

The effect of hydraulic residence time and initial COD concentration on color and COD removal performance of the anaerobic–aerobic SBR system

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Abstract

An anaerobic–aerobic sequencing batch reactor, SBR, was operated with a textile dyestuff (Remazol Rot RR) containing synthetic wastewater at different anaerobic–aerobic residence times ($\theta_{\text{Hanaerobic}} = 2\text{--}19\text{ h}$) and initial COD concentrations ($\text{COD}_0 = 400\text{--}1800\text{ mg l}^{-1}$). The total reaction time was kept constant at 23 h in all experiments. A dyestuff biodegrading facultative anaerobic bacterial consortium called PDW was used as the dominant bacterial culture. The environmental conditions were adjusted to $T = 28\text{ }^\circ\text{C}$ and $\text{pH } 7$. The experimental results indicated that anaerobic and aerobic residence times in SBR systems significantly affected the system's performance. Color was mainly removed under anaerobic conditions and it was almost completed within 4–6 h of the anaerobic residence time with about 90% decolorization efficiency for an initial dyestuff concentration of 60 mg l^{-1} . The initial COD concentration did not significantly affect the system and $\text{COD}_0 = 500\text{ mg l}^{-1}$ was determined as sufficient to obtain over 90% of the color, more than 85% COD removal efficiency in SBR. Higher concentrations did not improve color removal but decreased the COD removal performance of the system.

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1. Introduction

Dyestuffs present in textile industry wastewater cause significant problems in treatment plants since those compounds are hard to degrade by biological means. Chemical and physical methods including adsorption, coagulation–flocculation, advanced oxidation and electrochemical methods are very efficient in color removal [1–5]. These methods are quite expensive and have pose operational problems. Regeneration requirements and the cost of adsorbents make adsorption an unattractive method for decolorization purpose. However, recent reports indicated the possibility of using some natural or low cost adsorbents such as wood ash, soil, and powdered activated sludge for color removal [6–10].

Although it was known that dyestuffs are resistant to biological degradation, the isolation of new microbial stains has caused more attention to be devoted to biological methods [11–13]. Aerobic biodegradation of dyestuffs indicated that the removal

of dyestuffs by aerobic bacteria is at the level of 10% [14,15]. White-rot fungi can effectively biodegrade textile dyestuffs by their extracellular enzyme system [16–18]. However, it is difficult to keep them in a functional form in conventional wastewater treatment systems, because of their special nutritional requirements and environmental conditions.

Anaerobic dyestuff biodegradation bacterial cultures can effectively remove color by their azoreductase enzyme activity [19–21]. The advantages of anaerobic systems compared to aerobic ones are no aeration requirement, methane gas production and low sludge formation. Moreover, bacterial degradation is much faster than fungal degradation of textile dyestuffs. Studies indicated that color removal under anaerobic conditions is significantly affected by the dyestuff structure. Azo type dyestuffs are readily biodegradable while metal complex, antraquin and indigo group dyestuffs are not [20,22]. In addition, co-substrate is required for dyestuff biodegradation [19,23–25].

Anaerobic decolorization of textile dyestuffs has been carried out in different bioprocesses including UASB, fed-batch, fluidized bed, and packed bed, and high decolorization efficiencies were obtained [26–31]. The limitations in single step anaerobic decolorization processes are low COD removal and formation

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of toxic aromatic amines as a result of azodye biodegradation. However an aerobic unit sequential to anaerobic treatment provides enhanced COD and toxic substances removal from the anaerobic unit effluent, rather than decolorization. It has been shown that an aerobic unit after anaerobic decolorization is necessary in order to increase the effluent water quality [32–34].

Sequencing batch system combines both anaerobic–aerobic phases in one unit. It is widely used in nutrient removal from wastewater [35,36]. The application of SBR to color removal is rather a new approach compared to anaerobic–aerobic sequential treatment [37–42]. Therefore, this study was designed to investigate the potential of the SBR system in textile wastewater treatment. Effects of anaerobic–aerobic residence times and initial COD concentrations on color and COD removal in SBR system containing facultative anaerobic bacterial culture were evaluated.

2. Materials and methods

2.1. Microbial culture

The facultative anaerobic bacterial consortium, isolated at the Biotechnology Center of Ulster University, N. Ireland [21] was used in decolorization of dyestuff. The consortium called PDW consists of *Alcaligenes faecalis* and *Comamonas acidovorans* mixed bacterial cultures. The culture was grown in flasks under static conditions at its optimum growth temperature, $T = 28^\circ\text{C}$.

2.2. Media composition

Synthetic dyestuff containing wastewater was used throughout the experiments. The growth media was made up of $0.5\text{ g }(\text{NH}_4)_2\text{SO}_4\text{ l}^{-1}$; $4.32\text{ g NaHPO}_4 \cdot 2\text{H}_2\text{O l}^{-1}$; $2.66\text{ g KH}_2\text{PO}_4\text{ l}^{-1}$. Glucose was added to the media to provide a readily biodegradable carbon source. The concentration of glucose varied depending on the experimental conditions. The dyestuff used in the study was vinylsulphonyl (VS) and monochlorotriazine (MCT), reactive azo dye, Remazol Rot RR which was obtained from EKOTEN Co. Textile Industry, Izmir, Turkey.

2.3. Experimental set-up

The reactor was made up of Plexiglas with a reaction liquid volume of 3500 ml. The facultative anaerobic PDW culture was inoculated at the beginning of the experiments and then the system was operated batch-wise for 10 days to increase the biomass concentration. The SBR cycle consisted of fill (5 min), anaerobic/aerobic reaction (23 h), settle (30 min) and draw periods (10 min). The initial liquid volume in the reactor during the fill stage was 1 l. The system was first operated under anaerobic conditions. A slight mixing was provided during the fill stage and the anaerobic phase to obtain homogenous conditions. After the anaerobic residence time was completed, the system was aerated. The experiments were not conducted under sterile conditions. Oxidation–reduction potential and dissolved oxygen concentrations were $\text{ORP} = -300\text{ mV}$ and $\text{DO} < 0.1\text{ mg l}^{-1}$ for the anaerobic phase, and $\text{ORP} = +400\text{ mV}$ and $\text{DO} > 2\text{ mg l}^{-1}$ for

the aerobic phase. Each experimental condition was repeated at least three times. The pH was adjusted to pH 7 by adding 5% KOH and 1% H_2SO_4 when necessary. The temperature was controlled at $T = 28^\circ\text{C}$ by using a heating jacket.

2.4. Analytical methods

Samples withdrawn from the system were centrifuged 15 min at 5000–6000 rpm. COD and absorbance measurements were carried out on clear supernatants.

A scanning spectrophotometer (Novaspec II, Pharmacia Biotech) was used for absorbance measurements at $\lambda = 520\text{ nm}$ which is the maximum absorbance wavelength of the dyestuffs. Samples were diluted with distilled water prior to measurements if necessary. Dyestuff concentrations were determined from the developed absorbance–concentration curve. Chemical oxygen demand (COD) analysis was carried out according to standard methods [43]. The dissolved oxygen (DO) concentration was measured by Oxi 330/SET. The oxidation reduction potential was monitored by a WTW Electrode SenTix ORP probe connected to WTW Inolab pH meter.

3. Results and discussions

3.1. Effect of anaerobic–aerobic hydraulic residence time

The SBR was operated at 15 different anaerobic–aerobic residence times ($\theta_{\text{Hanaerobic}} = 2\text{--}19\text{ h}$, $\theta_{\text{Haerobic}} = 20\text{--}4\text{ h}$) in order to determine the optimum residence time for the highest color and COD removal. The sludge age, initial dyestuff and COD concentrations were kept constant at $\theta_c = 15\text{ days}$, $D_0 = 60 \pm 10\text{ mg l}^{-1}$, $\text{COD}_0 = 495 \pm 70\text{ mg l}^{-1}$, respectively.

Variation of color and COD removal with time in the SBR at $\theta_{\text{Hanaerobic}} = 4\text{ h}$ and $\theta_{\text{Haerobic}} = 19\text{ h}$ are depicted in Fig. 1. The experiment was repeated three times and the results of the last two replicates are given in the figure. Effluent dyestuff concentration was obtained as 7 mg l^{-1} with 89% color removal efficiency at the end of the anaerobic period. A slight decrease in the concentration from 7 to 3 mg l^{-1} was observed after 19 h of aeration. The anaerobic period did not provide significant COD

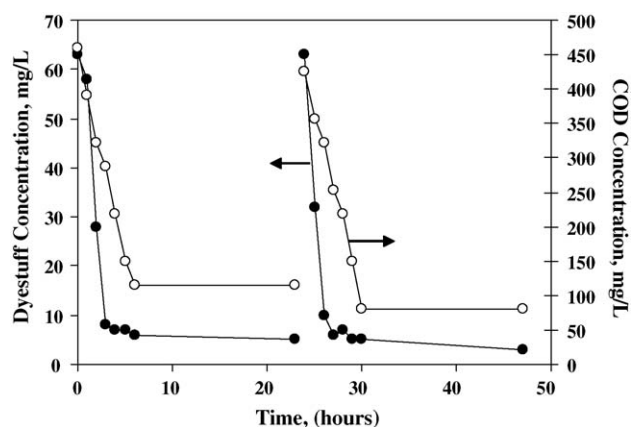


Fig. 1. Variation of effluent dyestuff and COD concentrations in the SBR with time at $\theta_{\text{Hanaerobic}} = 4\text{ h}$, $\theta_{\text{Haerobic}} = 19\text{ h}$. (—●—) Dyestuff; (—○—) COD.

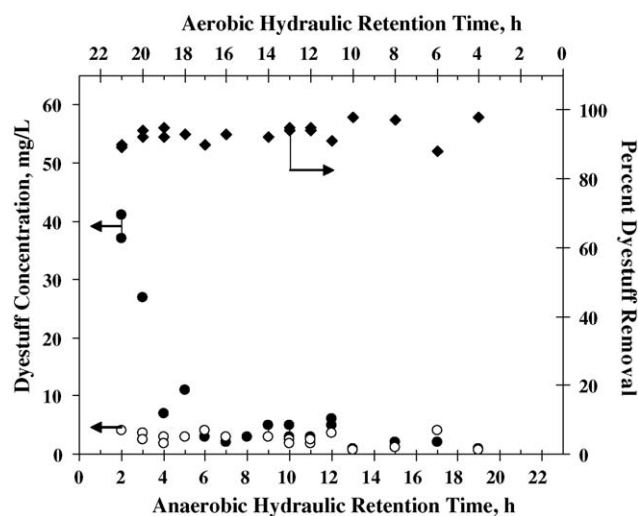


Fig. 2. Effect of anaerobic–aerobic hydraulic residence time on effluent dyestuff concentration and dyestuff removal efficiency in the SBR. (—●—) Effluent of anaerobic; (—○—) effluent of aerobic; (—◆—) total percent removal.

reduction. However, aeration enhanced the COD removal. No significant difference was detected between the repeated experimental conditions.

Fig. 2 depicts the effect of anaerobic–aerobic hydraulic residence times on effluent dyestuff concentration of each of the phases and the dyestuff removal efficiency of system. Anaerobic–aerobic hydraulic residence time in SBR has a significant effect on both color and COD removal. Color removal under anaerobic conditions was in the range of 40% at $\theta_{\text{Hanaerobic}} = 2$ h. However, aeration ($\theta_{\text{Haerobic}} > 17$ h) helped with color removal and 90% final removal efficiency was obtained. Increasing hydraulic residence time in the anaerobic phase ($\theta_{\text{Hanaerobic}} > 4$ h), resulted in less than 5 mg l^{-1} effluent dyestuff concentration. No further decrease in dyestuff concentration was obtained by aeration. The total color removal efficiency was more than 95%, but, the contribution of the aerobic phase to decolorization was around 10% for long anaerobic hydraulic residence times.

The studies of the anaerobic–aerobic sequential textile wastewater treatment system indicated that aeration provides improvement in COD removal and acts as a polishing step after anaerobic color removal. This general conclusion could be valid for low anaerobic hydraulic residence times in SBR especially between $\theta_{\text{Hanaerobic}} = 2$ –4 h. COD removal efficiency was around 50% under anaerobic conditions and reached to about 80% by the contribution of the aerobic phase to COD removal when $\theta_{\text{Haerobic}} = 19$ –20 h. As a result less than 150 mg l^{-1} effluent COD concentration was obtained (Fig. 3). However, as the anaerobic residence time was increased, the contribution of aerobic phase on COD removal was negligible. The main reason for this result could be the toxic effect of the dyestuff biodegradation end products of the anaerobic phase. Due to batch operation in SBR, they were accumulated in the system and long term exposure of the cultures to these products might have inhibited the activity of aerobic organisms. Alternatively, transition between anaerobic to aerobic phases might have not enhanced

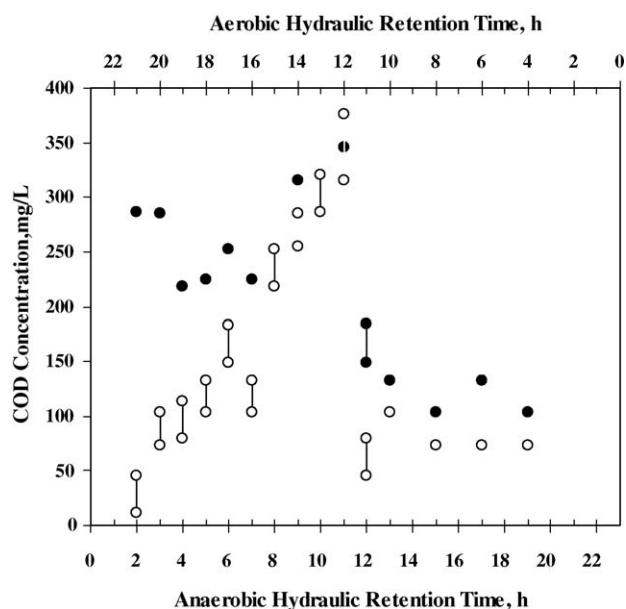


Fig. 3. Variation of effluent COD concentration of anaerobic and aerobic phases with anaerobic–aerobic hydraulic residence time in the SBR. (—●—) Effluent of anaerobic; (—○—) effluent of aerobic.

the growth of aerobic organisms and they were eliminated from the system. Lourenço et al. [37] observed the same result and concluded that changes in the relative duration of the anaerobic and aerobic phases could have caused alteration on the microbial population and also a lack of adequate aerobic microbial population in the mixed culture capable of metabolizing mineralization of azo dyestuff intermediates after anaerobic reduction. Similarly, Psukphun reported that an increase in the duration of the non-aeration phase could have brought about an alteration in the anaerobe population in SBR, positively affecting dyestuff reduction rates [39].

In summary, dyestuff removal takes place under anaerobic conditions and aeration provides a slight color removal if there is any remaining color in the liquid phase after anaerobic biodegradation. A similar conclusion was reported by Panswand et al. [40]. It was observed that color removal occurred mainly in an anaerobic environment while slight attenuation was noticed under the aerobic conditions for decolorization of Remazol Black B in the SBR system. Shaw et al. also observed an improvement in decolorization by aeration in the SBR [41].

Extension of the nonaerated phase more significantly affected the COD removal than decolorization. Low COD removal at short anaerobic periods leads to an increased aeration requirement to obtain less than 100 mg l^{-1} COD in the effluent. However, longer anaerobic periods ($\theta_{\text{Hanaerobic}} > 12$ h) makes the aeration unnecessary in terms of COD removal. Psukphun obtained a slightly higher COD removal with an anaerobic/aerobic cycle = 17.5/2.5 h (90%) compared to 14/6 h (87%) and concluded that the duration of the anaerobic phase should be long enough to obtain better COD and color removal [39]. Lourenço et al. investigated the effect of anaerobic–aerobic residence time on COD and decolorization of Remazol Brilliant Violet 5R in SBR at a 21 h reaction time and an increase in COD

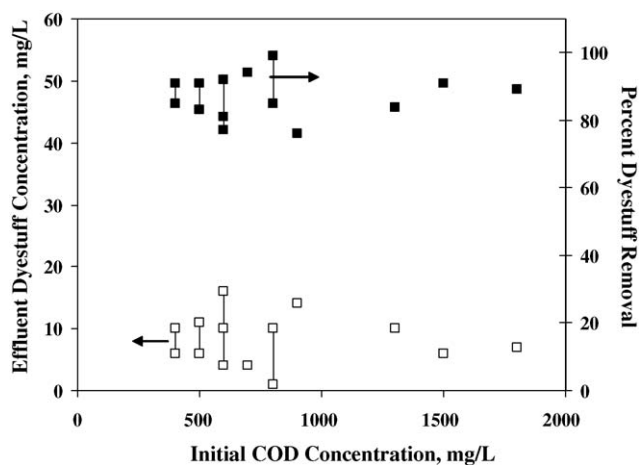


Fig. 4. Effect of the initial COD concentration on dyestuff removal. (—□—) Concentration; (—■—) efficiency.

removal from 30 to 80% was obtained with an 8 h aeration [37]. In the light of the experimental results of this study, the optimum residence times were determined as $\theta_{\text{Hanaerobic}} = 12$ h and $\theta_{\text{Haerobic}} = 11$ h for efficient color and COD removal.

3.2. Effect of initial COD concentration

In the second part of the study, the effect of initial COD concentration on dyestuff and COD removal performance of the SBR was investigated. The system was operated at eight different initial COD concentrations varying between 400 and 1800 mg l⁻¹. The residence times for the anaerobic and aerobic phases were 12 and 11 h, respectively, while the sludge residence time was 15 days. The initial dyestuff concentration was kept constant at 60 mg l⁻¹.

Fig. 4 depicts the variation of the anaerobic and the aerobic phase effluent dyestuff concentrations with the initial COD concentration in the SBR system. The dyestuff removal performance of the system was not significantly affected with increasing the initial COD concentration. The effluent dyestuff concentration varied between 5 and 15 mg l⁻¹ which resulted in over 85% decolorization efficiency at the end of the operating cycle. The effluent dyestuff concentrations at the end of the anaerobic and aerobic phases were almost the same. Therefore, it can be concluded that the contribution of the aerobic phase to color removal is insignificant.

The effect of the initial COD concentration on the effluent COD concentrations of the anaerobic and aerobic phases is given in Fig. 5. The effluent COD concentration was around 80 mg l⁻¹ up to $\text{COD}_0 = 500$ mg l⁻¹. The highest effluent COD concentration, $\text{COD}_e = 1184$ mg l⁻¹, was obtained at 1800 mg l⁻¹. As a result of these changes in the effluent COD concentration, the removal efficiency was less than 50% for the concentrations $\text{COD}_0 > 1300$ mg l⁻¹ and it was higher than 85% for $\text{COD}_0 < 800$ mg l⁻¹.

The significance of the anaerobic phase was as apparent in COD removal as in color removal. About 70% of COD was removed in the anaerobic phase when the COD concentration was between 400 and 800 mg l⁻¹. The COD removal perfor-

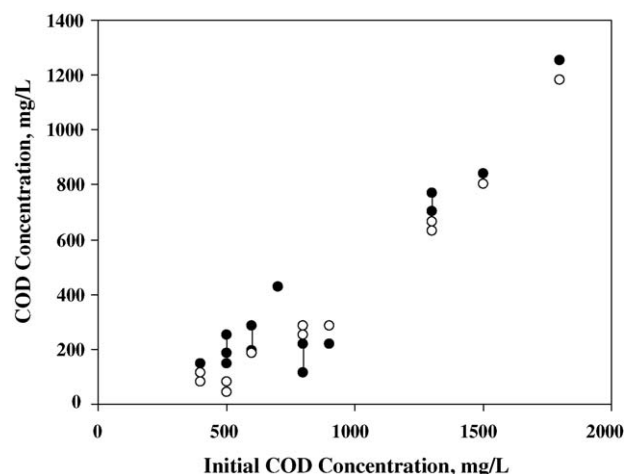


Fig. 5. Variation of anaerobic-aerobic phases effluent COD concentration with initial COD concentration in the SBR. (—●—) Anaerobic; (—○—) aerobic.

mance of the anaerobic phase decreased to 45% when the initial one was above 1300 mg l⁻¹. A significant part of the COD was removed under anaerobic conditions.

The initial COD concentration did not significantly affect the dyestuff removal performance of the SBR. The effluent dyestuff concentration was less than 15 mg l⁻¹ for all studied initial COD concentrations. Aeration provided a slight decrease in dyestuff concentration. The main purpose of increasing the initial COD concentration was to enhance the growth of the aerobic culture by providing more organic substance. Because it was thought that the remaining COD after the anaerobic phase was not enough to sustain the growth of aerobic microorganisms. However, a similar result was observed for COD removal as in anaerobic/aerobic phase hydraulic residence time experiments. There was only 5%, on average, COD removal in the aerobic phase. Although the amount of remaining carbon after the anaerobic phase was enough to sustain the growth of aerobic microorganisms, no significant contribution of aeration to COD removal was obtained. Therefore, the main reason for low COD removal under aerobic conditions might be the elimination of the aerobic culture during the transition between phases. Facultative anaerobic PDW culture needs longer aeration periods to be active under aerobic conditions, which means that the system should be aerated for longer. However, this is not feasible in the light of the demands of operational economy.

Substrate removal rates in anaerobic phase depending on initial COD concentration were calculated by using Eq. (1):

$$R_i = -[(S_0 - S_t)/(t_0 - t_t)] \quad (1)$$

where, R_i represents the initial rate, S_0 the initial substrate concentration, S_t the effluent substrate concentration at time “ t ” and t_0 is the starting hour of the experiment ($t_0 = 0$). The first 3 h ($t_t = 3$) of COD and dyestuff concentrations were considered in the calculation of the initial substrate removal rates. Fig. 6 shows the effect of the initial COD concentration on COD and dyestuff removal rates. The COD removal rate increased from 37.8 to 151.4 mg l⁻¹ h⁻¹ with increasing COD concentration from 390 mg l⁻¹ to around 1000 mg l⁻¹. Higher COD concen-

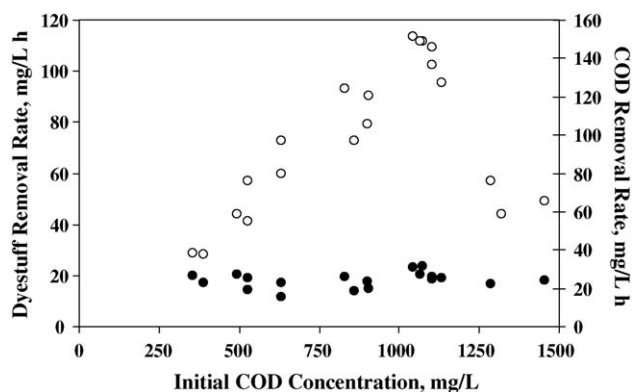


Fig. 6. Effect of initial COD concentration on COD and dyestuff removal rates. (—●—) Dyestuff; (—○—) COD.

trations caused a substrate inhibition effect decreasing the rate to around $60 \text{ mg l}^{-1} \text{ h}^{-1}$. The dyestuff removal rate was not significantly affected by the COD concentration. It varied between 15 and $23 \text{ mg l}^{-1} \text{ h}^{-1}$. Initial decolorization rates between 22.2 and 14.5 SU h^{-1} at 500 mg l^{-1} in the initial COD concentration were obtained by Panswad et al. [38].

4. Conclusions

Operating the sequencing batch reactor at different anaerobic–aerobic hydraulic residence times and initial COD concentrations indicated that the minimum hydraulic residence time in the anaerobic phase should be 6 h for efficient color removal. The SBR system requires long aeration periods to decrease the effluent COD concentration to less than 100 mg l^{-1} . The initial COD concentration does not significantly affect the system performance in terms of color removal. 500 mg l^{-1} is the minimum initial COD concentration to obtain over 90% color and more than 85% COD removal efficiency in the SBR system. Higher concentrations do not affect color removal but decrease the COD removal performance of the system.

Aeration does not contribute to color removal unless the remaining dyestuff concentration after the anaerobic decolorization period is high ($D_e = 40 \text{ mg l}^{-1}$). Transition from anaerobic to aerobic phases adversely affected especially the COD removal by aerobic organisms. It might have also caused elimination of them from the system.

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