

## REMOVAL OF REACTIVE BLUE 19 BY ADDING POLYALUMINUM CHLORIDE TO SEQUENCING BATCH REACTOR SYSTEM

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### ABSTRACT

The main objective of this study was to evaluate Reactive Blue 19 dye removal efficiency in aerobic sequencing batch reactor (SBR) process by adding polyaluminum chloride (PACl). PACl was added to the reactors in concentrations of 0, 1, 5, 15 and 30 mg-Al/L (SBR<sub>1</sub> to SBR<sub>5</sub>) after filling periods. Initial dye concentrations were selected to be 40 mg/L for all reactors. The averages of dye removal efficiencies were more than 57% in all reactors. The maximum and minimum dye removal efficiencies were  $71.7\% \pm 13.6$  and  $57.7\% \pm 34.3$  in SBR<sub>3</sub> and SBR<sub>4</sub>, respectively. According to the obtained results, PACl had not any significant effects on the COD removal efficiency. The MLSS and MLVSS concentration of SBRs had an increasing rate during whole operation time and reached from 2500 mg/L (1<sup>st</sup> day) to 4900 mg/L (39<sup>th</sup> day). The maximum increasing rate was 50% in SBR<sub>5</sub>.

**Key words:** Biological treatment, Sequencing batch reactor, Reactive Blue 19, Polyaluminum chloride

### INTRODUCTION

Textile companies, dye manufacturing industries, rubber, plastic, tanneries, cosmetics, food companies and many other industries discharge dye wastewater which cause environmental concerns (Amin, 2008). Wastewater generated by these industries is characteristically high in both color and organic content. Currently about 20–30% of the total market for dyes belong to reactive dyes because they are used to dye cellulosic fibers such as cotton which makes up about half of the worlds fiber consumption (Koyuncu, 2002; Papic *et al.*, 2004).

Two methods of dye removal, which are extensively used, are biological and physicochemical processes (Uddin *et al.*, 2003; Ong *et al.*, 2005a; Zee and Villaverde, 2005; Ong *et al.*, 2005a; Nabi Bidhendi *et al.*, 2007, Hasani Zonoozi *et al.*, 2008; Rezaee *et al.*, 2008, Wang *et al.*,

2009). The biodegradability of many reactive dyes, and textile effluents indicated that biological treatment is not always sufficient (Pala and Tokat, 2002). On the other hand, some operational problems such as high chemical and operation cost, regeneration problems, secondary pollutants and much energy consumption limit application of physicochemical processes (Lee *et al.*, 2003; Ong *et al.*, 2005b; Sirianuntapiboon *et al.*, 2006; Mohan *et al.*, 2007). Because of such these limitations, combined processes have been developed in last decades.

Effects of adding some adsorbents and chemicals into activated sludge process in order to enhance the treatment efficiencies of different industrial wastewaters have been investigated by several researchers (Pala and Tokat, 2002; Dosta *et al.*, 2007). In this study, polyaluminum chloride (PACl) is directly added into sequencing batch reactor (SBR) at different dosages to investigate

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its effect on Reactive Blue 19 dye removal efficiency.

## MATERIALS AND METHODS

Reactive Brill Blue KN-R (CI: Reactive Blue 19) was used for this study. The chemical composition of the simulated dye wastewater was as follows: Reactive Blue 19 (40 mg/L), powdered milk (1.78 g/L) as a carbon source and nutrients (46 mg/L of  $\text{KH}_2\text{PO}_4$ , 52 mg/L of  $\text{K}_2\text{HPO}_4$  and 198 mg/L of urea) to adjust COD about 1500mg/L. The maximum absorbance ( $\lambda_{\text{max}}$ ) of the dye with the background of deionized water was at 594 nm, which was determined by scanning pattern performed on HACH spectrophotometer DR/4000. During the experiments,  $\lambda_{\text{max}}$  was used for all the absorbance readings.

Five Plexiglas sequencing batch reactors with the total volume of 7L and working volume of 5.5L

were used in this study (Fig. 1). The operation program of all SBRs in one cycle (24 hours) is summarized in Table 1.

Bio-sludge was collected from Qeytarieh municipal wastewater treatment plant, Tehran (Iran) and was inoculated to the bioreactors. The reactors were initially operated for 10 days (10 cycles) to acclimatize microorganisms to simulated dye wastewater. PACl was also added at different dosages of 0, 1, 5, 15, 30 mg-Al/L (as variable) into the  $\text{SBR}_1$ ,  $\text{SBR}_2$ ,  $\text{SBR}_3$ ,  $\text{SBR}_4$ , and  $\text{SBR}_5$ , respectively (after filling phase) every day. The other main operational parameters such as hydraulic retention time (HRT) and solids retention time (SRT) of all SBRs were kept constant at 1.83 day and 10 day, respectively. After five days, first measurements were implemented which was selected as day 0 and the normal operation were continued for 46 days (more than three times of SRT).

The chemical oxygen demand (COD), dye absorbance ratio, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), total suspended solids (TSS), turbidity, dissolved oxygen (DO), pH and sludge volume index (SVI) of samples were measured using standard methods for examination of water and

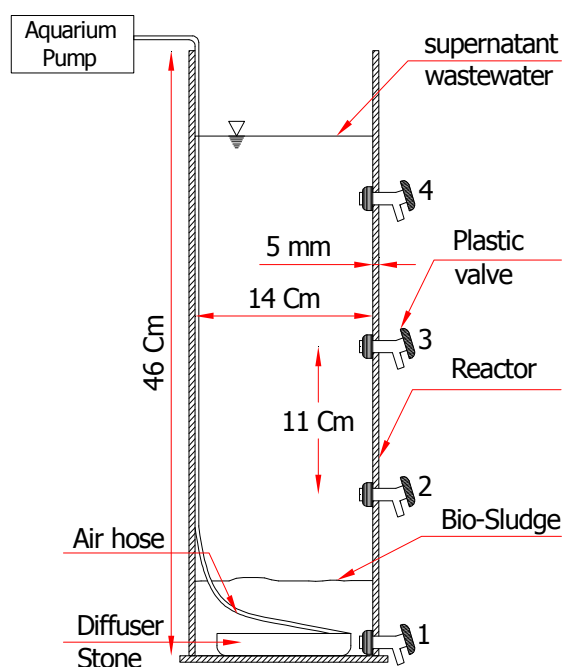


Fig. 1: A schematic of sequencing batch reactor used in this study

Table 1: Operation program of all SBRs in one cycle

Sequence phase	Phase period	Air supply
Fill	15 min	Off
React	20.5 h	On
Settle	2.5 h	Off
Draw	15 min	Off
Idle	30 min	Off

wastewater (APHA, AWWA, WPCF, 1992).

## RESULTS

### *Effect of PACl concentration on dye removal efficiency*

This study was conducted to investigate the influence of PACl dosages in SBR system on the Reactive Blue 19 removal efficiency. The variation of dye removal efficiency with different dosages of PACl (0-30 mg-Al/L) for SBR systems

during the operation period is shown in Fig. 2. As seen in Fig. 2, the dye removal efficiencies of SBRs increased gradually within first ten days and after that the process approximately remained in a stable condition except for SBR<sub>2</sub> and SBR<sub>4</sub>. The average dye removal efficiency of 68.3% was obtained in SBR<sub>1</sub> (without adding PACl). By adding of 1, 15, and 30 mg-Al/L PACl into the SBR<sub>2</sub>, SBR<sub>4</sub>, and SBR<sub>5</sub>, the average dye removal efficiencies reduced to 59.3% and 57.7%, and 67.5%, respectively. However, in the cases of SBR<sub>3</sub> with 5 mg-Al/L PACl, better efficiencies

of 71.7% was achieved. The minimum and maximum dye removal efficiencies were 27.3% and 85.5% in SBR<sub>2</sub> and SBR<sub>3</sub>, respectively. As it is shown in Fig. 2, no significant influence on the dye removal efficiency was observed by altering the PACl concentrations in the range of 0 to 30 mg-Al/L of PACl. In order to have more information regarding dye removal changes during a cycle time, the variation of dye removal efficiencies of SBRs were monitored in the last day of normal operation (day 46) which is presented in Fig. 3.

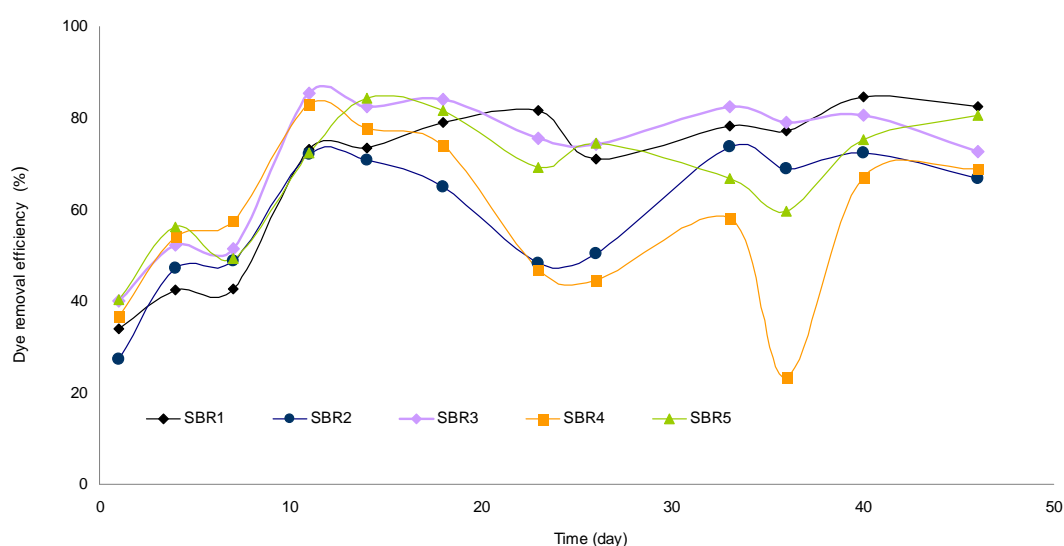


Fig. 2: The variation of dye removal efficiencies of SBRs during operation period

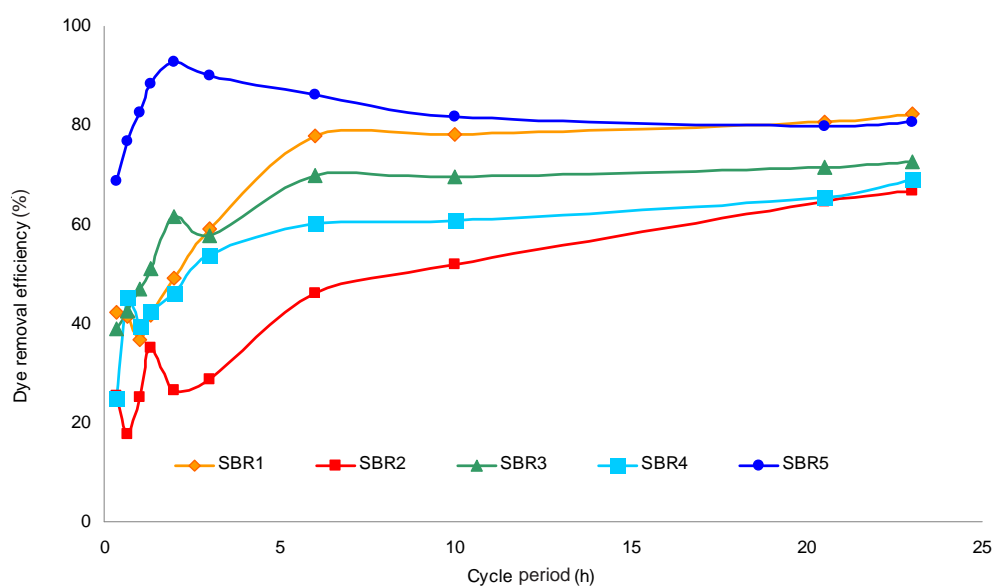


Fig. 3: Variation of dye removal efficiencies of SBRs during a cycle time (day 46)

Some fluctuations were observed during first six hours of the cycle time in dye removal efficiencies of all SBRs, then the curves relatively approached plateau until the end of the cycle. In the case of SBR<sub>5</sub> with the highest dosage (30mg-Al/L PACl), the dye removal efficiency increased up to 93% within the first two hours and decreased gradually to about 81% at the end of the cycle period.

#### *Effect of PACl concentration in SBR performance*

The main experimental data of SBRs performance including COD removal efficiency, effluent turbidity and TSS and the main sludge characteristics are summarized in Table 2.

Table 2: Main experimental data of SBRs during the operation period

Reactors		SBR <sub>1</sub>	SBR <sub>2</sub>	SBR <sub>3</sub>	SBR <sub>4</sub>	SBR <sub>5</sub>
COD	Effluent (mg/L)	67.5 ± 42.5	104.7 ± 60.3	79.2 ± 34.8	76.3 ± 22.7	56.2 ± 39.8
	Removal (%)	95.5 ± 2.8	93 ± 4	94.7 ± 2.3	94.9 ± 1.6	96.2 ± 2.6
Effluent TSS (mg/L)		35.6 ± 45.4	37.6 ± 37.4	41.2 ± 36.8	44.7±78.3	47.5± 68
Effluent Turbidity (NTU)		6 ± 5.7	11 ± 15	8.9 ± 7.72	13±12.2	8.3 ± 17.9
MLSS (mg/L)		2120 ± 466	2243 ± 503	2485 ± 593	2815 ± 587	2959 ± 919
MLVSS/MLSS (%)		79 ± 19.1	83 ± 3.1	81.1 ± 5.7	79.2 ± 7.2	79.5 ± 11.2
SV <sub>30</sub> (mL/L)		173.6 ± 33.6	189 ± 19.1	160 ± 50	206.4 ± 76.4	144.54 ± 44.5
SVI (mL/g of bio sludge)		66.2 ± 26	71 ± 17.9	52.5 ± 10	57.3 ± 7.3	40.8 ± 19.14
F/M (1/d)		0.38 ± 0.07	0.33 ± 0.08	0.29 ± 0.1	0.25 ± 0.09	0.24 ± 0.1

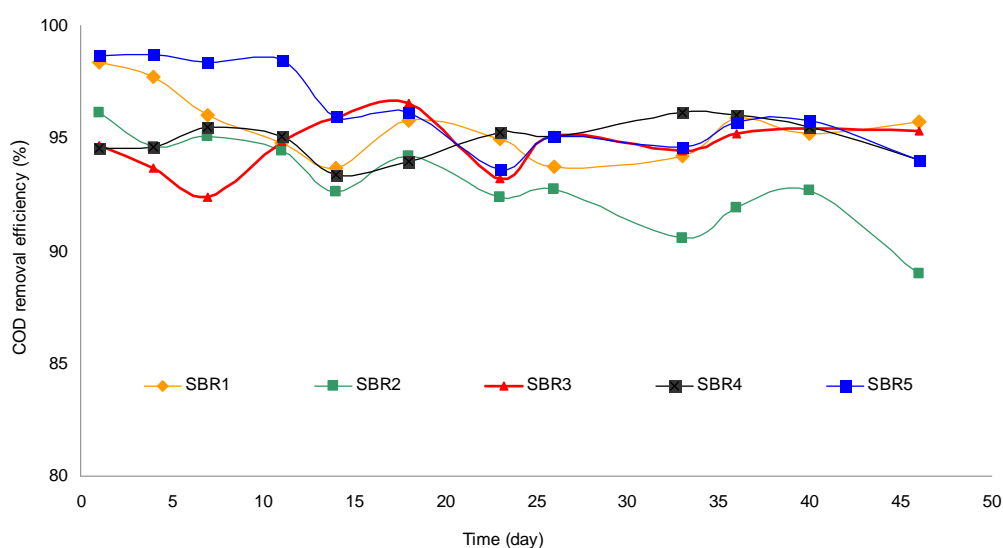


Fig. 4: Variation of COD removal efficiencies of SBRs during operation period

One of the parameters that evaluate the performance of SBR is COD removal efficiency. As it is shown in Table 2, the average COD removal efficiencies of all reactors were in the range of 93-96 percent, which it may be due to prolonged aeration period in SBRs cycles (20.5 hours).

The average COD removal efficiency had no regular trend with increasing PACl concentration in SBRs. The maximum and minimum averages of COD removal efficiencies were observed in SBR<sub>5</sub> and SBR<sub>2</sub> with PACl concentrations of 30 and 1 mg-Al/L, respectively.

The variation of COD removal efficiencies of all

SBRs during operation period is shown in Fig. 4.

The maximum COD removal efficiency was 99%, obtained in SBR<sub>5</sub> with 30 mg-Al/L on fourth day of operation and the minimum COD removal efficiency was 89% in SBR<sub>2</sub> with 1 mg-Al/L on the last day of operation (day 46). Generally, no significant influence on COD removal efficiency was observed by adding PACl at different dosages. Variation of COD removal efficiencies of SBRs were monitored on the last day of operation (day 46) to find COD removal pattern during a cycle time which is shown in Fig. 5.

It is evident from the experimental results that

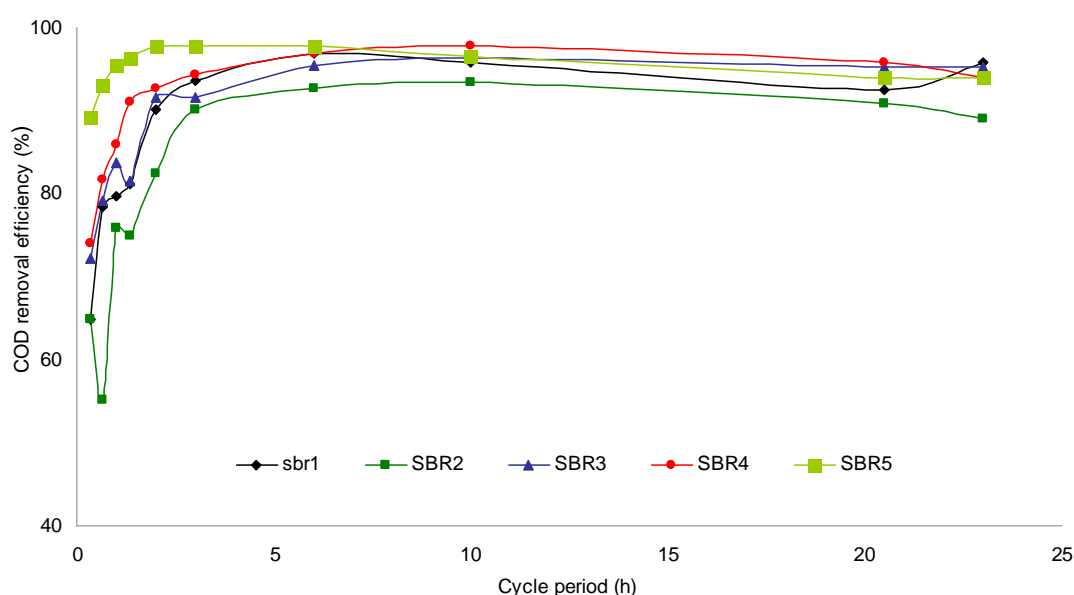


Fig. 5: The variation of COD removal efficiencies of SBRs during a cycle time (day 46)

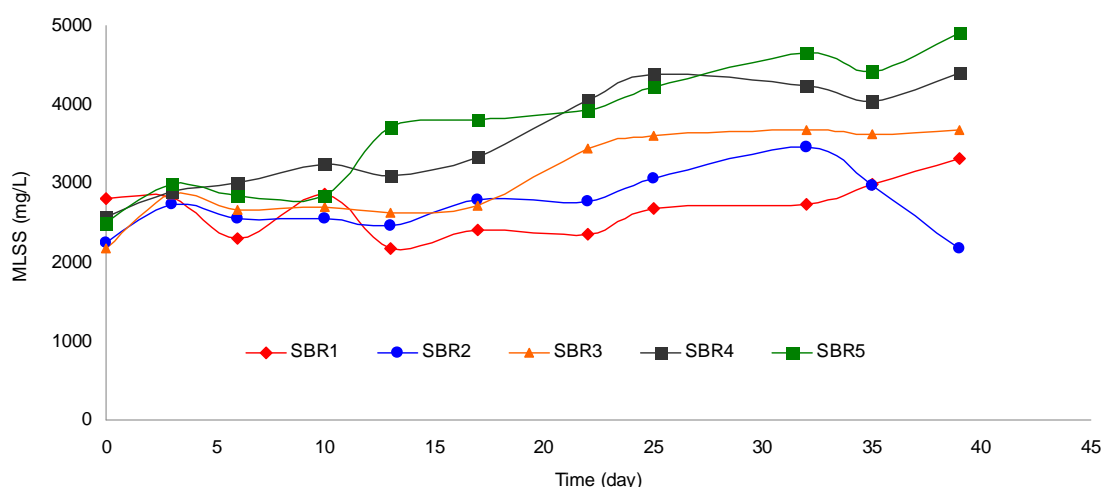


Fig. 6: MLSS variations during SBR operation

over 90 percent of influent COD were eliminated during the first two hours of aerobic phase ; the curves nearly approached plateau.

Effluents characteristics of all SBRs including average effluent TSS and effluent turbidity are reported in Table 2. Average effluent TSS of reactors increased by increasing PACl concentration. No influence on effluent turbidity was observed by adding PACl at different dosages. However, the value of effluent turbidity of all SBRs were less than Iranian national effluent discharge standards (<50 NTU) (Iranian environmental protection regulations & standards, 2004).

In order to determine the effects of PACl at different dosages on bio-sludge, the MLSS in SBRs were monitored during operation period which are illustrated in Fig. 6.

As shown, the MLSS gradually increased during the normal operation of SBRs and at the highest level, it reached 4900 mg/L in SBR<sub>5</sub> in day 39. The maximum and minimum averages of MLSS were observed 3700 and 2670 mg/L in SBR<sub>5</sub> and SBR<sub>1</sub>, respectively.

MLSS and MLVSS variations of PACl dosage are illustrated in Fig. 7. As it is shown in this Fig., with the increase of PACl concentration from 0 to 30 mg-Al/L, MLSS and MLVSS increased slightly.

The maximum and minimum average sludge volume index of SVI were 71 and 40.8 in SBR<sub>2</sub> and SBR<sub>5</sub>, respectively. SVI for all SBRs was in the range of 41-71 mL/g and no relationship was found between SVIs in SBR<sub>1</sub> (without adding PACl) and other SBRs.

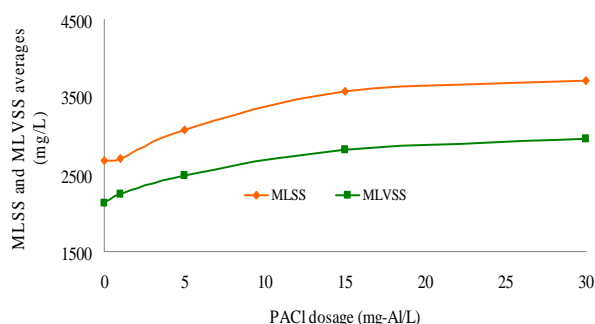


Fig. 7: Influence of PACl dosage on MLSS and MLVSS averages

## DISCUSSION

The average dye removal efficiency for SBR<sub>1</sub> to SBR<sub>5</sub> with PACl concentration of 0, 1, 5, 15, and 30 mg-Al/L were 68.3%, 59.3%, 71.1%, 57.7%, and 67.5%, respectively. In spite of SBR<sub>3</sub>, the other reactors showed a similar decreasing tendency to dye removal in comparison with SBR<sub>1</sub> (without adding PACl). No significant influence on the dye removal efficiency was observed by altering the PACl concentrations in the range of 0 to 30 mg-Al/L. In another study which was carried out by Pala and Tokat, (2002), the dye removal efficiency was 78% after addition of 120 mg/L of a specific organic flocculants (Marwiche DEC) in activated sludge process.

The removal efficiency of Reactive Blue 19 with concentration of 40 mg/L is reported 35% in aerobic biological process by Vaigan group (Vaigan *et al.*, 2009). In our study, a better performance of 68.3% was achieved in SBR<sub>1</sub> (without adding PACl). Longer settling phases (2.5 h), applied in this study, may have increased the dye removal efficiency due to anoxic condition in this stage. In a different study by Panswad and Luangdilok, removal efficiency of Reactive Blue 19 was 64% when a long anaerobic time (18 h) was used to maximize the decolorization potential. Generally, a better performance in dye removal is achieved in anaerobic system in comparison with aerobic process (Panswad and Luangdilok, 2000). Additionally, in another study by Wang, reduction of Reactive Blue 19 was 90% by batch hydrolytic-aerobic recycling process with the recycling rate of 10 mL/min (Wang *et al.*, 2009).

In our study, the average COD removal efficiencies of all reactors were in the range of 93-96 percent. Generally, no significant influence on COD removal efficiency was observed by adding PACl at different dosages (0-30 mg-Al/L). When the anaerobic residence time is low, the contribution of aerobic phase on COD removal is significant. In this condition, SBR system requires long aeration period to eliminate COD from the wastewater (Kapdan and Oztekin, 2006). In another study, the average COD removal efficiency was 97%, obtained in aerobic phase without addition of any chemicals in SBR (Vaigan *et al.*, 2009). Similar results are observed by Pala and Tokat which



found that the addition of some materials like powdered activated carbon (PAC), bentonite, activated clay and a specific organic flocculants (Marwiche DEC) did not change COD removal significantly (Pala and Tokat, 2002).

According to the experimental results (Fig. 5), more than 90 percent of influent COD were eliminated during the first two hours of aerobic phase. This is compatible with other research of that found the major part of COD is removed during the first hours of aeration period (Vaigan, 2008; Hajiabadi, 2009).

According to obtained results, the MLSS increasingly varied during the normal operation of SBRs. Furthermore, as it shown in Table 2, the average MLSS was increased from 2120 to 2960 mg/L with the increase of PACl concentration from 0 to 30 mg-Al/L. In another study, carried out by Pala and Tokat, MLSS concentration did not change significantly during addition of a specific organic flocculants (Marwiche DEC) in the applied dosage of 120 mg/L (Pala and Tokat, 2002).

Average SVI of all SBRs was in the range of 41-71 mL/g and no relationship was found between SVIs in SBR<sub>1</sub> (without adding PACl) and other SBRs.

The main aim of this study was to evaluate dye removal efficiency in aerobic sequencing batch reactor process by adding polyaluminum chloride (PACl). The main conclusions of this study can be summarized as follows:

- The averages of dye removal efficiencies were more than 57% in all SBRs. The maximum and minimum averages of dye removal efficiencies were obtained 71.7% and 57.7% in SBR<sub>3</sub> and SBR<sub>4</sub> with 5 and 15 mg-Al/L PACl, respectively. No significant influence on the dye removal efficiency was observed by altering the PACl concentrations in the range of 0 to 30 mg-Al/L of PACl.

- COD removal efficiency was obtained more than 93% in all SBRs. No significant influence on COD removal efficiencies was observed by adding different concentrations of PACl in the range of 0-30 mg-Al/L.

- Adding PACl to the SBR system increased effluent TSS and had no significant influence on effluent turbidity of SBRs. The values of effluent

turbidity of all SBRs were less than Iranian national effluent discharge standards.

- Average MLSS and MLVSS of all reactors slightly increased during the operation time. The maximum MLSS was related to SBR<sub>5</sub> which reached 4900 mg/L on day 39.

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