15)	7.58 (0.13)	7.63 (0.12)	7.47 (0.15)	7.70 (0.43)
Substrate total COD _{cr}	mg/L	940 (106)	1,060 (270)	1,990 (80)	3,520 (760)	9,720 (1,050)
Effluent total COD _{cr}	mg/L	307 (34.5)	159 (59)	213 (25)	268 (56)	1,520 (774)
COD removal	%	78.1 (5.9)	85.2 (2.0)	89.3 (1.4)	92.2 (1.7)	84.2 (8.3)
Substrate total BOD	mg/L	N.D.*	N.D.	N.D.	2,135 (727)	6,340 (1,010)
Effluent total BOD	mg/L	N.D.	N.D.	N.D.	94 (37)	554 (321)
BOD removal	%				95.6 (0.8)	91.3 (4.8)
NaHCO ₃ addition	mg/L	3,000	3,000	3,000	3,000	1,000
Effluent recirculation ratio						2
Addition of mineral solution		+	+	+	+	-

The numbers in parentheses represent the standard deviation.

*Not determined

constituent of VS is natural rubber; further, a high concentration of SDS inhibits anaerobic treatment. Hence, as a pre-treatment, SDS and residual rubber in DPNR wastewater were coagulated and removed by addition of CaCl₂. To determine the appropriate CaCl₂ concentration, the amount of CaCl₂ required for removing SDS and natural rubber latex was determined separately. It was found that coagulation of SDS occurred in the SDS/Ca²⁺ molar ratio of about 2. Thus, SDS could be removed by addition of CaCl₂ in the Ca²⁺/SDS mass ratio of 0.070 (g/g). Coagulation of natural rubber occurred immediately after the addition of CaCl₂ to natural rubber latex (36,000 mg VS/L). When CaCl₂ was added at concentrations greater than 400 mg-Ca²⁺/L, the fluid remaining after rubber recovery became clear; addition of CaCl₂ at concentrations over 1990 mg-Ca²⁺/L resulted in COD and VS removal efficiencies of 100 and 80%, respectively. Therefore, we concluded that most of the rubber had coagulated. Thus, natural rubber could be coagulated and recovered by addition of CaCl₂ in the Ca²⁺/rubber mass ratio of 0.055 (g/g).

The effects of CaCl₂ dosage on SDS removal and rubber recovery from DPNR wastewater are shown in Fig. 2. The results indicate that maximum recovery of SDS and rubber occurred at a CaCl₂ dosage of 2380 mg-Ca²⁺/L. This value is close to the dosage of 2620 mg-Ca²⁺/L, which is calculated from the experimentally determined values of the mass ratios of 0.070 and 0.055 for SDS and rubber recovery, respectively. Hence, the amount of CaCl₂ required for SDS removal and rubber recovery from the DPNR wastewater could be estimated from the SDS and VS concentrations in the DPNR wastewater. This may indicate that SDS agglomeration and rubber coagulation occur independently in DPNR wastewater. The initial pH of the DPNR wastewater had little influence on the SDS and rubber removal

efficiencies (data not shown); therefore, initial pH was adjusted to 7 for preparation of P-DPNR wastewater, because a pH of around 7 is suitable for coagulation of rubber through the addition of electrolytes (John, 1971) and also suitable for anaerobic treatment. Under these conditions, residual rubber in the DPNR wastewater could be recovered continuously throughout the experimental period (Fig. 2B).

The compositions of P-DPNR wastewater produced from pre-treatment of DPNR wastewater using CaCl₂ are listed in Table 1. SDS was completely removed to below the detection limit (0.5 mg/L) and the BOD/COD ratio of the P-DPNR wastewater improved to 0.71 from 0.15 of DPNR wastewater. The methane conversion ratio of P-DPNR wastewater (5000 mgCOD/L) was 57 and 72% in the case of incubation for 15 and 30 days, respectively. On the contrary, methane production ceased at DPNR wastewater concentrations over 3000 mgCOD/L. The surfactant SDS has an inhibitory effect on microorganisms; only low concentrations of SDS such as below a few hundreds mg·L⁻¹ are anaerobically degradable (Shcherbakova et al., 1999; Wagener and Schink, 1987). In fact, obvious methane production was only observed below the DPNR wastewater concentration of 1000 mgCOD/L, which corresponded to an SDS concentration of 60 mg/L, in the methane production batch test (data not shown). Thus, SDS removal and rubber recovery from DPNR wastewater using CaCl₂ are suitable pre-treatment processes for DPNR wastewater prior to its anaerobic treatment.

Table 2 presents operating conditions of the UASB reactor, and Fig. 3 shows the time course of total COD and BOD removal and methane gas production. During the first 116 days of operation (phases A to D), influent P-DPNR wastewater was appropriately diluted by tap

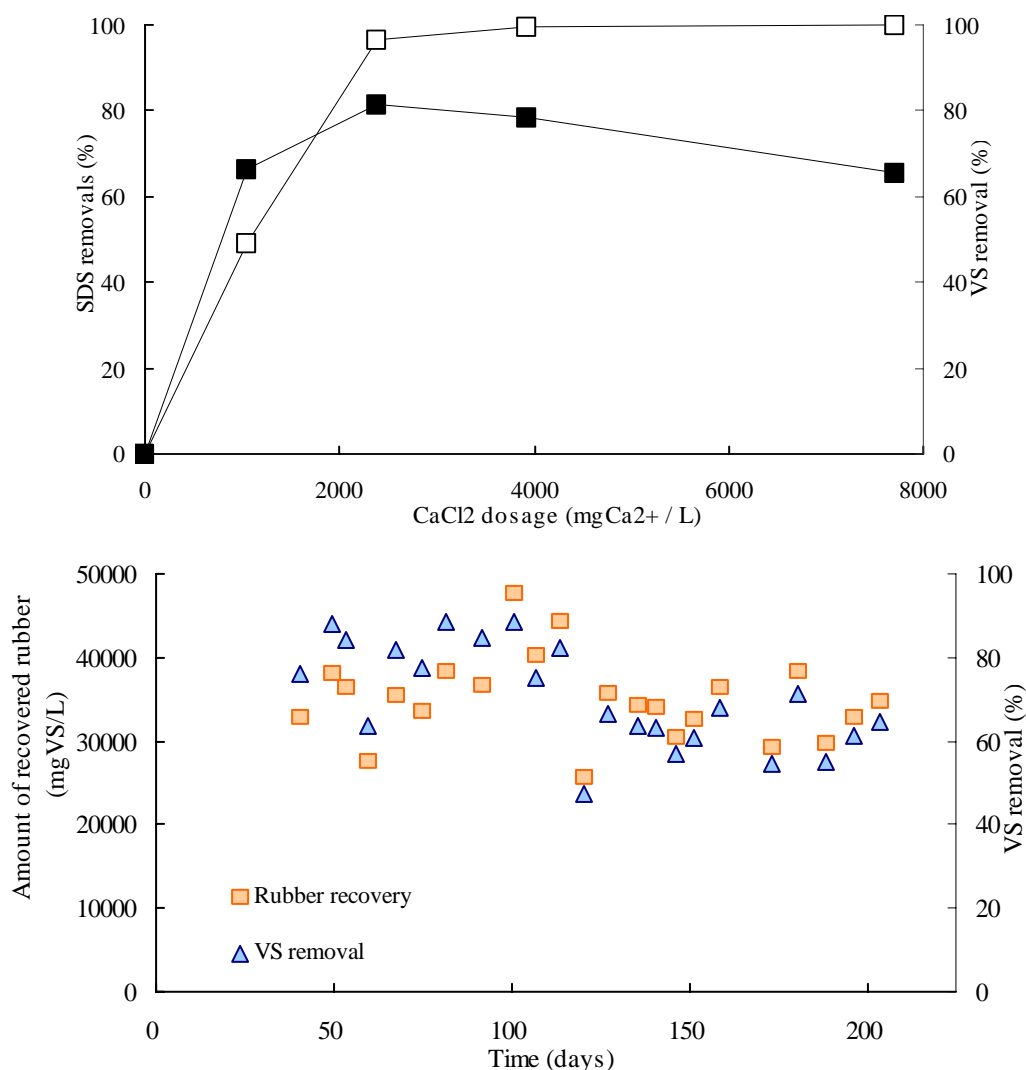


Fig. 2. SDS removal and rubber recovery from DPNR wastewater. Effect of calcium concentration on SDS removal and rubber recovery (A). Amount of recovered rubber from DPNR wastewater and ratio of VS removed from DPNR wastewater (B)

water. The reactor was started up at a hydraulic retention time (HRT) of 22.3 d with influent total COD of 940 mg/L and after day 25, the COD loading rate could be increased by increasing the influent total COD concentration and shortening the HRT. During the operation of the reactor with diluted influent P-DP NR wastewater (phases A to D), the reactor exhibited a COD removal efficiency of $92.2 \pm 1.7\%$ at the loading rate of $6.83 \pm 1.76 \text{ kgCOD/m}^3/\text{d}$ and HRT of 12 h for 2 months (phase D). The effluent total COD was reduced to $268 \pm 56 \text{ mg}\cdot\text{L}^{-1}$ during this period. The total BOD removal ratio was over 95% and the effluent BOD concentration reached to $94 \pm 37 \text{ mg/L}$ in phase D. Thus, in phase E, effluent recirculation was started instead of tap water dilution of P-DP NR wastewater. In addition, supplementation of the influent P-DP NR wastewater with mineral solution was stopped and

influent NaHCO_3 concentration was reduced to 1000 mg/L. In phase E, the total COD removal efficiency was slightly lower than that in phase D but averaged to 84% under an almost same COD loading rate of $6.43 \pm 1.71 \text{ kgCOD/m}^3/\text{d}$ over a hundred-day operation period. The total BOD removal was also slightly lower than that in phase D but it averaged to 91%. These treatment efficiencies were comparable to those in other biological rubber wastewater treatment systems (Anotai *et al.*, 2007; Saritpongteeraka and Chairapat, 2008; Mohammadi *et al.*, 2010). The methane concentration of the produced biogas was around 70%, except during the startup period of phase A (Fig. 3C), and the methane conversion ratio was 50–60%. The methane production rate was $1.47 \text{ Nm}^3\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ in phase E. During the entire reactor operation except for phase E, the effluent pH was maintained at around 7. In phase E, the effluent pH was about 6.8.

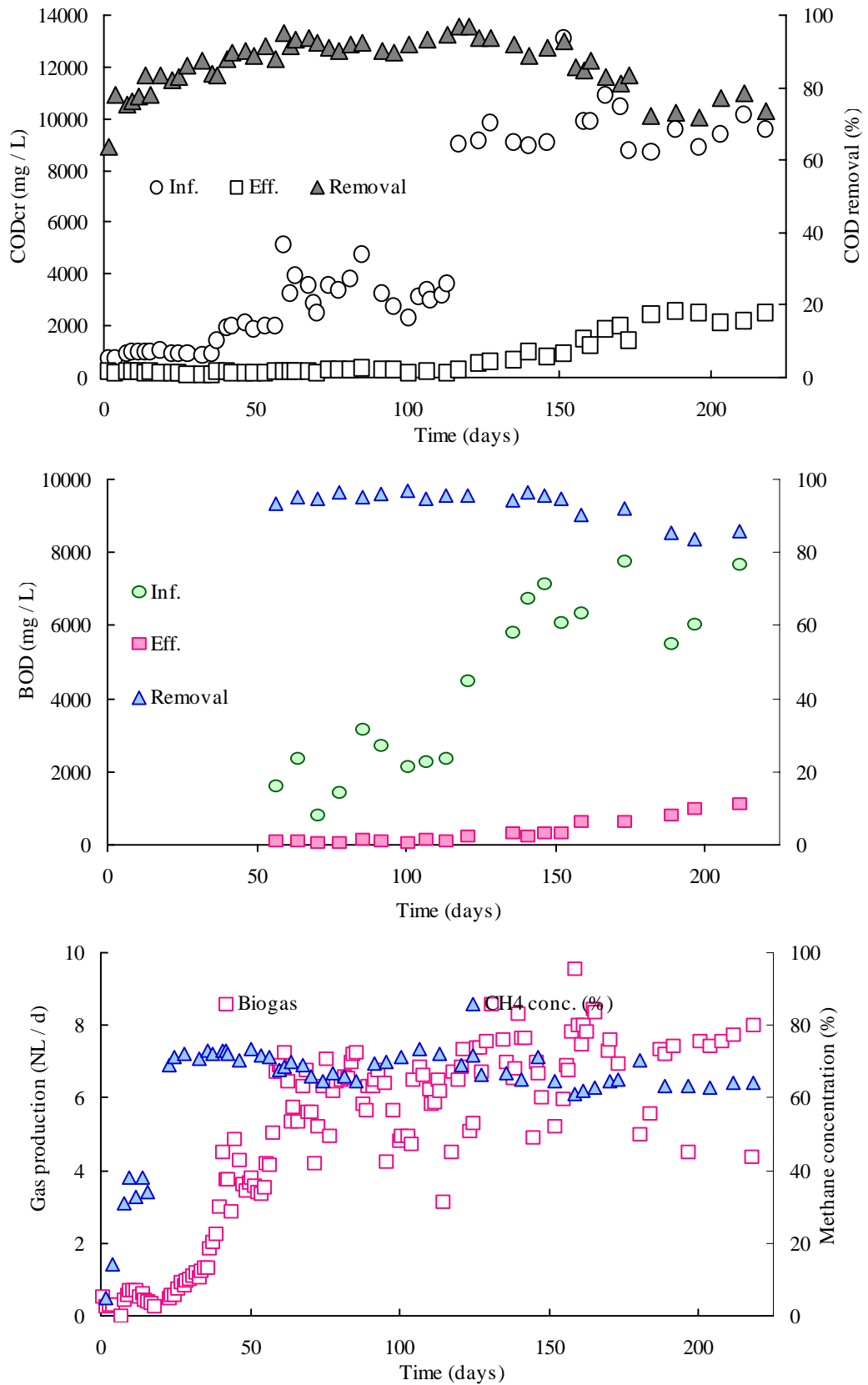


Fig. 3. Results of P-DPNR wastewater treatment using a mesophilic UASB reactor. Total COD concentrations of influent and effluent and COD removal efficiency (A). Total BOD concentrations of influent and effluent and BOD removal efficiency (B). Biogas production rate and methane concentration (C)

Usually, wastewater generated in the rubber manufacturing process contains a high concentration of sulfate, so application of anaerobic treatment results in the formation of high concentration of H₂S. Therefore, sulfate and/or H₂S removal from wastewater and biogas is quite important and a prerequisite for successful reactor operation (Anotai *et al.*, 2007; Saritpongteeraka and Chaiprapat, 2008; Mohammadi *et al.*, 2010). In contrast, there is no such concern about the P-DPNR wastewater, because it has a low sulfate concentration (Table 1). However, the P-DPNR wastewater contains a relatively high concentration of calcium (Table 1). It is known that calcium precipitates when the waste stream contains a

high concentration of calcium and calcium carbonate that accumulated in the reactor (Chen *et al.*, 2008; El-Mamouni *et al.*, 1995; Speece, 1996). Under the diluted influent conditions of phases A to D, significant calcium accumulation was not observed. However, in phase E, calcium was found to accumulate and the difference in Ca²⁺ concentrations between the influent and the effluent was about 1500 mg-Ca²⁺/L (Fig. 4). Thus, at the end of the reactor operation, whitish-gray particles accumulated at the bottom of the reactor. This was not a major problem in our relatively short operation period, but periodic removal would be needed in long-term operation.

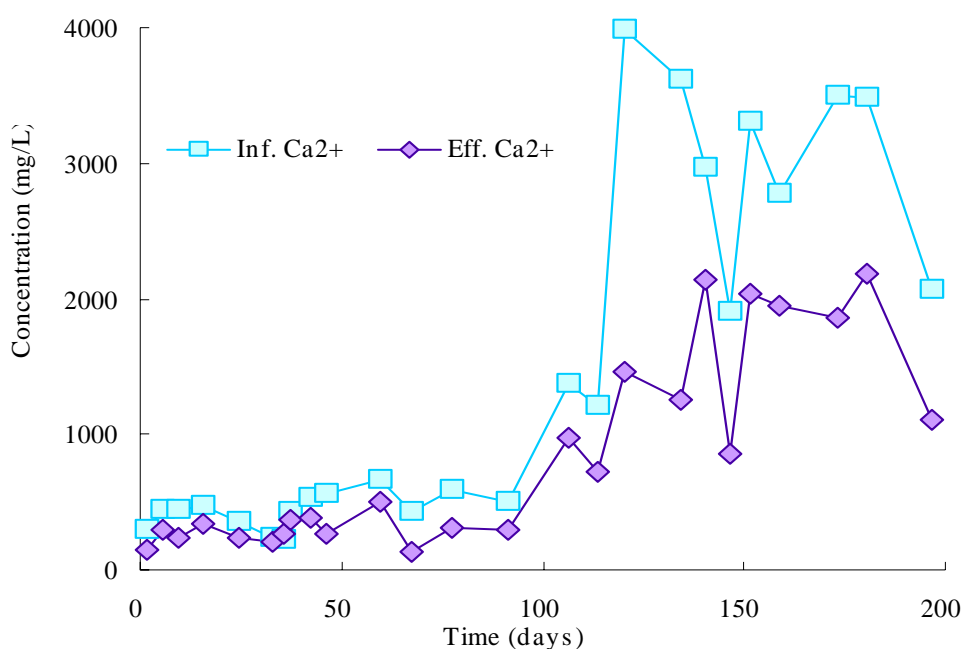


Fig. 4. Time course of influent and effluent calcium concentration

CONCLUSION

In this study, a resource recovery process for DPNR wastewater (an intermediate product of a newly developed natural rubber deproteinization process) was developed. The residual rubber in the DPNR wastewater was recovered by addition of CaCl₂ in a Ca²⁺ to SDS mass ratio of 0.07 and VS wastewater concentration of 0.055. The remaining P-DPNR wastewater was effectively treated using a mesophilic UASB reactor at HRT of 39 h and recirculation ratio of 2 over a period of 100 days. Under these conditions, a total COD removal efficiency of 84% and a total BOD removal efficiency of 91% were achieved at a loading rate of 6.4 kgCOD·m⁻³·d⁻¹; methane recovery was 1.47 Nm³/m³/d. Thus, the newly developed resource recovery process is suitable for the DPNR wastewater treatment.

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