

# Effect of operating parameters on color and COD removal performance of SBR: Sludge age and initial dyestuff concentration

Ilgi Karapinar Kapdan\*, Rukiye Ozturk

Dokuz Eylül University, Department of Environmental Engineering, Tinaztepe Campus, Buca, 35 160 İzmir, Turkey

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## Abstract

Effect of sludge and initial dyestuff concentration on color and COD removal performance of anaerobic–aerobic sequential batch reactor was investigated. Remazol Red RR a vinylsulphonyl (VS) and monochlorotriazine (MCT), reactive azo dye was used in the study. Sludge age was varied between  $\theta_c = 12$  days and  $\theta_c = 30$  days and dyestuff concentration was between  $D_0 = 50$  and  $D_0 = 500$  mg l<sup>-1</sup>. The maximum color and COD removal was obtained as 95% and 70% for  $D_0 = 60$  mg l<sup>-1</sup> and COD<sub>0</sub> = 800 mg l<sup>-1</sup> at 15 days sludge retention time, respectively, and no further improvement was observed when sludge age was increased to 30 days. The main color removal phase in this operation system was the anaerobic phase. Because, the color removal efficiency was already above 95% under anaerobic condition and therefore, the contribution of aerobic phase to color removal was negligible. Increasing dyestuff concentration did not significantly affect the decolorization. It was possible to obtain over 90% dyestuff removal even at  $D_0 = 500$  mg l<sup>-1</sup>. SBR system reduces 1000 mg l<sup>-1</sup> initial COD concentrations to about 400 mg l<sup>-1</sup> for dyestuff concentration up to 150 mg l<sup>-1</sup>. COD removal efficiency decreased from 70% to 60% by increasing initial dyestuff concentration from 100 to 500 mg l<sup>-1</sup>. The results indicated that dyestuff and COD are mainly used by anaerobic organisms and aeration does not improve the performance of SBR system.

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## 1. Introduction

Dyestuffs present in textile industry wastewater causes significant problems in treatment plants since those compounds are hard to degrade by biological means. Chemical and physical methods including coagulation-flocculation, advanced oxidation and electrochemical methods are very efficient in color removal [1–5]. These methods are quite expensive and have operational problems such as high sludge formation in chemical methods. Regeneration requirement and cost of adsorbent 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, for color removal [6–8]. Moreover,

it was also reported that powdered sludge and live activated sludge have high dyestuff adsorption capacity [9,10].

Studies on biological decolorization of dyestuff concentrate on utilization of anaerobic bacteria [11–14]. White-rot fungi can also effectively biodegrade textile dyestuffs by their extracellular enzyme system [15–17]. However, it is difficult to keep them in functional form in conventional wastewater treatment systems, because of their special nutritional requirements and environmental conditions. Although most of the dyestuffs are resistant to aerobic biodegradation [18], Coughlin reported the aerobic degradation of azo dyes [19] and Ekici showed that degradation under aerobic conditions proceeds via oxidation of the substituents located on the aromatic ring or on the side chain [20].

Anaerobic dyestuff biodegradation bacterial cultures can remove color by their azoreductase enzyme activity [21–24]. The advantages of anaerobic systems compared to aerobic ones are no aeration requirements, low sludge formation and

\* Corresponding author. Fax: +90 232 453 11 53.

E-mail address: ilgi.karapinar@deu.edu.tr (I.K. Kapdan).

methane gas formation. Moreover, bacterial degradation is much faster than fungal degradation of textile dyestuffs.

Anaerobic decolorization of textile dyestuffs have been carried out in different bioprocesses including fluidized bed, UASB, packed bed, fed-batch and high decolorization efficiencies were obtained [25–29]. The limitations in single step anaerobic decolorization processes are low COD removal, formation of toxic aromatic amines as a result of azodye biodegradation. Alternatively, an aerobic unit sequential to anaerobic treatment has advantageous in terms of enhanced COD and toxic substances removal from the anaerobic unit effluent, rather than decolorization. It has been shown that aerobic unit after anaerobic decolorization is necessary in order to increase the effluent water quality [30–32].

Sequencing batch system combines both anaerobic–aerobic phases in one reactor. It is widely used in nutrient removal from wastewater by providing alternated anaerobic–aerobic–anoxic phases [33–34]. The application of SBR to color removal is rather a new approach compared to anaerobic–aerobic sequential treatment [35–41]. Therefore, effects of sludge age and initial dyestuff concentration on color and COD removal in facultative anaerobic bacterial culture containing SBR system were evaluated, in this study.

## 2. Materials and methods

### 2.1. Microbial culture

The facultative anaerobic bacterial consortium, isolated at Biotechnology Center of Ulster University, N. Ireland [23] was used in decolorization of dyestuff. The consortium called as PDW consists of *Alcaligenes faecolus* and *Commomonas acidourans* 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 containing  $1\text{ g glucose l}^{-1}$ ,  $0.5\text{ g (NH}_4)_2\text{SO}_4\text{ l}^{-1}$ ;  $4.32\text{ g NaHPO}_4 \cdot 2\text{H}_2\text{O l}^{-1}$ ;  $2.66\text{ g KH}_2\text{PO}_4\text{ l}^{-1}$ . Glucose was added into the media to provide readily biodegradable carbon source. 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

Sequencing Batch Reactor was made of Plexiglas with total reactor volume of 4750 ml and the reaction liquid volume of 3500 ml. At the beginning of the experiments, anaerobic PDW culture was inoculated and the system was operated as batch for 10 days to increase the biomass concentration.

SBR cycle consisted of fill (5 min), anaerobic/aerobic reaction (23 h), settle (30 min) and draw periods (10 min). The liquid volume in the reactor during fill stage was 1 l. A slight mixing was provided during fill stage and anaerobic phase to obtain homogenous conditions. The system was completely mixed in aerobic stage by aeration. Oxidation–reduction potential and dissolved oxygen concentrations were continuously monitored and they were  $\text{ORP} = -300\text{ mV}$  and  $\text{DO} < 0.1\text{ mg l}^{-1}$  for anaerobic phase,  $\text{ORP} = +200\text{ mV}$  and  $\text{DO} > 2\text{ mg l}^{-1}$  for aerobic phase. Each experimental condition was repeated at least three times. pH was adjusted to pH 7 by adding 5% KOH and 1%  $\text{H}_2\text{SO}_4$ . The temperature was adjusted to  $T = 28^\circ\text{C}$  by using a heating jacket.

### 2.4. Analytical methods

Daily samples withdrawn from system were centrifuged at 5000–6000 rpm until clear supernatant was obtained. COD and absorbance measurements were carried out on supernatants.

A scanning spectrophotometer (Novaspec II, Pharmacia Biotech) was used for absorbance measurements. Absorbance measurements were done 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 concentration was evaluated from the developed absorbance–concentration curve. Dyestuff concentration was used in decolorization efficiency calculations. Chemical Oxygen Demand (COD) Analysis were carried out according to Standard Methods [42]. The dissolved oxygen (DO) concentration was measured by Oxi 330/SET. Oxidation Reduction Potential was monitored by WTW Electrode SenTix ORP probe connected to pH meter.

## 3. Results and discussions

### 3.1. Effect of sludge age on color and COD removal

In order to determine the optimum sludge age for maximum COD and color removal, SBR system was operated at six different sludge retention times (SRT) between  $\theta_C = 12$  days and  $\theta_C = 30$  days. Effluent dyestuff and COD concentrations and removal efficiencies for each retention times were determined. The initial dyestuff and COD concentrations, were kept constant at  $\text{COD}_0 = 800 \pm 50\text{ mg l}^{-1}$  and  $D_0 = 60 \pm 10\text{ mg l}^{-1}$ , respectively. The anaerobic/aerobic phase operation period was 12 and 11 h, respectively. Sludge age was adjusted by withdrawing certain volume of biomass/liquid mixture under completely mixed conditions.

Fig. 1 depicts the variation of dyestuff concentration and removal efficiency with time at 15 days SRT in SBR system. Dyestuff concentration reduced from  $60$  to  $8\text{ mg l}^{-1}$  resulting in around 90% removal efficiency within 3 h in anaerobic phase in the third cycle. It further decreased to  $4\text{ mg l}^{-1}$  at the end of 6 h of anaerobic phase. However, no color removal

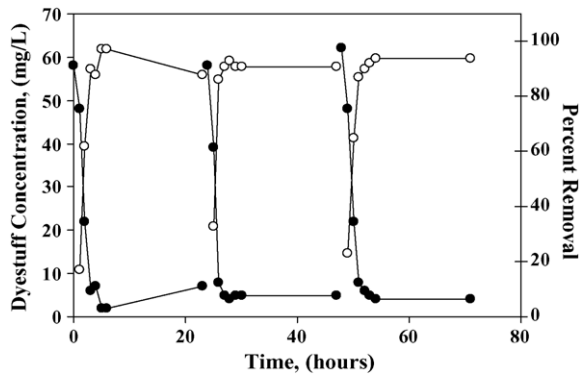


Fig. 1. Variation of effluent dyestuff concentration and dyestuff removal efficiency in SBR with time (—●—, concentration; —○—, efficiency).

was obtained by aeration. As a result, removal efficiency remained around 94%. Although total COD removal efficiency was over 75%, about 70% of COD was removed in the first 5 h of anaerobic stage (Fig. 2). These results indicate that almost 90% of color removal can be obtained within 3–4 h of anaerobic period. It was reported that color removal was mainly achieved within 4 h [36] and 2 h [39] of anaerobic period of SBR system. However it could reach to 30–48 h in batch operations depending on dyestuff type and concentration [14,43].

Fig. 3 shows the final dyestuff concentration and removal efficiencies at different sludge ages in anaerobic and aerobic phases of SBR. As seen from the figure, increasing SRT from 15 to 30 days did not affect the color removal. It was possible to obtain more than 95% decolorization efficiency or to reduce  $60 \text{ mg l}^{-1}$  initial dyestuff concentration to less than  $5 \text{ mg l}^{-1}$  by anaerobic–aerobic sequencing batch reactor. Lower sludge age adversely affected the color removal. The efficiency decreased to 57% in anaerobic phase at 12 days sludge age. Since, 95% of color was removed by anaerobic organisms, it has to be stated that, the main color removal phase in this operation system is the anaerobic phase. Therefore it can be concluded that the contribution of aerobic phase

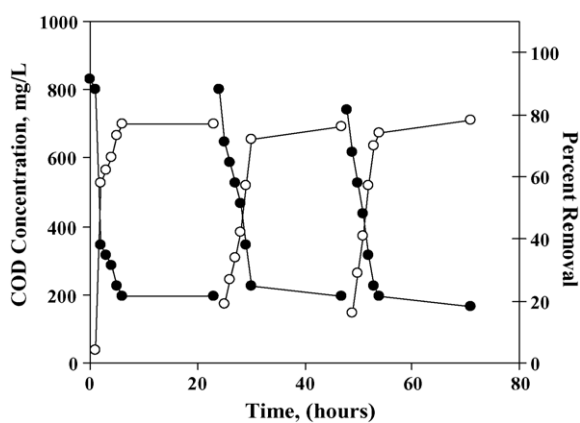


Fig. 2. Variation of effluent COD concentration and COD removal efficiency in SBR with time (—●—, concentration; —○—, efficiency).

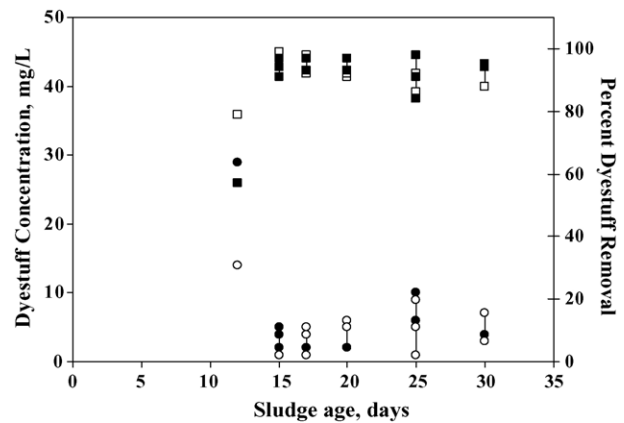


Fig. 3. Effect of sludge age on color removal in SBR system (concentration in —●—, anaerobic effluent; —○—, aerobic effluent; efficiency in —■—, anaerobic phase; —□—, aerobic phase).

to decolorization was almost none or negligible. The results are in good agreement with the other SBR studies. Increasing sludge age from 12 to 22 days did not provide better color removal [41]. Panswand reported around 70% color removal in anaerobic phase while it was maximum 12.8% aerobic phase of SBR system [39]. About 90% of color was removed under anaerobic condition and no further improvement in effluent dyestuff concentration was obtained by increasing aeration period. Even an increase in absorbance of aerobic effluent was observed [36]. On the contrary, improvement in decolorization by aeration has been also reported [38].

The final COD concentration and removal efficiencies in SBR system is given in Fig. 4. The effluent COD concentration was around  $250 \pm 50 \text{ mg l}^{-1}$  for sludge ages between  $\theta_C = 12$  days and  $\theta_C = 30$  days. Anaerobic phase was able to remove  $70 \pm 5\%$  of initial COD concentration (Fig. 4). The same conclusion can be drawn for COD removal as in color removal. The effect of anaerobic phase on COD removal is

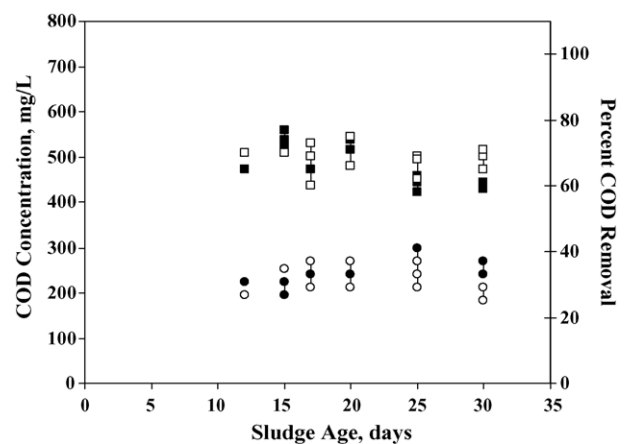


Fig. 4. Variation of effluent COD concentration and COD removal efficiency with sludge age in SBR (concentration in —●—, anaerobic effluent; —○—, aerobic effluent, efficiency in —■—, anaerobic phase; —□—, aerobic phase).

stronger than that of aerobic phase. Since the first stage exposed to limited amount of organic substrate in the media is the anaerobic stage, the main fraction is consumed by the anaerobic organisms for growth and to obtain energy. Therefore high COD removal was observed in anaerobic phase. The low COD removal in aerobic phase could be because of the insufficient amount of organic substances remained ( $\text{COD} = 200 \text{ mg l}^{-1}$ – $250 \text{ mg l}^{-1}$ ) after anaerobic phase. This amount of organic substance may not have sustained the growth of aerobic organisms and hence no improvement in COD removal was observed in aerobic phase. The reported organic substance removal efficiencies in SBR vary depending on dyestuff type, amount of initial COD concentration, anaerobic–aerobic phase retention times etc. For example, Shaw reported 65% TOC removal in 18.5 h anaerobic retention time [38]. Panswand obtained overall 97% COD removal [39]. Low initial COD concentration ( $500 \text{ mg l}^{-1}$ ) and dyestuff concentrations ( $10 \text{ mg l}^{-1}$ ) or longer anaerobic period (18 h) could be the main reasons for better COD removal compared to the results of this study. Over 80% COD removal in total of SBR was observed by Pasukphun and Vinitnantharat [41]. However, there are also reports about no efficient COD removal in anaerobic phase of SBR system. Under 24 h batch anaerobic condition, 22% of COD was removed, but 12 h shaking provided almost complete COD removal [35]. Similarly, The efficiency was only 30% in anaerobic phase while it was 80% in aerobic phase when SBR was operated at 15 days sludge age [36].

### 3.2. Effect of initial dyestuff concentration on color and COD removal

Initial dyestuff concentration was changed in order to understand the response of the system to higher dyestuff concentrations and to determine the maximum concentration that can be tolerated by the system. Dyestuff concentration was varied between  $D_0 = 50$  and  $500 \text{ mg l}^{-1}$ . Sludge age was adjusted to 15 days and anaerobic–aerobic hydraulic retention times were 12 and 11 h, respectively. Initial COD concentration was around  $1000 \text{ mg l}^{-1}$  in most of the experiments.

Fig. 5 summarizes the effect of initial dyestuff concentration on dyestuff removal performance of the system. As seen from the figure, increasing dyestuff concentration did not significantly affect the effluent dyestuff concentration and removal efficiency. It was possible to obtain less than  $15 \text{ mg l}^{-1}$  effluent dye concentration up to  $D_0 = 300 \text{ mg l}^{-1}$ . The highest effluent concentration was  $44 \text{ mg l}^{-1}$  which was observed at  $500 \text{ mg l}^{-1}$ . Although, it seems that system performance decreases at high dyestuff concentrations, 90% of the dyestuff was removed from the media. This result indicates that system can be operated efficiently at high dyestuff concentrations. However, it has to be stated here again that significant amount of dyestuff is removed under anaerobic conditions, since the contribution of aerobic phase to color removal could be maximum 5% or none at all.

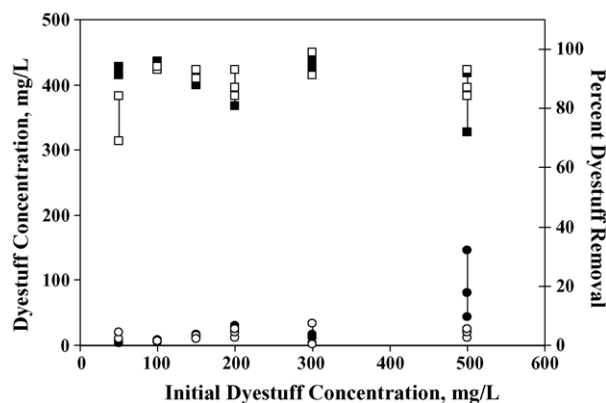


Fig. 5. Effect of initial dyestuff concentration on dyestuff removal in SBR system (concentration in —●—; anaerobic effluent; —○—, aerobic effluent, efficiency in —■—, anaerobic phase, —□—, aerobic phase).

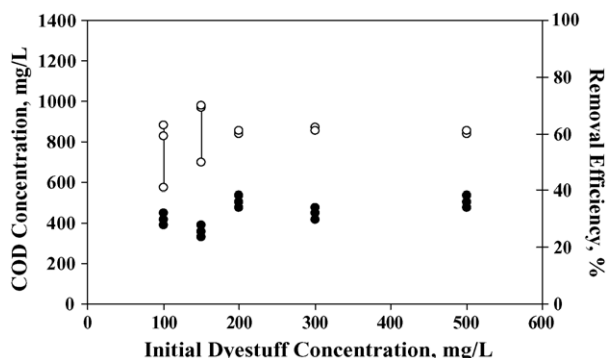


Fig. 6. COD removal performance of SBR system at different initial dyestuff concentration (—●—, concentration; —○—, efficiency).

Fig. 6 depicts the variation of effluent COD concentration and removal efficiencies with initial dyestuff concentration. Increasing dyestuff concentration caused a slight rise in the effluent COD. SBR system reduced around  $1000 \text{ mg l}^{-1}$  initial COD concentrations to about  $400 \text{ mg l}^{-1}$  for dyestuff concentrations up to  $150 \text{ mg l}^{-1}$ . However, the COD concentration in the effluent was around  $500 \text{ mg l}^{-1}$  for  $\text{DO} > 150 \text{ mg l}^{-1}$ . As a result removal efficiency varied between 60% and 70%. If the results are compared with Fig. 7,

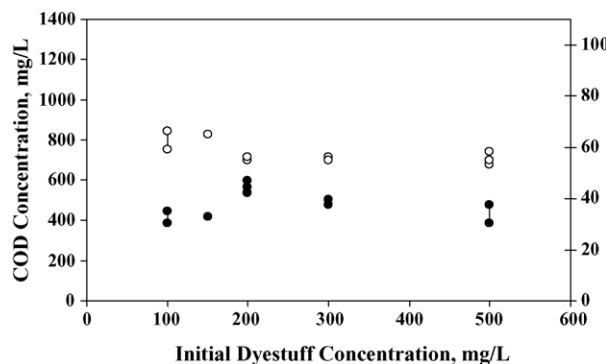


Fig. 7. COD removal in anaerobic phase of SBR system at different initial dyestuff concentration (—●—, concentration; —○—, efficiency).

which indicates the effluent COD concentration and removal efficiencies of anaerobic phase at different dyestuff concentrations, it could be concluded that COD is mainly used by anaerobic organisms.

#### 4. Conclusions

Increasing sludge from  $\theta_C = 15$  to  $\theta_C = 30$  days did not significantly affect the dyestuff removal performance of anaerobic phase and aerobic phases. The most significant effect was observed at 12 days sludge age at which both color and COD removal decreased. Although dyestuff concentration was reduced from  $60 \text{ mg l}^{-1}$  to around  $25 \text{ mg l}^{-1}$  in anaerobic phase, aeration provided further decrease resulting in  $12 \text{ mg l}^{-1}$  effluent dyestuff concentration. The low level of color and COD removal could be because of decreasing in biomass concentration at low sludge age. The effect of sludge age on decolorization in SBR system has been investigated by Lorenzo [36]. An improvement in COD and decolorization of Brilliant Violet 5R by increasing sludge age from 10 to 15 days was obtained while there were no differences in the performance of the system for Remazol Black B for sludge retention times of 15 days and 20 days. Similarly, better color and COD removal were observed at 15 days SRT compared to 10 days SRT in SBR [37]. Moreover, Pasukphan concluded that increasing sludge age from 12 to 22 days resulted in an increase of COD and color removal [41]. The results of this study indicated that at least 15 days sludge retention time is required for efficient decolorization of Remazol Rot RR and COD removal in SBR system.

Aerobic phase contributes to color removal if only remaining dyestuff concentration after anaerobic operation is high. It could be because of partial degradation of dyestuff, which produces, as a result, low concentration of toxic degradation end products. So, aerobic cultures might have remained active to be able to tolerate and to remove the remaining dyestuff after anaerobic phase. But removal of dyestuff by adsorption on the culture in aerobic stage could also be the possible mechanism.

SBR system can tolerate high concentration of dyestuff. The anaerobic phase was capable of removing over 95% of dyestuff even at  $500 \text{ mg l}^{-1}$  initial dyestuff concentration. At low concentrations almost complete decolorization was obtained. However, COD removal performance slightly decreases with increasing initial dyestuff concentration.

In summary, SBR system has advantages in terms of tolerance to high dyestuff concentrations up to  $D_0 = 500 \text{ mg l}^{-1}$ , low sludge ages ( $\theta_C = 15$  days) and low external carbon requirement ( $\text{COD}_0 = 800 \text{ mg l}^{-1}$ ) to obtain over 85% decolorization efficiency. However, the contribution of aerobic phase to total system performance can be evaluated as insignificant. The aeration is necessary as long as remaining dyestuff concentration is high after anaerobic biodegradation.

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