Combined Membrane-Trickling Filter Wastewater Treatment System

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Domestic wastewater is a main cause of water pollution. The idea of this research is to manage wastewater with an on-site treatment system. The proposed system is a modified trickling filter with a chitosan membrane coated matrix bed at the bottom, followed up by a conventional matrix bed. The system is called a combined membrane–trickling filter system. A ϕ0.5 m × H1.15 m unit was made as the studied model. The matrix materials were ϕ0.5 inch × 1 inch rigid PVC elements formed into a perforated wall of 35 openings each. The coated matrix was prepared by casting a chitosan solution synthesized from shrimp shells on the matrix as a thin membrane layer. The characteristics of the chitosan solution were as follows: viscosity 4200-4500 centipoise, degree of deacetylation 84.4%, and molecular weight 1.8×10^{6} Dalton. Raw domestic wastewater was taken from the equalization tank of the Sipraya Water Quality Improvement Factory in Bangkok. Using a bar screen and rotating fine screen, large and fine objects were removed. It was found that the chitosan membrane acted as the initial organic layer for the microbial adherence and developed to become a biofilm for wastewater treatment. The developed biofilm in the lower portion of the tower provided better efficacy of the combined system. The culture balance between autotrophs and heterotrophs in the developed biofilm was controlled by raw wastewater characteristics.

Key words: Chitosan membrane, trickling filter, domestic wastewater, onsite treatment system.

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น้ำเสียจากชุมชนเป็นสาเหตุหลักประการหนึ่งที่ก่อให้เกิดมลพิษทางน้ำ งานวิจัยนี้มีแนวคิดของการจัดการน้ำเสียด้วยระบบบำบัดแบบติดกับที่ประเภทถังโปรยกรอง แต่มีการดัดแปลงใช้ชั้นตัวกลางที่ได้เคลือบผิวด้วยเยื่อแผ่นไคโตแซนทางด้านล่างของถังโปรยกรองและมีชั้นตัวกลางตามแบบถังโปรยกรองปกติอยู่ถัดขึ้นไป เรียกระบบนี้ว่าระบบร่วมเยื่อแผ่น-ถังโปรยกรอง งานวิจัยนี้ได้ออกแบบและสร้างถังโปรยกรองขนาดเส้นผ่านศูนย์กลาง 50 เซนติเมตร สูง 1.15 เมตร เลือกใช้ตัวกลางเป็นท่อพีวีซีขนาดเส้นผ่านศูนย์กลาง 0.5 นิ้ว ยาวท่อนละ 1 นิ้ว (2.54 เซนติเมตร) เจาะรูจำนวน 35 รูต่อท่อน เยื่อแผ่นได้จากการเคลือบสารละลายพอลิเมอร์ไคโตแซนซึ่งสังเคราะห์ขึ้นเองจากเปลือกกุ้งบนตัวกลาง โดยสารละลายพอลิเมอร์ไคโตแซนมีลักษณะสมบัติคือ ความหนืดประมาณ 4200-4500 เซนติพอยส์ การกำจัดหมู่อะเซติลร้อยละ 84.4 มวลโมเลกุลประมาณ 1.8 ล้านดัลตัน น้ำเสียที่ใช้ในการศึกษาเป็นน้ำเสียชุมชนจากบ่อปรับสภาพน้ำเสียของโรงงานปรับปรุงคุณภาพน้ำสี่พระยาในกรุงเทพมหานครซึ่งได้ผ่านขั้นตอนเครื่องดักขยะขนาดหยาบและละเอียดมาแล้ว จากการศึกษาพบว่าเยื่อแผ่นไคโตแซนทำหน้าที่เป็นชั้นสารอินทรีย์เริ่มต้นเพื่อให้จุลินทรีย์เจริญเติบโตติดกับตัวกลาง เมื่อพัฒนาเป็นชั้นไบโอฟิล์มจะทำหน้าที่บำบัดน้ำเสีย ชั้นไบโอฟิล์มที่บริเวณส่วนล่างนี้ทำให้ประสิทธิภาพการบำบัดของระบบรวมเยื่อแผ่น-ถังโปรยกรองสูงขึ้น โดยคุณภาพน้ำเสียจะเป็นตัวกำหนดสมดุลชนิดของจุลินทรีย์ระหว่างออโทโทรบและเฮเทอโรโทรบในชั้นไบโอฟิล์มนี้

คำสำคัญ เยื่อแผ่นไคโตแซน ถังโปรยกรอง น้ำเสียชุมชน ระบบบำบัดแบบติดกับที่

INTRODUCTION

Virtually all of the aqueous wastes produced by humans are returned to the environment with the result that water supplies may be polluted, eutrophication may occur, and aquatic forms of life may suffer. In primitive ages, the self-purification capacity of nature was much greater than the rate of water pollution caused by human activity. However, as time passed with the increasing density of population, the rate of environmental pollution has exceeded the rate of natural purification. The Bangkok Metropolitan Administration (BMA) already has central sewage treatment plants in practice. They rely on biological oxidation. Most modern biological processes are capable of removing organic pollutants efficiently, but it is difficult to remove nitrogen and phosphorus compounds efficiently, causing eutrophication in the receiving body of water. Additionally, the central treatment plant concept cannot be serve the whole country.

It is challenge to develop on-site systems for treating overflows from the existing septic tanks, grey water (i.e., from baths, showers or washbasins) and rainwater replacement of the central plant. It should be stated here that the treatment scenario consists of same pretreatment steps as in the existing central treatment plant. The difference is in the secondary treatment system, which should be much smaller, effective and easily operated.

The trickling filter is a biochemical wastewater treatment process that relies on the microorganisms growing on a matrix to assimilate the biodegradable organic substances in the wastewater as it trickles down. This process was one of the first biochemical operations developed for the treatment of domestic and industrial wastewaters.[1,2]

Chitosan, a natural biodegradable polymer, is of interest for its potential value in biotechnological applications. It can be prepared from shrimp shells. The expansion of aguaculture and seafood processing in Thailand generates a large amount of waste containing sources of chitin and chitosan. Thus, chitosan prepared from seafood wastes is an interesting choice.

Our aim is to develop the trickling filter as an alternative scenario for secondary treatment of an on-site treatment system. It is observed that on any surface submerged in water for a period of time, a layer of microorganisms develops forming a biofilm. It is expected that the thin film application of a hydrophilic polymer to enhance surface hydrophilicity is a technique to develop biofilm formation faster. The unit that contains a coated matrix bed is here called a combined membrane–trickling filter system. In order to enhance the treatment capacity, the hydrophilic membrane coated matrix is placed only at the bottom region where biofilm thickness is reduced due to substrate limitations.

MATERIALS AND METHODS

Preparation of chitosan

Chitosan, a natural biopolymer, was prepared following Benjakula et al.[3] This was performed through the deproteinization of ground shrimp shells with 3% w/v of NaOH at 100°C for 1 hour. Demineralization was executed with 1.25 N HCl at ambient temperature for 1 hour, drying at 65°C. The solid materials obtained were chitin. Deacetylation was performed with 50% w/v of NaOH at 100° C under vacuum for 30 minutes. The resulting chitosan flakes were washed with tap water until neutral and dried at 65°C.

Molecular weight, viscosity, and degree of deacetylation are the normal parameters to characterize chitosan.[4-6] Molecular weight was measured by gel permeation chromatography. Several methods were proposed for N-deacetylation of chitin and chitosan(4,11) of which NMR measurement is a choice. Only viscosity was measured in the laboratory. GPC and NMR were performed at the National Metal and Materials Technology Center (MTEC).

The chitosan solution of 1% by weight in 1% by weight acetic acid was prepared by dissolving 1 g of chitosan flakes in 99 g of 1% by weight acetic acid. The dispersion was slowly stirred at room temperature until complete dissolution and left to stand to get rid of bubbles.

Trickling filter unit

The studied unit was designed corresponding to the low-rate trickling filter.(12) The hydraulic loading of 2 m^3 m^{-2} d^{-1} was used to treat screened domestic wastewater taken from the equalization tank of the Sipraya Water Quality Improvement Factory. No recirculation option was developed. The matrix was made from rigid PVC pipes of 0.5 inch diameter. Each piece was cut into 1 inch lengths. To increase the roughness of the filter matrix pieces, they were punctured to give perforated walls with 2- millimeter diameter holes. The array was arranged as 7 columns by 5 rows. The features of a filter matrix piece, are shown in Figure 1. Both studied systems are shown in Figure 2. The difference is in the bottom portion. In the combined membrane-trickling filter system, the matrix was separated into two parts; i.e., conventional matrix and membrane-coated matrix. The membrane-coated matrix was prepared by spreading the chitosan solution onto each matrix piece. Any coating method is possible but coating with a brush was used here to obtain uniform thickness. This is a matter of experience. The film was left for drying at room temperature.

Opening diameter = 2 mm
Number = 35 holes (7 columns × 5 rows)

Figure 1. Filter matrix piece.

Figure 2. Trickling filter unit.
(Left) Conventional trickling filter system
(Right) Combined membrane-trickling filter system

The uncoated matrix was kept submersed in raw wastewater in a separated tank. It was kept there for 3-4 days to cultivate the microorganisms attached onto the matrix. An air diffuser was used to obtain the aerobic culture. It is expected that a faster steady state condition could be achieved.

Both the pre-biofilm and membrane-coated matrix would be dumped into the studied system randomly. The pre-biofilm matrix height in the conventional trickling filter system was set for two cases; i.e., at 0.8 and 1. In the combined membrane–trickling filter system, the membrane-coated matrix would be dumped to the specified height of 0.1 or 0.2 followed up by the pre-biofilm matrix of 0.8.

Water quality parameters in this study were 5-day biological oxygen demand (BOD_5), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and total phosphate-phosphorus (TP). Standard Methods[13] were used for all the analytical procedures.

RESULTS AND DISCUSSION

Characteristics of chitosan

Yields and other properties of prepared chitosan, i.e., viscosity, % deacetylation, and molecular weight, were presented in Table 1. Characteristics from other sources are also presented for comparison. It was shown that chitosan could be extracted from the dried shrimp shells in the same range as others. It was equivalent to a high molecular weight type. The molecular weight of the present chitosan was very different from others. This was due to the different process conditions. A severe degradation of the chain could take place during the demineralization step, when the shells were submitted to the action of acid solutions at high concentrations and at room temperature, or during the deacetylation step, which involved harsh treatment with alkaline solution at high concentration and at high temperature.(16) The viscosity of chitosan solution from this study was lower than reparted by Benjakula et al.(3) This might be due to the effect of the acetic acid concentration. It has been stated that the viscosity in acetic acid tends to increase with increasing acid concentration.(16)

The viscosity is related to the molecular weight in the Staudinger equation(16) :

$$\text{Log}[\eta] = \log [K] + a \times \log [MW] \quad \ldots(1)$$

where a is a constant that is unity for a long molecule kinked in a random fashion, and approaches zero for a chain coiled into ball. Based on the Staudinger equation, K values for commercial Fluka chitosan are in the range $5\text{x}10^{-4}$ to $6.7\text{x}10^{-4}$. It was increased to $2.5\text{x}10^{-3}$ for the present chitosan. This presented the more linear, unbranched molecules of the present chitosan.

Table 1. Characteristics of chitosan.

Parameters	Unit	Present study	Ref. [14]	Ref. [3]	Commercial Fluka chitosan [15]		
					High MW type	Medium MW type	Low MW type
Av. yield based on shells	%	22	24.3	21.0	-	-	-
based on chitin		75	82.3	78.4			
Molecular weight	Dalton	1.8×10^6	0.5×10^6	-	0.6×10^6	0.4×10^6	0.15×10^6
Viscosity	centipoise (cP)	4200-4500[a]	540[b]	10,183[c]	400[a]	200[a]	100[a]
Degree of deacetylation	%	84.4	82.3	-	-	-	-

[a]At 1% chitosan solution in 1% acetic acid
[b]At 0.5% chitosan solution in 0.5% acetic acid
[c]At 1% chitosan solution in 2% acetic acid

The degree of deacetylation varied with the conditions used. It was found to influence the physical and chemical properties and biological activity of chitosan.(7) The degree of deacetylation of the present chitosan was 84.4%.

Membrane-coated matrix

The consistency of the chitosan membrane coated on the matrix was evaluated by observing the uniform appearance during coating and the resulting membrane weight. Two portions of the matrix were sampled randomly. The membrane coating on each matrix piece as well as on a number of matrix pieces was weighed as presented in Tables 2 and 3, respectively. It could be stated that a uniform coating was obtained and the average membrane weight coated on the matrix was 0.0135 g.

Characteristics of raw wastewater

The average characteristics of 10 runs were shown in Table 4 together with the design criteria. There were great fluctuations in the characteristics because the raw wastewater in this study was real domestic wastewater and the test was run discontinuously for almost a year. The BOD_5 loading was relatively low, in the range of 0.03-0.12 with an average value of 0.07 kg m^{-3} d^{-1}. This might be due to the dilution effect of storm water. The average BOD/COD ratio was 0.37, on the low range of typical untreated domestic wastewater, i.e., 0.4-0.8.[12]

Evaluation of the steady state

The lag time to reach a steady state condition was measured for the combined membrane-trickling filter system. This test was performed because the biofilm was not pre-cultivated on the membrane coated matrix bed portion. The raw wastewater was fed to the combined membrane-trickling filter with a 0.2 meter coated matrix bed. The effluent parameters were analyzed periodically as shown in Figure 3. This shows that the steady state was reached within 1 day. It could be concluded that by replacing with precultivated matrix, the assimilation time was shortened. The surface modification with hydrophilic chitosan membrane could enhance the microorganism immobilization. As a result, the steady state condition was achieved more quickly.

Table 2. Weight of chitosan membrane coating on individual matrix pieces.

Matrix Piece	Weight (g)		
	Before coating	After coating	Membrane weight
1	4.6506	4.6629	0.0123
2	4.7396	4.7526	0.013
3	5.0157	5.0298	0.0141
4	4.8186	4.8323	0.0137
5	5.7598	5.7739	0.0141
Average	**4.9969**	**5.0103**	**0.0134**
STDEV	0.4473	0.4478	0.0008

Table 3. Weight of chitosan membrane coating on a number of matrix pieces.

Matrix	Weight (g)		
	Before coating	After coating	Membrane weight
11 pieces	52.7033	52.8533	0.15
Average/piece	-	-	0.0136

Table 4. Characteristics of raw wastewater during the runs.

Parameters	Unit	Design criterion [6]	Raw wastewater		
			Range	Average	STDEV
BOD_5 loading	kg m^{-3} d^{-1}	0.08-0.4	0.03-0.12	0.07	0.0283
COD loading	kg m^{-3} d^{-1}	-	0.12-0.27	0.19	0.0458
TKN-loading	kg m^{-3} d^{-1}	-	0.01-0.025	0.02	0.0045
P-loading	kg m^{-3} d^{-1}	-	0.02-0.03	0.02	0.0033
Hydraulic loading	m^3 m^{-2} d^{-1}	1-3.7	2		

Figure 3. Measures of water quality vs. time.

Performance evaluation of the systems

The performance of both systems is shown in Table 5. The designed matrix depth was 1 meter. It was known that the diminished treatment capacity in the lower portion of the tower was due to the limitation of reduced biofilm thickness on the substrate.(2) As a result, the replacement with chitosan membrane coated matrix in the lower portion to some level would be expected to compensate this drawback. The effect of coated bed height on the treatment capacity was tested at 0.1 and 0.2 m in the combined systems with using a constant conventional matrix bed height of 0.8 m. The conventional systems at the designed height and 0.8 m were studied for comparison purposes. All parameters were within standard ranges, except the effluent BOD_5 from conventional systems, which was higher than the lower standard value.

Both conventional systems showed similar results. The reduction of the matrix bed by 0.2 m did not deteriorate the system performance. The low organic content in the raw feed benefited the system by promoting the growth of autotrophic bacteria more than heterotrophic bacteria. The ratio of BOD:N:P used by the biofilm in both conventional systems showed concurrently. The ratio was increased from 100:5:1, a typical ratio for active heterotrophic cultures, to be 100:13.8:4.4 in the conventional trickling filter systems of this study.

Table 5. Performance of systems.

Table 6. Long operation performance of the combined system containing 0.2-m membrane coated matrix.

Batch		0-4	5-8	9-12	13-16	17-20
Influent [mg l^{-1}]	BOD_5	42.8	71.7	14.2	26.1	23.7
	COD	60	164	84	84	80
	TKN	9.1	14.3	8.1	8.2	7.5
	TPO_4^{3-}-P	10.7	11.1	11.7	12.6	11.9
Effluent [mg l^{-1}]	BOD_5	17.2	32.4	6.4	21.7	12.4
	COD	16	76	48	76	56
	TKN	5	6.9	4.5	2.2	3.2
	TPO_4^{3-}-P	7.9	8.7	10.3	11.6	10.8
$(BOD:COD)_{inf}$		0.71	0.44	0.17	0.31	0.3
$(BOD:N:P)_{inf}$		100:21.3:25	100:19.9:15.5	100:57:82.4	100:31.4:48.3	100:31.6:50.2
$(BOD:N:P)_{biofilm}$		100:16:10.9	100:18.8:6.1	100:46.1:17.9	100:136.4:22.7	100:38:9.7
BOD removal efficiency [%]		59.8	54.8	54.9	16.8	47.7
COD removal efficiency [%]		73.3	53.7	42.9	9.5	30
TKN removal efficiency [%]		45	51.7	44.4	73.2	57.3
TPO_4^{3-}-P removal efficiency [%]		26.2	21.6	12	7.9	9.2

The efficacy of the combined systems was better for all four parameters, particularly nutrient removal. Higher removal efficiencies in all parameters than those of conventional systems were obtained in both combined systems. The removal efficiencies for BOD_5, COD, TKN, and TPO_4^{3-}-P were increased from 50.2-50.6, 55.2-56, 32.3-34.4, and 7.9-8.5 in the conventional systems to 57.2-62.5, 65.1-67.2, 35.9-48.2, and 14-21.8 in the combined systems, respectively. Higher nutrient removals were observed in the combined system concomitant with ratios of biofilm BOD:N:P changing to 100:18.6:7.3 and to 100:21.9:15.2 for the combined systems containing 0.1 and 0.2 m depth of membrane coated matrix bed, respectively. On similar ratio of BOD/COD; i.e., between combined system at 0.8:0.1 and conventional system at 1 meter or between combined system at 0.8:0.2 and conventional system at 0.8 meter, higher performance was obtained in the combined system as shown in higher removal efficiencies of all four parameters. However, it was not clear to compare the performance between both combined systems in terms of removal efficiency because of different raw waste characteristics. The better view should be on biofilm BOD:N:P. It could be stated that the role of the chitosan membrane coated matrix accounts for the better treatment capacity. The chitosan membrane behaved as the prerequisite organic layer for the microbial attachment. The biofilm development began later. The adherence should take place immediately and the steady-state biofilm thickness resulted in rapid steady-state condition. Based on the low organic content of the raw wastewater, the autotrophs could compete favorably with the heterotrophs. As a consequence, more of nutrients were removed from the wastewater.

Operation life of chitosan coating

The operation life of the chitosan membrane was tested because of its biodegradable nature. Quantities of raw wastewater adequate for 3-4 days each were fed continuously to the combined system containing 0.2-m membrane coated matrix bed. The results are shown in Table 6. The culture balance between autotrophs and heterotrophs corresponded with the raw wastewater characteristics. The BOD_5/COD ratio in the raw feed of batches 9-12 was very low. This was due to the dilution effect of storm water. The influent BOD_5 of batches 9-12 was as low as 14.2 mg l^{-1}. The influent BOD:N:P, 100:57:82.4, indicated a high nutrient content, resulting in more development of autotroph biofilms that was present for a biofilm BOD:N:P ratio of 100:46.1:17.9. This changed continuously to the next batch, becoming 100:136.4:22.7. As a consequence, the organic content removal efficiency dropped from 54.9% to 16.8% but nutrient (especially TKN) removal efficiency rose from 44.4% to 73.2% for batches 13-16. The new culture balance on the attached biofilm was changed again for batches 17-20, resulting in a new pattern of removal efficiency. This treatment capacity scenario would be repeated the same way even it all the chitosan membrane were consumed. This is because the chitosan membrane functioned only in the initial stage.

CONCLUSION

The on-site wastewater treatment concept is proposed in place of the central treatment concept. The trickling filter was adopted as the proposed on-site treatment system. To improve the removal efficacy of the conventional trickling filter system, the matrix surface modification with chitosan membrane was applied in the lower portion of the combined system. The following conclusions could be drawn:

1. The prepared chitosan was of high molecular weight type with viscosity, molecular weight and degree of deacetylation of 4200-4500 cP, 1.8×10^6 Dalton, and 84.4%, respectively.
2. The removal efficiencies of BOD_5, COD, TKN, and TPO_4^{3-}-P were improved from 50.4, 55.6, 33.3, and 8.2% in the conventional trickling filter systems to be 57.2-62.5, 65.1-67.2, 35.9-48.2, and 14-22%, respectively, in the combined membrane-trickling filter systems containing 0.1-0.2 m coated matrix beds.
3. A suitable biofilm in the lower portion of trickling filter column could be developed by the action of chitosan as a pre-existing organic layer for microbial adherence.
4. The culture balance in the developed biofilm corresponded with the raw wastewater characteristics. A low organic content in raw feed resulted in the favorable competition of autotrophs.
5. A combined system containing 0.2-m membrane coated matrix could be run continuously for at least 20 days in this study.

The application of chitosan for enzyme immobilization is known. This study showed that a chitosan membrane on trickling filter matrix, usually made of an inorganic material, could improve the wettability and enhance the adherence of microorganisms useful for wastewater treatment.

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