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Treatability of Dye Wastewaters by Conventional and Anoxic + Anaerobic/Aerobic SBR Processes

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ABSTRACT Several studies have reported that the color in dye wastewaters could be removed effectively by a combined biological treatment, ie, anaerobic digestion followed by aerobic degradation. Therefore, the Phoredox or anaerobic/aerobic process, which is a biological phosphorus (BPR) system, seems to be a very good combination for the decolorization of dye wastewater from the textile industry. This study compared the performance of conventional and anoxic+anaerobic/aerobic (A+A/A) sequencing batch reactors (SBRs) in removing organic matter, total kjeldahl nitrogen and color. The two SBR systems with 8 days of sludge age were operated under the same feeding, reacting, settling and withdrawal periods. However, the 10-hour reaction period of the conventional SBR was totally aerobic whereas that of the A+A/A system was separated into 2 hours of anoxic+anaerobic followed by 8 hours of aerobic conditions. The feed wastewaters contained specific target dyes, ie, disperse, sulfur and reactive dyes, which were collected directly from the treatment plants of local textile factories. At the steady state, it was found, as expected, that both systems were able to reduce the chemical oxygen demand (COD) and total Kjeldahl nitrogen (TKN) of the wastewaters to the same extent. The phosphorus removal efficiency of the A+A/A system was not so good, approximately only twice as high as that of the conventional system due to limited volatile fatty acids and anaerobic contact time. The visual color removal of the A+A/A system was impressive and seemed to be a step ahead of the conventional system. The anaerobic digestion is considerably a necessary step for decolorization of dye wastewaters. Disperse dye was degraded to form non-color by-products whilst the sulfur and reactive dyes were degraded to yield colored by-products which were readily degraded under aerobic environment. The apparent color removal efficiencies of both models measured in terms of color intensity as space unit (SU) and ADMI were, however, not convincing. This is probably due to turbidity and/or solute interference during the color measuring process.

KEYWORDS: Color removal, decolorization, dye wastewater, anoxic+anaerobic/aerobic process, SBR.

INTRODUCTION

The textile industry is one of the largest water users and polluters that still threaten the environment with its highly colored discharge. This colored wastewater is perceived by public as highly toxic. As a result, it is an urgent task to lessen the obnoxious appearance in the receiving water. In general, activated sludge systems and other traditional aerobic biological processes used in most textile factories, though able to remove organic carbon effectively, cannot reduce color satisfactorily. This is because the dyes ordinarily used in the coloring process are rarely biodegradable or are even non-biodegradable under an aerobic environment[1]. However, Porter and Snider (1976)[2] and Dohanyos *et al.* (1978)[3] reported that certain dyes could be removed by adsorption onto microbial cells or flocs under a high mixed liquor suspended solids (MLSS) concentration and long contact time. In addition, it was later discovered that some particular dyes especially those with an azo group were anaerobically biodegradable. The color removal is believed to be due to the chemical reductive cleavage of azo bonds within the dye molecules under the anaerobic conditions.[4,5] Nonetheless, the inter mediate products of these sequent reactions are carcinogenic aromatic amines which need to be further degraded to more stable and inert substances.[6,7] Under the aerobic conditions, certain dyes and by-products from the anaerobic degradation including carcinogenic aromatic amines can be hydroxylated by breaking down the aromatic ring, which results in the formation of several stable end products such as CO_2 and H_2O. Aerobic color removal, however, was found to be less effective than anaerobic means. In general, the modification of any existing conventional system to an anoxic+anaerobic/aerobic (A+A/A) process is quite simple and inexpensive; hence, it is of interest to evaluate and compare the performance between the conventional and A+A/A systems.

It was the aim of this study to investigate the color as well as organic carbon measured in terms of chemical oxygen demand (COD) and total Kjeldahl nitrogen (TKN) removal efficiencies of disperse, sulfur, and reactive dye wastewaters by the facultative microorganisms existing in the A+A/A system and compare them with those of aerobic microbes in a conventional process both of which were operated in the sequencing batch reactor (SBR) mode.[8,9]

Materials and Methods

Two identical bench-scale systems of conventional and A+A/A SBRs were set up as shown in Fig 1. Each system consisted of a 14 litre acrylic tank (20x20x35 cm^3) and was automatically controlled by a microprocessor at the sludge age of 8 days with an operating cycle as indicated in Table 1. The wastewaters from three sources which contain different types of dyes, namely disperse, sulfur, and reactive dyes, were used to feed the experimental systems. The wastewaters were collected from the equalizing tanks of two treatment plants located approximately 50 and 60 km east of Bangkok once a week and stored at 4°C in the dark until used. The preserved wastewaters were allowed to reach room temperature of 24 to 27°C before being fed into the test units. Typical characteristics of all three dye-wastewaters are illustrated in Table 2. If necessary, the appropriate amounts of nitrogen (urea, $(NH_4)_2CO$), phosphorus (KH_2PO_4), and sulfuric acid were added to the wastewaters to maintain the COD:N:P (chemical oxygen demand:nitrogen: phosphorus) ratio of 150:5:1 and to adjust the pH to be within 6.5-7.5. All experimental systems were inoculated to achieve the initial MLSS of 1,500 mg l^{-1} with the sludge from the treatment plants of the same dye houses where the wastewaters were collected to ensure the acclimation of the microbes. An appropriate portion from the 10-litre mixed liquor in the reactor vessels was collected at the end of each stage and analyzed for concerned parameters following the procedures described in Standard Methods.[10] The measurement of color in space units (SU) and ADMI was performed according to the methods specified by Eckenfelder *et al.* (1992)[11] and Allen *et al*. (1973),[12] respectively. The samples were, however, not filtered so that the 'apparent' color under actual conditions was determined. The experimental systems took 20 cycles or more to reach the steady state and the samples were collected and analyzed after another 12 cycles at the steady state.

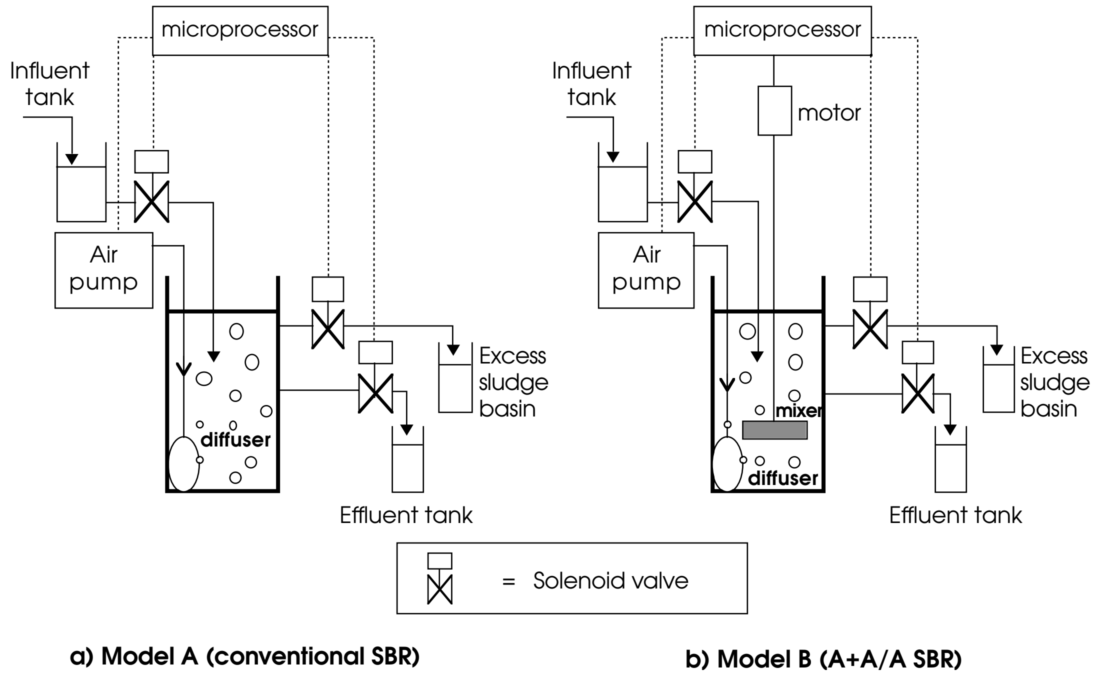

Fig 1. Experimental setup for Models A and B.

Table 1. Operating cycle of the experimental systems.

Operational step	Model A (Conventional SBR)	Model B (A+A/A SBR)
feeding	0.08 hour (3.33 litres)	0.08 hour (3.33 litres)
anoxic+anaerobic	-	2 hours
aerobic	10 hours	8 hours
excess sludge withdrawal	near the end of aerobic stage	near the end of aerobic stage
settling	1.88 hours	1.88 hours
effluent withdrawal	0.04 hour	0.04 hour
Total	**12 hours per cycle**	**12 hours per cycle**

Table 2. Typical characteristics of the feed wastewaters used in this study.

Parameters	Disperse dye	Sulfur dye	Reactive dye
BOD_5 (mg l^{-1})	420	190	140
$COD_{Filtrate}$ (mg l^{-1})	1120	1213	940
SS (mg l^{-1})	61	70	56
$TKN_{Filtrate}$ (mg l^{-1})*	27.4	41.2	40.6
$TP_{Filtrate}$ (mg l^{-1})*	5.91	5.74	7.04
COLOR: SU	142	761	298
COLOR: ADMI	791	1064	1973

*After supplementing with $(NH_4)_2CO$ and KH_2PO_4

Results and Discussion

The removal efficiencies and operational parameters at the steady state are summarized in Table 3. The steady-state MLSS values of the systems fed with the disperse, sulfur, and reactive dye wastewaters were 1070, 439, and 597 mg l^{-1}, respectively, for Model A, and were 1119, 377, and 657 mg l^{-1}, respectively, for Model B. The high MLSS in the systems fed with disperse dye wastewater is reasonable since the BOD_5 (5-day biochemical oxygen demand) of this particular wastewater is approximately two-fold greater than for the others. Relatively low MLSS concentrations similar to those found in this study have been commonly experienced and reported in many textile treatment plants.[2]

The removal efficiencies in terms of COD and TKN of the two models were comparable as shown in Table 3. Fig 2 represents a typical profile of the remaining COD in each cycle for both models. Two steps COD removal occurred in A+A/A system which suggests certain non-anaerobic-degradable by-products were formed which were degraded later in the aerobic environment. A low degree of phosphorus removal has been observed; however, Model B, which is the BPR configuration, obviously exhibited a better performance than Model A. The low phosphorus removal of the A+A/A process in this study was expected since the majority of organic substances contained in the wastewater are not short-chain volatile fatty acids (SCVFAs) which are essential for the BPR process but are rather starch which is slowly biodegraded to SCVFAs; thus not enough VFAs were readily available for phosphate accumulating organisms (PAOs). In addition, the short retention time under the anaerobic environment might also hinder the phosphorus release activity of the PAOs. The small amount of phosphorus reduction observed in Model A was on the other hand mainly due to the cell synthesis. A slight drop in pH values was observed, which may be due to the degradation of the VFA portion in the wastewaters. The dissolved oxygen (DO) and oxidation-reduction potential (ORP) correlated with each other very well which assured the required conditions for anoxic, anaerobic, and aerobic stages. As anticipated, Model B with an anoxic stage was able to reduce nitrogen to a greater extent than Model A as illustrated by the nitrate concentrations in the effluents. Small variations in mixed liquor temperature resulted from the seasonal changes in ambient temperature.

Of greater concern is the finding that both Models A and B were able to remove color in the wastewater better than a more expensive chemical treatment by

Table 3. Removal efficiencies and operational parameters of Models A and B for three dye wastewaters.

Dye Types	System	Removal Efficiency (%) COD_F	TKN_F	P^*	MLSS ($mg\,l^{-1}$)	pH	DO ($mg\,l^{-1}$)	ORP (mV)	NO_3^- ($mg\,l^{-1}$)	Temp (°C)
1.Disperse	Model A	82.1	94.8	12.3	1070	8.6	7.1	167	13.1	25.8
	Model B									
	-Anoxic+Anaerobic	23.8	19.1	-47.7		8.3	<0.1	-306	0.7	26.7
	-Aerobic	79.1	93.7	29.8	1119	8.7	7.4	101	4.8	25.7
2. Sulfur	Model A	64.0	95.2	6.5	439	8.1	7.6	149	12.1	24.4
	Model B									
	-Anoxic+Anaerobic	12.2	9.3	-23.3		8.3	< 0.1	-247	2.1	25.3
	-Aerobic	59.8	95.3	23.9	377	8.2	7.4	160	5.3	24.4
3. Reactive	Model A	61.2	94.8	12.3	597	7.7	7.5	166	15.4	24.6
	Model B									
	-Anoxic+Anaerobic	21.5	3.2	-24.0		8.4	< 0.1	-133	1.5	25.8
	-Aerobic	60.6	94.9	25.7	657	8.1	7.0	164	4.5	25.0

*efficiency = ((total $P_{influent}$ - soluble $P_{effluent}$)/total $P_{influent}$) x 100
negative value indicates phosphorus release occurrence.

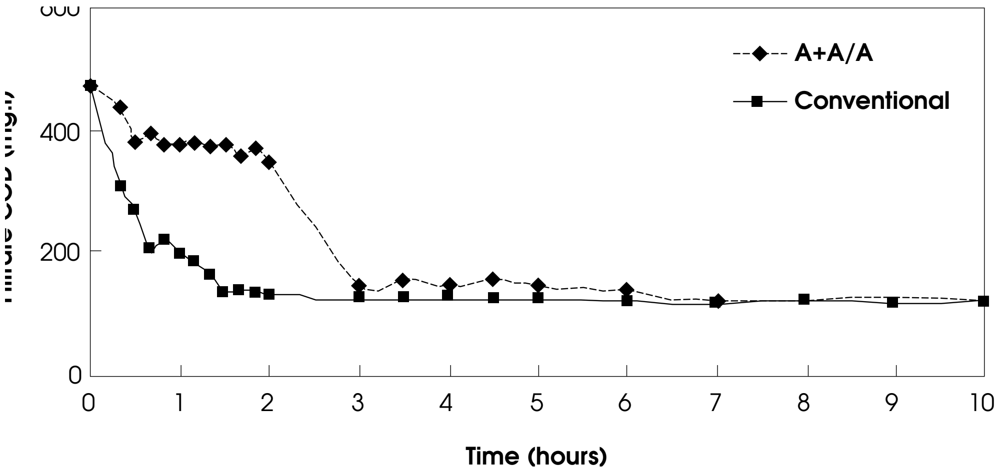

Fig 2. Filtrate COD profile of the experimental systems fed with disperse dye wastewater at the steady state.

alum or lime. However, the A+A/A Model B showed significantly greater color reduction as shown in Fig 3, 4, and 5 for disperse, sulfur, and reactive dye wastewaters, respectively. Shaul *et al.* (1985)[13] noticed that the color in wastewater containing insoluble dyes such as disperse and sulfur dyes was able to be removed effectively by a biosorption process. Nonetheless, that is not the case for this study since the differences in the efficiency based on visual justification of both models were obvious whereas the steady-state concentrations of the mixed liquor suspended solids in both systems were comparable. Hence, this implies that the biodegradation process, which occurred after biosorption, should be an important step that enhanced the degradation of the dyes and controlled the decolorization effectiveness. Furthermore, it was found that anaerobic digestion is the important stage for biological decolorazation. The A+A/A system fed with disperse-dye wastewater indicated an intensive color removal during anaerobic period of less than two hours rather than 8-hour aerobic contact time. Although the anaerobic decolorization of sulfur- and reactive-dye wastewaters was not as appearent as that of disperse-dye wastewater, certain dye cleavages occurred during anaerobic environment. The by-products were later degraded readily under the following aerobic stage. As a result, better decolorization was achieved in the A+A/A configuration than in solely aerobic system. This

Table 4. Color removal performance of Models A and B.

Systems	Color removal efficiency								
	Disperse dye			Sulfur dye			Reactive dye		
	SU %	ADMI %	Visual	SU %	ADMI %	Visual	SU %	ADMI %	Visual
Model A	73.6	11.2	good	3.2	5.2	moderate	30.2	7.8	moderate
Model B	75.0	3.8	very good	15.7	5.1	good	31.2	8.0	good

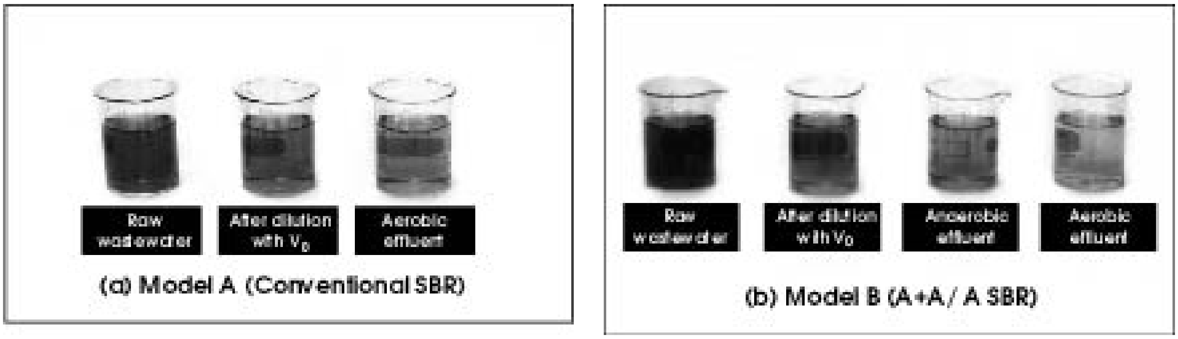

Fig 3. Color removal at various stages for disperse-dye wastewater.

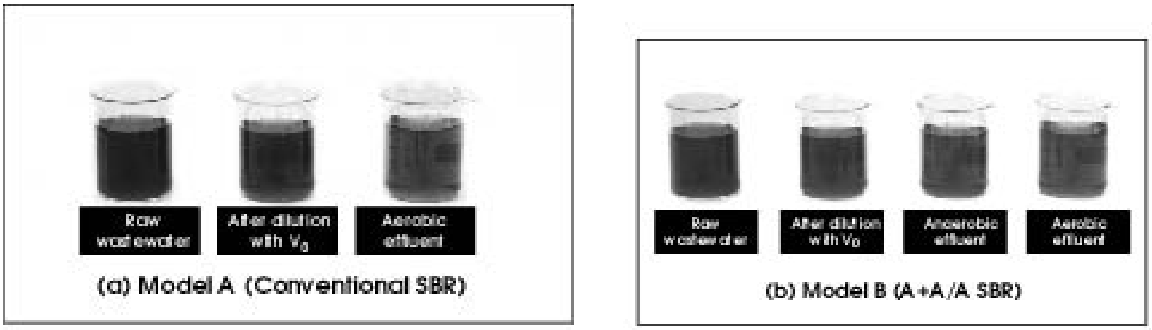

Fig 4. Color removal at various stages for sulfur-dye wastewater.

Fig 5. Color removal at various stages for reactive-dye wastewater.

observation was in agreement with the COD reduction mentioned previously as well as confirms the results from the studies of Meyer (1981)[4] and Carliell *et al.* (1994).[5]

The removal efficiencies in terms of color intensity, expressed in SU and ADMI as shown in Table 4, were, however, contrary to the convincing visual observations; in other word, the scientific data indicated a worse process performance than in reality. This discrepancy may be due to certain sources of interference such as turbidity, as mentioned in the study of Carliell *et al.* (1994).[5] Hence, this suggests that one should be cautious when using color intensity in terms of SU and ADMI to determine the decolorization efficiency and only "true" color (after filtration) should be used as the basis for comparison.

Conclusion

In terms of COD and TKN reduction, both conventional and A+A/A SBR systems showed comparable efficiencies. Even though the phosphorus removal efficiencies of the A+A/A units in this study were lower than those of other BPR systems reported in the literature due to the lack of volatile fatty acids in the feed wastewater and the limited anaerobic detention time, they were still approximately twice as efficient as those of conventional systems. The color removal efficiency measured scientifically in terms of SU and ADMI for both models was found to be unsatisfactory and contrary to the impressive visual observations as summarized in Table 4, perhaps due to turbidity interference in the color measurement.

A modification of an existing aerobic system to an A+A/A system is practical and economical since the initial investment cost for system alteration will be finally offset by the reduction in the aeration cost. Additionally, it was found that A+A/A operation could reduce the sludge-bulking problem as well as provide an anoxic environment for the denitrification process. In summary, the A+A/A process proved to be a better alternative for decolorization of dye wastewaters as compared to the ordinary aerobic process and chemical precipitation. As a result, any existing textile factories that currently use conventional processes should consider investing and modifying their systems to the A+A/A path. The improvement in color and nitrogen removal as well as the reduction in power consumption for aeration is believed to be a worthwhile investment.\

Acknowledgments

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