Investigation of Decolorization of Textile Wastewater in an Anaerobic/Aerobic Biological Activated Carbon System (A/A BAC)

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Abstract: The aim of this study is to investigate the decolorization in anaerobic/aerobic biological activated carbon (A/A BAC) system. The experiment was divided into 2 stages; stage I is batch test for preliminary study of dye removal equilibrium time. The preliminary experiment (stage I) provided the optimal data for experimental design of A/A BAC system in SBR (stage II). Stage II is A/A BAC system imitated Sequencing Batch Reactor (SBR) which consist of 5 main periods; fill, react, settle, draw and idle. React period include anaerobic phase followed by aerobic phase. The BAC main media; Granular Activated Carbon (GAC), Mixed Cultures (MC) and Biological Activated Carbon (BAC) were used for dye and organic substances removal in three different solutions; Desizing Agent Solution (DAS), dye Solution (DS) and Synthetic Textile Wastewater (STW). Results indicate that GAC adsorption plays role in dye removal followed by BAC and MC activities, respectively. In the presence desizing agent, decolorization by MC was improved because desizing agent acts as co-substrates for microorganisms. It was found that 50% of dye removal efficiency was achieved in Fill period by MC. GC/MS analysis was used to identify dye intermediate from decolorization. Dye intermediate containing aniline group was found in the solution on BAC surfaces. The results demonstrated that combination of MC and BAC in the system promotes decolorization and dye intermediate removal. In order to improve dye removal efficiency in an A/A BAC system, replacement of virgin GAC, sufficient co-substrates supply and the appropriate anaerobic-aerobic period should be considered.

Key words: Dye removal, reactive dye, sequential batch reactor, desizing agents, biosorption, adsorption

INTRODUCTION

Dyes are generally synthetic organic compounds with complex molecular structure and large molecular weight, which is difficult to remove from the textile wastewater. Azo dyes are considered to be resistant to attack by aerobes, however there are reports of the possibility of decolorization by anaerobic process from which aromatic anilines were produced as dye intermediate. These dye intermediates are believed to be also carcinogenic which could be mineralized in aerobic condition (Panswad and Luangdelok, 2000). This brought about the idea to improve the conventional biological treatment system for complete dye removal.

Anaerobic-aerobic biological process has been studied and developed continuously for dye treatment. There are two patterns of operation, single unit or 1-stage operation and 2-stages operation. However, 1-stage operation using Sequencing Batch Reactor (SBR) shows many advantages such as good operational flexibility, simple running, compact layout and all necessary processes are taking place time-sequenced in a single basin; therefore, it is comfortable to set anaerobic-aerobic periods (Mahvi et al., 2004). Luangdelok and Panswad (2000) and Shaw et al. (2002) reported color removal efficiency in the range of 66-95% by using anaerobic/aerobic SBR system for treating a synthetic wastewater with glucose and desizing agents as carbon sources together with azo dyes. Besides, there are some reports on operating the anaerobic-aerobic SBR systems in the treatment of textile wastewater for efficient color and COD removal more than 85% (Chan et al., 2009). Furthermore, activated carbon is a supporting media used widely in wastewater treatment, particularly for dye removal. Adding activated carbon in the biological treatment system was suggested in term Biological
Activated Carbon (BAC) system. BAC provides simultaneous adsorption of non-biodegradable matter and oxidation of biodegradable contaminants (Walker and Weatherley, 1999). Long service life of activated carbon in BAC process had also been reported by several authors due to bioregeneration of spent carbon by microorganisms (Zhao et al., 1999). There is a report on adding supporting media such as plastic beads, slag and granular activated carbon in anaerobic-aerobic SBR, it shows possibility to increase dye removal efficiency by adding granular activated carbon (Pasakphan and Vinitpantharat, 2003). The previous work studied the use of BAC process for color removal in an aerobic reactor configuration such as Granular Activated Carbon (GAC) adsorption, bacteria immobilized on GAC and free bacteria cells (Walker and Weatherley, 1999). Besides, Ong et al. (2008) studied decolorization by GAC-biofilm configured sequencing batch reactor (SBCR) operation. About 100 and 60% color removal was observed in living biofilm-GAC and dead biofilm-GAC, respectively. The increasing in living biofilm-GAC over dead biofilm-GAC was a result of the combination of adsorption and biological degradation of dye. However, studies on biosorption and living BAC sorption in BAC process are limited.

Therefore, this research aims to investigate decolorization and organic substance removal in A/A BAC system by operation on SBR technique. The experiments were divided into 2 stages, stage I proceeded to determine the optimal retention time and media concentration which would be useful for the following stage. Stage II aims to study the removal ability of the main media in BAC system on their phenomena such as GAC adsorption, MC biodegradation/biosorption and BAC activity. It was separately investigated on three different solutions, Desizing Agent Solution (DAS), Dye Solution (DS) and Synthetic Textile Wastewater (STW). Effect of solution composition, SBR periods, kind of media to decolorization were studied to understand the nature of BAC system. Moreover, dye intermediate from decolorization in BAC system was studied by GC/MS analysis. The result from this research is expected to bring about improve dye removal efficiency and decrease toxic discharge from BAC system or textile treatment plant in the future.

MATERIALS AND METHODS

Dyes: The red tone reactive azo dyes chosen for this research were reactive red 180 (RR180) and reactive red 141 (RR141), azo and diazo structures, respectively. The dyes were supplied from year 2006-2007 by Winimex Industry Company Limited, Thailand and used in dissolved form. The hydrolyzed stock solutions (100 mg L\(^{-1}\)) were prepared by dissolving in distilled water room temperature and stirring at 100 rpm for 8 h. Dyes structures are shown in Fig. 1a and b.

Tested solutions: Three different solutions were used for this research namely Desizing Agent Solution (DAS), Dye Solution (DS) and synthetic textile wastewater (STW). The composition of each solution is shown in Table 1. To convert each desizing agents into the forms normally used in textile industry, modified starch (100 g L\(^{-1}\)), 20% (w/v) PVA (1000 ml L\(^{-1}\)) and acryllic size (100 ml L\(^{-1}\)) was hydrolysed with 4.0% NaOH overnight at room temperature overnight. COD and dye concentrated supplement was included in the ratio of each desizing agent and dye as shown in Table 1 which was adapted from O’Neill et al. (2000) and Shaw et al. (2002). The pH of the solutions were adjusted to 7.0±0.2 before using in each experiment.

![Fig. 1: The structure of reactive azo dyes. (a) Reactive red 141 (RR141-Diazox) and (b) Reactive red 180 (RR180-Monoazo)](image)

<p>| Table 1: The composition of the tested solutions |</p>
<table>
<thead>
<tr>
<th>Solutions</th>
<th>Mixture</th>
<th>A+C+D</th>
<th>B+C+D</th>
<th>A+B+C+D</th>
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<tbody>
<tr>
<td>DAS</td>
<td>Unit</td>
<td>mg COD L(^{-1})</td>
<td>~900</td>
<td>~150</td>
</tr>
<tr>
<td>DS</td>
<td>Unit</td>
<td>mg COD L(^{-1})</td>
<td>~150</td>
<td>~150</td>
</tr>
<tr>
<td>STW</td>
<td>Unit</td>
<td>mg COD L(^{-1})</td>
<td>~50</td>
<td>~50</td>
</tr>
<tr>
<td>A (Desizing agents)</td>
<td>Compositions</td>
<td>mg COD L(^{-1})</td>
<td>~900</td>
<td>~150</td>
</tr>
<tr>
<td>B (Dyes)</td>
<td>Unit</td>
<td>mg Dye L(^{-1})</td>
<td>~100</td>
<td>~100</td>
</tr>
<tr>
<td>C (Nutrients)</td>
<td>Unit</td>
<td>mg L(^{-1})</td>
<td>~67</td>
<td>~26</td>
</tr>
<tr>
<td>D (Trace element mixture)</td>
<td>Unit</td>
<td>g L(^{-1})</td>
<td>~5</td>
<td>~0.011</td>
</tr>
<tr>
<td>FeSO(_4),7 H(_2)O</td>
<td>Unit</td>
<td>mg L(^{-1})</td>
<td>~0.392</td>
<td>~0.248</td>
</tr>
<tr>
<td>ZnSO(_4),7 H(_2)O</td>
<td>Unit</td>
<td>g L(^{-1})</td>
<td>~0.025</td>
<td>~0.025</td>
</tr>
</tbody>
</table>
Media: The composition of BAC in this study consisted of microorganisms, granular activated carbon and biological activated carbon. They were prepared to be used in the experiment as follows:

Microorganisms: Microorganisms used in this research were derived from the Mixed Culture (MC) in the aeration tank of a domestic wastewater treatment plant. The seed was separately acclimatized by DAS or STW (RR180 or RR141) over 1.5 months (45 cycles). Acclimatization was done using sequential anaerobic-aerobic conditions consisting of 12, 8, 3 and 1 h for anaerobic, aerobic, settle and drain, respectively in each cycle. The removal ability at equilibrium of both non-acclimatized and acclimatized MC were studied comparatively to indicate the appropriate MC type and retention time for using in the experiments for studying the phenomena of biosorption and biodegradation.

Granular activated carbon (GAC): GAC bituminous based from SIGMA-ALDRICH, USA was chosen. It had average diameter of 0.25-0.5 mm. It was washed with distilled water to remove the fine particles. Then, it was dried at 110°C in an oven for 24 h. Finally, it was stored in a sealed container prior to using. Effect of GAC dosage and sequential anaerobic-aerobic operation were investigated to determine GAC dose for using in 1 cycle SBR batch test. Furthermore, changeable dye concentration was also observed among sequential anaerobic-aerobic operation in order to consider GAC exhaust time.

Biological activated carbon (BAC): BAC was separately prepared in reactor feed by DAS or STW (RR180 or RR141). Prepared GAC was added into the reactor containing mixed cultures. The procedure was the same as for MC acclimatization. After 1.5 months, BAC was collected and sifted from excess sludge (outside BAC) by plastic sieve and rinsed with distilled water. This preparation was performed no later than 1-2 h before using in the experiments. Removal ability of BAC vis-à-vis biosorption and biodegradation were studied in SBR batch test.

Anaerobic-aerobic batch decolorization operations: Batch test operation was divided into 2 stages; stage I sequential anaerobic-aerobic system and stage II, 1 cycle of SBR operation. Stage I was employed to identify the optimal times and concentration for adsorption and biodegradation of dyes and organic substances from STW using virgin GAC and MC, respectively. Then, the optimal data obtained from stage I were used for stage II experimental design to investigate dyes and organic substances removal using BAC system with various mechanisms such as adsorption, biosorption and biodegradation in SBR operation. The glass bottles of 480 mL were used with the total volume of the solution was 250 mL. The tested bottles were shaken in an incubator at 100 rpm and 30°C.

Stage I: Sequential anaerobic-aerobic operation: Two kinds of MC, non-acclimatized and acclimatized MC and virgin GAC were used for dyes removal evaluation in order to determine the optimal times and media concentration for dye biodegradation and adsorption. The various media concentrations of 1000, 3000 and 5000 mg L⁻¹ were comparatively studied for dye removal ability from STW which including RR180 or RR141. Dye concentrations were measured at influent and throughout the operations. The experiments were preformed in anaerobic phase until it was attained or dye concentrations were stable. After that, the tested bottles were continuously operated in aerobic condition until it reached the equilibrium time. Dye removal efficiency, system running possibility and economic concerns were considered to determine the optimal retention times and media concentration for stage II.

Stage II: 1 cycle of SBR operation: The optimal times and media concentrations obtained from the experiments in Stage I were used for this stage. The SBR operation consisted of 5 steps; Fill, React (anaerobic/aerobic), Settle, Draw and Idle. As for the React period, the optimal times required for anaerobic/aerobic were selected from the result of Stage I. Dyes and organic substances removal using BAC-SBR with virgin GAC, MC and BAC were investigated for the following mechanisms: adsorption, biosorption and/or biodegradation and BAC sorption and/or BAC bioactivities. The experiments were operated with three different solutions; DAS, DS and STW. Dyes and COD removal efficiencies were evaluated by difference between influent and effluent (Draw). Dye and COD concentrations were measured in all the SBR steps.

Controlling of anaerobic and aerobic conditions: In order to maintain anaerobic conditions, the experiments followed the method used by Ning et al. (1988). The tested bottles including media and the solutions were purged with nitrogen gas to replace air in the head space. Then, they were covered with lids and sealed with plastic cap and put in the incubator shaker. As for aerobic phase controlling, the tested bottles were opened and aerated through air diffusers in order to reach 4-6 mg L⁻¹ of dissolved oxygen.
Unactivation or minimization of bioactivities: All GAC adsorption experiments required aseptic conditions therefore 0.5% and 1% (w/v) NaN₃ was added to the solutions in order to minimize bioactivity for RR 180 and RR 141, respectively. In addition, 0.1% (w/v) NaN₃ was used for biosorption experiments in order to inactivate the biological activity (Ning et al., 1988).

Dye intermediate study in A/A BAC-SBR: Lab scale A/A BAC-SBR was set up in stage II with unlimited sludge retention time and hydraulic retention time of 1.5 days. The STW with RR141 was fed into the reactor by peristaltic pump to reach the working volume of 4.5 L in Fill period. An overhead stirrer was used for mixing and aeration was supplied by air pump diffusers. After 15 cycles, dye intermediates were detected in solution as well as in BAC. The solution in reactor was sampled at the end of anaerobic phase on the steady state, while BAC was sampled at the last studied cycle.

Dye intermediate extraction: Immobilized MC on BAC was extracted by sonication technique at 20°C for 10-15 min. Then, the organic species present on the BAC surface were extracted by soxhlet apparatus. Hexane was used as solvent; 1 g (wet weight) of prepared BAC was placed in the extraction thimble and extracted with 300 mL solute. The process was carried for 24 h at 20 cycles h⁻¹. Finally, the extracted liquid was studied by GC-MS analysis.

As for the solution, 100 mL of filtrated solution was extracted by liquid/liquid extraction following Isik and Sponza (2004). The sample was then extracted 3 times with 100 mL of methyl-tert-butyl-ether. The fraction was combined for GC/MS analysis.

GC/MS analysis: The extracted sample of 1 µL was injected manually in splitless mode via GC inlet. An optima-5-MS capillary column, 30 m long, 0.25 mm i.d., 0.25 µm film thickness was directly connected to mass spectrometer. The oven temperature was maintained at 40°C for 10 min and then increased at the rate 10°C min⁻¹ to 300°C and kept at 300°C for 10 min.

Analytical methods: The samples were centrifuged at 4000 rpm for 10-15 min in order to separate liquid and solid phases. Then, COD and dyes concentrations were determined the liquid phase. The COD was measured by closed reflux titration method (Clasen et al., 1998). Color measurements were performed April 1, 201 using UV-VIS spectrophotometer at maximum absorption wavelengths of 540 and 545 nm for RR 180 and RR141, respectively. Calibration graphs of absorbance versus dye concentration were constructed from the solutions of each reactive dye in distilled water for calculation of the individual dye concentrations.

RESULTS

In stage I, the performance of non acclimatized and acclimatized MC towards the degradation of RR180 and RR141 from STW was evaluated by observation of dye concentration under sequential anaerobic-aerobic conditions (Fig. 2a, b). It was found that both MC types could effectively remove dyes. Dye removal efficiency of 61-96% and 68-96% were achieved for RR141 using non-acclimatized and acclimatized MC, respectively. Similarly, the removal efficiencies of RR180 were in the range of 73-88% for 53-145 h. Furthermore, RR180 removal efficiency (70%) in the first 25 h in acclimatized MC experiment was higher than RR141 (50%).

Besides, it was found that COD removal using non-acclimatized MC was ineffective. At the highest of non acclimatized MC dosages of 5000 mg L⁻¹, only 18% and 33% were found for total COD removal in STW containing RR140 and RR180, respectively. On the contrary, acclimatized MC could achieve 69 and 77% of COD removal in the same condition.

As for the effect of GAC dosage on dye removal (Fig. 3a, b), it was revealed that increasing of GAC dosage from 1000 to 3000 mg L⁻¹ could clearly bring about increasing total dye removal in STW in the range of 59-79 and 55-88% for RR141 and RR180, respectively. Dyes were removed in anaerobic condition, while dye removal in aerobic condition was insignificant. However, dye removal in the first 10th h of aerobic phase was found in the range of 0-13% and 0-4% for RR141 and RR180, respectively, then dye concentration increased till it reached equilibrium.

In stage II, the experiments aimed to investigate dye removal mechanism with BAC system by evaluation of COD and dye removal ability by means of adsorption, biosorption, biodegradation and BAC activity. The total COD and dye removal efficiencies evaluated the overall removal from influent to Settle period. Figure 4a and b show the total COD and dye removal of BAC-SBR compositions by different removal mechanisms under one cycle of A/A BAC-SBR operation. It was found that both RR141 and RR180 can be removed by GAC and BAC. This can be seen in DS where the high COD removal was due to effective dye removal resulting in COD reduction (Fig. 4a). However, BAC sorption only plays a role in RR180 removal while RR141 was removed by BAC (biodegradation and biosorption). Microorganism activity can be noticed to be the main cause for degradation and
Fig. 2: Dye removal equilibrium time of non-acclimatized and acclimatized MC on sequential anaerobic-aerobic operation. (a) Reactive Red 141 and (b) Reactive Red 180

Fig. 3: Dye removal equilibrium time of GAC on sequential anaerobic-aerobic operation. (a) RR141 and (b) RR180

Fig. 4: COD and dye removal efficiencies with different removal mechanisms on A/A SBR operation in a cycle

Absorption of desizing agents. A removal of 91% was achieved for biodegradation and 60% for biosorption. Additionally, microorganisms attached on GAC (BAC) also participate in degradation of desizing agents. The adsorption of desizing agents by GAC was observed to be 19%.

Furthermore, the profile of dye removal in one cycle under SBR operation with the different BAC system mechanisms was studied. The profiles as shown in Fig. 5a and b revealed that treatability with GAC and MC in STW experiments were similar. The profiles clearly show that most dye concentration was removed in Fill
Additionally, the acclimatized MC provided the higher organic substance degradation than non-acclimatized MC with effective dye removal on the shorter retention time. This ability of acclimatized MC can be considered in tolerate toxic of dye intermediates during anaerobic condition. Besides, a lower F/M ratio can bring about a higher removal rate. This is similar to the previous work that reported that no lag phases were observed in any acclimatized sludge experiment (Rodriguez et al., 2006) and the lower F/M ratio influenced the biodegradation of toxic substances such as dye or phenol by promoting more effective removal (Rodriguez et al., 2006; Zissi and Lyberatos, 1996). However, Challoner et al. (2000) found the similar effective azo dye (reactive red 31) removal efficiency at 75 and 90% with mineral salts and without mineral salts operation, respectively by using non acclimatized sludge within 50 h of retention time. This shows that some non acclimatized sludge has no lag phase and do not need acclimatization for decolorization depend on sludge source, dye and co-substrate. While, Moreno et al. (1999) could observe a higher decolorization rate was obtained for the lower F/M ratio with the same initial co-substrate concentration. Therefore, these results demonstrate that there exists an optimal value for F/M ratio (initial co-substrate concentration and MC concentration) under decolorization. Besides, Supaka et al. (2004) indicated the decolorization rate is affected by dye structures, decolorization of diazo dye was much lower than monoazo dye. It was also obvious that diazo dye was less decolorized in contrast to monoazo dye by using algal (Omar, 2008). This can be used to explain the observation that RR180 removal in acclimatized MC experiment was higher than RR141 in the first 25 h of retention time. It was also obvious that diazo dye was less decolorized in contrast to monoazo dye by using algal (Omar, 2008). However, Luangdick and Paysawaw (2000) used glucose (860 mg L\(^{-1}\)) as co-substrate for azo dye removal, it found that the diazo dye (reactive black 5) was rapidly reduced with high decolorization rate in the first 2 h of retention time. Besides, Samthima and Khammuang (2008) reported that Pleurotus sajor-caju could decolorize Indigo dye above 90% within 180 min, whereas azo dye could be decolorized only 3.5% and it was observed that increasing initial dye concentration the decolorization ability was either slower or lower decolorization levels. This can be considered that the high decolorization rate is relatively to co-substrate type which easily biodegradable, microorganism type, dye structure and initial dye concentration. On the other hand, it was found that decolorization mostly occurred in anaerobic condition. It may be because the electrons sufficient for decolorization.

**DISCUSSION**

Selection of the optimal times for removal of RR180 and RR141: From results in stage I, it can be noted that acclimatized MC and the higher MC concentration or the lower F/M ratio could improve dye removal by shortening the time to reach equilibrium in anaerobic condition. This is because the acclimatized MC does not require lag phase as clearly observed in RR180 experiment with non-acclimatized MC that needed almost 50 h for lag phase.
are provided by an electron donating carbon source such as desizing agents. On the other hand, dyes were not significantly removed in aerobic conditions; this may be because the carbon source consumed in anaerobic condition resulted in lack of electron donor in aerobic condition.

For the case of GAC, dyes were removed in anaerobic condition whereas removal in aerobic condition was insignificant. The possible explanation of this is the exhaustion of GAC which reached equilibrium in anaerobic condition resulting in very little dye removal in aerobic phase. However, dye removal was found within the first 10 h of the aerobic phase. This revealed that dye adsorption can occur in aerobic condition as reported by Vidic and Makram (1991) that oxygen molecular can be first adsorbed on GAC surface, then used in polymerization of dye molecules.

Result from stage I shows anaerobic retention time was more than 50 h for achieving maximum dye removal. In order to adjust the results to possible application in textile wastewater treatment plant, the 48 h cycle with 35 h anaerobic react period were employed for SBR operation as these conditions showed over 80% of dye removed at 30-35 h. It showed that 5000 mg L⁻¹ of acclimatized MC could provide the highest dye removal in that duration with F/M ratio of 0.2 which is within the typical range of F/M ratio in SBR at 0.05-0.30 (Tchobanoglous and Burton, 1991). Similarly, GAC dye removal is significant in anaerobic condition due to exhaustion during anaerobic conditions which needs very long retention time phase to achieve 50% and 80-90% of dye removal for RR141 and RR180, respectively. Although, the dye removal using 3000 mg L⁻¹ of GAC was not over 70% at 35 h, it was expected to promote dye removal in combination with microorganisms.

Due to the above reasons, the SBR operation was set at 48 h/cycle and the sequencing batch mode consisted of Fill 1.5 h, React (anaerobic/aerobic) 43 (35:8) h, Settle 2 h, Draw 1 h and Idle 0.5 h.

**Removal mechanisms in BAC system:** Desizing agents included modified starch, polyvinyl alcohol (PVA) and acrylic size which have large molecular size and can not be effectively adsorbed on GAC. Especially starches were reported to be weakly adsorbed by activated carbon (Rice and Robson, 1982). As for acrylic size is mainly composed of polyacrylate ester which can easy soluble in water as same as modified starch. Whereas, large structure size and low solubility of PVA has a significantly higher adsorption. Therefore, it can be suggested that DAS removal by GAC is possible to be PVA adsorption.

RRR141 adsorption by GAC was decreased by the effect of desizing agent. This may be because the desizing agents contend with dye molecules to adsorb on GAC surface and it hydrolyzed in sodium hydroxide solution including hydroxide ion which might react with dye molecules (Shore, 1990). It might bring about the larger molecular substances which hardly and slowly adsorbed on GAC. Anyhow, there is no effect of desizing agent on RR180 adsorption that may be due to the smaller structure size of RR180 which is more easily adsorbed on GAC.

However, the combination of desizing agents and dye in STW can increase dye degradation by MC and BAC by means of increasing COD removal. The reason for this is that desizing agents play role as co-substrate or auxiliary substrate for breaking azo bond (N = N) to colorless compound. Desizing agents functions as electron donor and dye is electron acceptor in the reaction (Yoo et al., 2001). Compare to the presence of only DAS and DS, it is clear that the performance of MC in the combination with desizing agent and dye increased decolorization of RR141 and RR180 (Fig. 4b). O’Neill et al. (2000) and Shaw et al. (2002) also used desizing agents as co-substrate for RR141 removal by mixed cultures in anaerobic-aerobic reactors, 77 and 94% overall dye removal w as achieved, respectively. However, Carliell et al. (1995) could also achieve 85-90% of RR141 removal by using glucose as co-substrate in anaerobic condition. While, Telke et al. (2008) studied the effect of carbon and nitrogen source on decolorization of RR141 by *R. radiobacter* MTCC 8161 in anaerobic condition. It found that a maximum of 85% dye removal was achieved with urea+yeast extract, whereas using glucose+ yeast extract, glucose+urea and starch+ yeast extract could decolorize at 11%, 2 and 10%, respectively. From the presented results and the reviews, it can be note that co-substrate for RR141 removal is not fixed depend on system operation and cultures. However, desizing agents are advantaged because they are waste from textile process that bring about the lower operation cost. In the addition, it was also found that the intermediates from decolorization were accumulated in the system causing low COD removal (Fig. 4a).

Besides, dyes were mainly removed in Fill period therefore it was wondered whether all dye removal should be due only to adsorption or biosorption without biodegradation. However, the previous works reported that dye biodegradation resulted in changing maximum wavelength absorbance. Similarly, this work found that maximum wavelength absorbance of the influent changed from 500-400 nm (data not shown) according to Manu and Chaudhari (2003). Therefore, the following dye removal mechanism is suggested for this experiment. Dye molecules were rapidly adsorbed into the cell membrane in the Fill period and then gradually degraded in the cells releasing byproducts to the system resulting in increased COD in bulk.
Dye intermediate from decolorization was found in solution and on BAC which suggested that the rapid decolorization in Fill period might be due to biosorption; then dye degradation plays a role in conversion of dye to amine byproduct. It can also be noted that BAC plays a role in COD and dye removal including dye intermediate removal that can result in decreased accumulation of dye intermediate and consequently toxicity level in the system.

In conclusion, the results indicated that acclimatization of microorganisms can decrease required retention time to achieve higher dye removal efficacy. F/M ratio is suggested to be considered for design dye removal system; the lower F/M ratio showed higher removal in this study (F/M ratio = 0.2). Dye removal in SBR system from sole dye source is due to GAC adsorption and BAC activity. However, the combination of dye and desizing agents can enhance dye removal by microorganism activity. Dye removal profile showed rapid dye reduction in Fill period of SBR operation and then dye concentration decreased gradually throughout the react period. This suggested dye removal mechanism in SBR for the 2 steps as follows: biosorption of dye in Fill period and degradation of dye in React (mostly anaerobic). The release of dye intermediates resulted in low COD removal in the system. Besides the result from GC/MS analysis showed that BAC can adsorb dye intermediate from decolorization in the system. Therefore, it is proposed that adding virgin GAC or replacement in A/A BAC SBR should be a choice to support dye intermediate adsorption and decreasing toxic level in the system. Moreover, replacement should be carried out almost at the end of the anaerobic phase in order to avoid the effect of desizing agent to GAC adsorption ability.

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