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Color removal from wastewater by using two-step (biological and chemical) aerobic filter reactors

Uysal Y.[1,*] and Bilgiç M.[2]
[1]Kahramanmaras Sutcu Imam University, Faculty of Engineering and Architecture, Dept. of Environmental Engineering, Kahramanmaras, Turkey
[2]General Directorate of State Hydraulic Works, Kahramanmaras, Turkey
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*to whom all correspondence should be addressed: e-mail: yagmuruysal@gmail.com

Abstract

The discharge of colored textile wastewaters containing dyes with different chemical characteristics into the receiving streams is a problem for toxicological, ecological and also esthetical reasons. Most of dyes are stable, and not easily degradable by the conventional treatment methods, so removal of dyes from the textile effluents is a major problem. This study aimed to investigate color removal efficiency of two aerobic filter column reactors operated as sequencing as biological and chemical treatment steps. Biological column reactor (BR) filled with basaltic lava (Scoria) as supporting media for microorganisms, and second column reactor (CR) was filled with lime and textile fly ash mixture (1:3, w/w) used as chemical treatment step especially for phosphate and color removal. The reactors were operated at batch mode to investigate the effect of hydraulic retention times (HRT), aeration time and initial dye concentration (Everzol Blue BB) on treatment efficiencies. The results of the study showed that this system has quite high removal efficiencies for soluble organics and nutrients from wastewater. COD, TOC, NH_4-N and PO_4-P removal rates were obtained as 94.2 %, 94.8 %, 84.7 % and 97.5% in HRT of 24 h, respectively. In addition, this two-step treatment system reached to quite high color removal efficiencies of 96.4 % Pt/Co, 96.4 % DFZ-436 nm, 99.5 % DFZ-525 nm, and 99.8 % DFZ-620 in initial dye concentration of 800 ppm.

Keywords: Aerobic, Color, Filter Reactor, Pt-Co, DFZ, Wastewater

1. Introduction

Textile industry is an industry producing high volume wastewater containing a large variety of dyes and chemical additions. Pollutants in textile wastewater come mainly from the dyeing and finishing processes which have high biological oxygen demands (BOD), chemical oxygen demands (COD), high concentrations of suspended solids, high salt content and high levels of color caused by residual dyes (Chen *et al.* 2016). In the textile industry, up to 50% of the synthetic dyes are lost after the dyeing process, and approximately 10%-15% of the dyes are discharged in effluents (Vaidya and Datye, 1982). Synthetic dyes are important organo-pollutants contaminating the water environment, often due to a massive release from the textile dyeing process into the effluents. Besides potential hazardous effects of dyes, very low concentrations of these pollutants negatively affect aesthetic value of stream waters, reducing also the amount of light entering in the water with an adverse effect on photosynthesizing organisms (Novotny *et al.*, 2011). Because of the serious risk posed to humans and aquatic organisms, it is imperative to develop an efficient method for removing these chemicals from wastewater (Chen *et al.*, 2016).

Submerged biofilm systems are fixed film reactors packed with natural or synthetic media with a high specific surface area where the microorganisms can grow (El-Shaddai and Zahid, 2013). These systems are very effective in organic carbon and nutrient removal by means of the attached growth biofilm. They exhibit lots of advantages as compared with activated sludge process such as stability and long retention time of microorganisms which enable removal of recalcitrant pollutants (Guo *et al.*, 2009). The hydraulic mixing regime in a fixed-bed bioreactor is less turbulent compared with the Continuous Stirred Tank Reactor (CSTR) (Chu *et al.*, 2016). However, the physicochemical properties of the packing material also strongly influence hydrodynamics and bioavailability of the contaminant for degradation (Iffat *et al.*, 2015; Ji *et al.*, 2015; Krüner and Rosenthal, 1983; Sharvelle *et al.*, 2008; Wang *et al.*, 2006; Yue *et al.*, 2009).

The support packing material serves as a holding medium for microorganisms in the biodegradation of organic pollutants, and it should be inexpensive, easily accessible, with high area/volume ratio, good mechanical resistance and suitable for microorganism attachment. So, the choice of support material is very important (Li *et al.*, 2016). Among the natural packing materials, volcanic scoria stones reasonably meet these criteria due to their high natural porosity, relative resistance and abundance (Sagastume and Noyola, 2008).

Discharging wastewater containing high concentrations of nutrients especially phosphorus is a major cause of eutrophication in many freshwater ecosystems. The excessive phosphate ion content in industrial wastewater causes water eutrophication. It is therefore very important to explore cost-effective technologies for the removal of nutrients from wastewater. In the present study, the development of a sequencing packed-bed column reactors (PCR) packed with basaltic lava and ash/lime mixture for the effective treatment of color and phosphorus from wastewater is described. Two packed-bed column reactors (PCRs) have been used to investigate their efficacy in decolourization and reduction in other water pollution parameters such as total organic carbon (TOC), chemical oxygen demand (COD), nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_4-N), sulfate (SO_4) and phosphate (PO_4) from textile wastewater.

2. Materials and Methods

2.1. Microbial Culture

The bacterial culture was obtained from Kahramanmaras Paper Industry wastewater treatment plant, Kahramanmaras, Turkey.

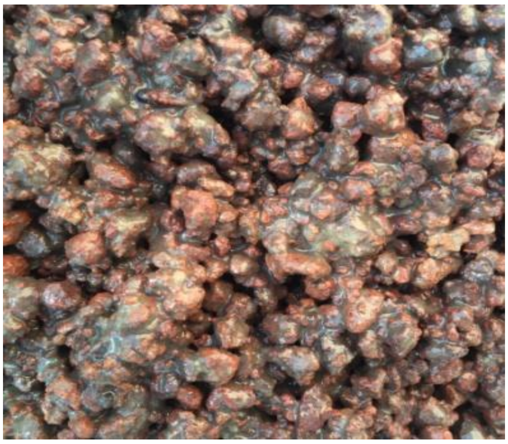

Figure 1. Scoria used for support material in order to immobilize microorganisms

The support particles used to immobilize microorganisms were Scoria which is an extremely vesicular basaltic lava with very small (< 1mm) vesicles. The seed culture was conditioned over a 21-day acclimation period to allow the biomass to adapt to culture medium and to obtain successful immobilization. During this acclimation period, the reactor was fed with synthetic wastewater, and controlled for MLSS, pH and DO parameters.

2.2. Experimental Setup

Figure 2 presents the schematic diagram of the pilot scale reactors. Two Plexiglas packed-bed column reactors with effective volume of 2 L were fabricated with an internal diameter of 7 cm and a height of 50 cm. The first column reactor (PCR-1) was filled with basaltic lava-Scoria and operated as biological while, the second column reactor (PCR-2) was filled with textile fly ash and lime mixture (1:3 v/v) and operated as a chemical treatment step to remove color and phosphate from wastewater. Scoria was used as support media for microorganisms. PCR-1 was inoculated with aerobic sludge taken from an aeration tank operated in a wastewater treatment plant belonging to a paper and paper mill industry in Kahramanmaras, Turkey. The system was fed from the bottom with dyestuff containing synthetic wastewater by a peristaltic pump with the volumetric organic loading rate (OLR) of 2.5 kg COD m^3/d, and the effluent was collected from the top. Aeration was supplied by air compressors via a porous membrane diffuser at the bottom of the reactors. The solid–liquid separator was also kept in the bottom of the reactor to prevent the loss of granules from the reactor. The reactors were operated at 23 ± 2 °C, and pH was set at 7.8. The reactors were run in sequence. A sedimentation tank was used after the biological reactor and fed with the effluent of it. Sludge age (θ_C) was adjusted to 10 days by removing certain amount of sludge from the biological column daily. pH was adjusted to 7.8 by adding of diluted NaOH and H_2SO_4 solutions. Schematic diagram of pilot plant is given in Fig. 2. In order to test the treatment capacity of the PCR-1 (biological), different aeration times (2-24 h) were tried to determine optimum retention time. Similarly, different retention times (5-30 min) were also tried for chemical reactor (PCR-2) to determine optimum retention time especially for phosphate and color removal.

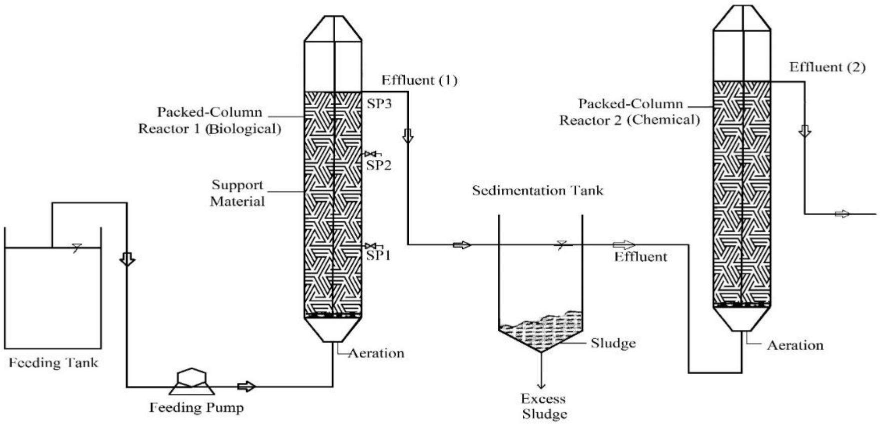

Figure 2: Biological-chemical sequencing packed-column reactors

2.3. Wastewater Characteristics

The synthetic textile wastewater used as feed solution was prepared by diluting the carbon source ($C_2H_3NaO_2$-sodium acetate) stock solution in distilled water to a COD content of 2500mg/L, and supplementing it with pH buffering phosphates and other nutrients: 1000 mg/L Na_2HPO_4, 1000mg/L K_2HPO_4, 500 mg/L $(NH_4)_2SO_4$, 50 mg/L Ca $(NO_3)_2.4H_2O$, 5000 mg/L Yeast extract. All salts were analytical grade. Everzol Blue BB was used as a model reactive dye as a concentrated solution in deionized water (100-800 mg/L). Macro, micro and buffering solutions were prepared separately once every six days and stored below 4 °C to prevent degradation, and diluted as required when necessary. Carbon sources and yeast extract were added immediately before to feeding as powder.

2.4. Analytical Methods

pH, total suspended solids (TSS), conductivity, total organic carbon (TOC), chemical oxygen demand, nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_3-N), sulfate (SO_4), and phosphate (PO_4) parameters were determined according to Standard Methods (APHA, 2005). Standards of European Norm EN ISO 7887 were considered as basis and DFZ parameter was also chosen for color measurements with a HACH Lange DR-5000 spectrophotometer. The measured absorbance values at three wavelengths of 436, 525 and 620 nm were converted to 'Indices of Transparency' (DFZ = Durchsichts-Farb-Zahl). DFZ calculation was made as follows (Eq. 1):

$$DFZ = 100\,(E\lambda/d) \qquad (1)$$

Where Eλ; is extinction (at a known wavelength) and d; the thickness of cell in cm. All the samples were filtered (0.45 µm) before color measurement test.

3. Results and Discussion

3.1. Effect of hydraulic retention time for continuous aeration study

The treatment system containing of the aerobic biological-chemical sequencing packed-bed column reactors were firstly operated with continuously aeration at different hydraulic retention times (HRT) between 2 h and 24 h. PCR-2 was fed with the effluent of PCR-1, and it was operated at HRT of 30 min. This experimental run was made to determine optimum treatment period of biological system with continuous aeration. The change of the wastewater parameters in the effluents of the system were shown in the Fig. 3.

According to the results shown in Figure 3, it is shown that NO_2-N concentrations increased in the effluent of PCR-1 with respect to influent concentration at HRT values of 2-6 h, and then they decreased again in the effluent of PCR-2. However, nitrite removal occurred after 6 hours of HRT for PCR-1. These results indicated that nitrification reaction did not occur at HRT values of lower than 6 hours. Nitrite removal percentage of the system occurred mainly in the effluent of second reactor (PCR-2) in the range of 45.5-71.2 %. The efficiency of the nitrate removal of the system was higher than nitrite, and it mainly occurred biologically in the range of 61.1-66.5%. PCR-2 reactor did not show any nitrate removal, and PCR-1 reached to high nitrate removal values (71.2%) at first 2 hour of the experimental run.

Ammonium removal efficiency of the system occurred mainly biologically, and increased with increasing HRT values of the system. The maximum ammonium removal efficiency (84.7%) was obtained in the HRT of 24 h. However, contrary of the ammonium removal, sulfate removal did not occur in the system, significantly. Sulfate removal efficiency of the system was found to be low, and these values remained only in the range of 10.9-16.4%. One of the main objectives of this study was the phosphate removal from wastewater. PCR-2 containing ash/lime mixture was used for this purpose. It was found that this system was quite successful in the removal of phosphate ions from wastewater. Total phosphate removal rate of the system occurred in the range of 94.6-97.5%, and there was no relationship between phosphate removal and HRT values of the system. In addition to this, system reached to maximum phosphate removal rate at first 2 h. PCR-2 reactor showed the highest removal efficiency for phosphate ions, and removed phosphate ions from the effluent of the PCR-1 reactor in the range of 48.2-52.2%. The high removal efficiency of the PCR-2 reactor resulted from its ash/lime mixture bed.

The percentages removal of COD for PCR-1 was in the range of 5.5-80.5 % while, it was in the range of 5.5-32.2 % for PCR-2 at HRT range of 2-24 hours. The total COD removal efficiency of the system was found in the range of 48.9 to 86.8%. COD removal efficiencies showed that the maximum removal occurred for 24 hours of full aeration. TOC removal occurred mainly in the first reactor (PCR-1) at high removal rates of 62.3-94.8 % while, this value was obtained as 70.1-95.8 % for all of the system. TOC removal efficiency was also the maximum for HRT of 24 h similarly for COD.

The conductivity and pH values showed an increase in the effluent of PCR-2 reactor. Effluent pH values for PCR-1 reactor did not change and remained stable in the range of 8.4-8.8 while, they increased up to 12.7 in the effluent of PCR-2 because of its basic lime bed. Similarly, cationic structure of ash/lime mixture caused to increase of conductivity in the effluent.

3.2. Effect of aerobic/anoxic sequencing operation mode on the system performance

The results of the study which aimed to determine optimum HRT value for the system showed that the maximum treatment performance for carbon removal was obtained at HRT of 24 h. However, this value is high when the aeration costs are taken into consideration. Thus, it was decided to use an HRT of 12 h because of the system could reached to quite high removal efficiencies for COD and TOC (57.7% and 69.5%, respectively). In order to investigate the aerobic/anoxic sequencing operation mode on the treatment performance of the system, HRT was applied for 4 and 8 hours (2 h aeration/2 h anoxic and 4 h aeration/4 h anoxic), and the results of this study are shown in Table 1.

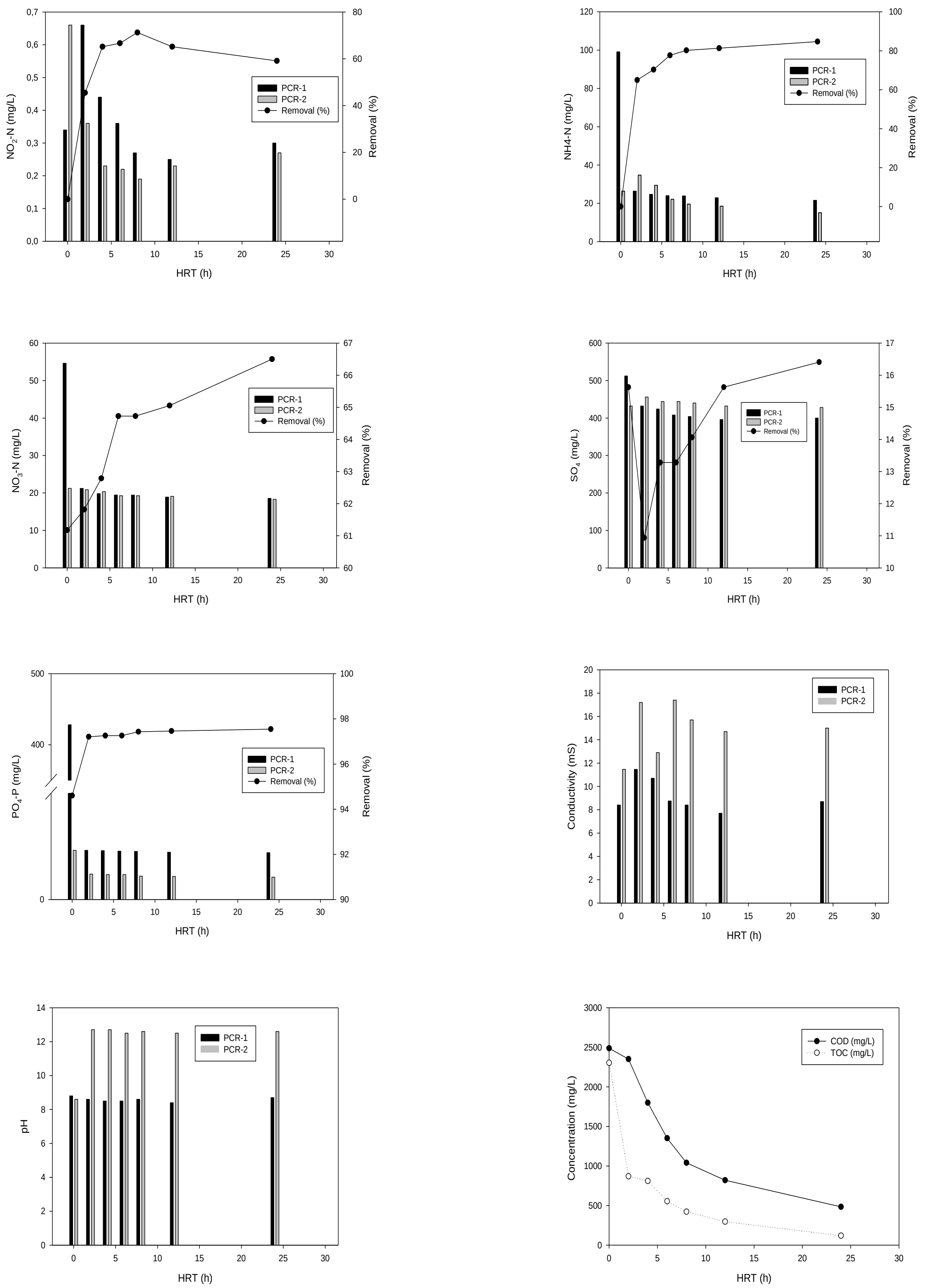

Figure 3. Wastewater characteristics in the influent and effluent of the reactors for different HRT values

The results showed that no differences were observed between two sequencing aeration operation mode of 2 h and 4 h. When these results were compared with the results of continuous aeration mode, COD and TOC removal efficiencies of 12 h of HRT (67% and 87%, respectively) were found to be higher than those of sequencing aerobic/anoxic mode for HRT of 2 h (60% and 70.1%) and 4 h (57.7%, 69.5%), respectively. There were also no differences between the results of nutrient removal rates for sequencing and continuous aeration modes. For example, ammonium removal efficiencies of the system for sequencing modes (2 h aeration/2 h anoxic and 4 h aeration/4 h anoxic) were found as 75.4% and 68.7%, respectively. These values were obtained as 75.8% and 75.1% for full aerobic modes of HRT of 4 h and 8 h, respectively. Similar results were also obtained for nitrate removal performance of the system. In the sequencing mode, 61.9% and 63.02% nitrate removal values were obtained for the system operated as 2 h and 4 h aeration/ anoxic modes, respectively. These values were found for full aeration mode as 63.8% and 64.4% for HRT of 4 and 8 h, respectively.

3.3. Effect of hydraulic retention time on the treatment performance of PCR-2

Packed-bed (ash/lime) column reactor of PCR-2 was operated with at different hydraulic retention times between 5-45 min. PCR-2 was fed with the effluent of PCR-1 treated with continuous aeration at HRT of 24 h. This experimental run was made to determine optimum treatment period of chemical system. The treatment performance of this run is shown in Table 2. According to the results shown in Table 2, the optimum HRT was found to be 15 min (with a 94.1 removal efficiency), and PCR-2 was found to be quite effective to remove PO_4 ions from wastewater especially in a short hydraulic retention time of 5 min (with 84.5% removal). Thus, we decided to continue other experiments by operating PCR-2 at HRT of 15 min.

Table 1. Influent and effluent characteristics of wastewater for PCR-1 reactor with aerobic/anoxic sequencing mode

	COD (mg/L)	TOC (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	PO_4-P (mg/L)	pH
Influent	2488	2304	0.34	99.10	54.63	512	428.2	8.0
Effluent PCR-1 (2 h aeration/2 h no-aeration)								
Aerob 1	1052	809	0.7	35.33	20.3	468	384	8.6-8.7
Anoxic 1	1525	1403	0.68	31.7	28.9	436	452	8.6-8.7
Aerob 2	1056	783	1.03	34.96	22.1	409	384	8.6-8.7
Anoxic 2	1250	906	0.77	30.73	20.1	458	452	8.6-8.7
Aerob 3	980	622	0.82	33.75	21.3	435	471	8.6-8.7
Anoxic 3	995	672	0.78	24.33	20.8	628	418	8.6-8.7
Effluent PCR-1 (4 h aeration/4 h no-aeration)								
Aerob 1	1152	891	0.84	30.85	21.2	465	412	8.6-8.7
Anoxic 1	1485	1166	0.8	32.42	20.3	463	403	8.6-8.7
Aerob 2	1052	703	0.76	30.97	20.2	460	437	8.6-8.7

Table 2. Influent and effluent characteristics of wastewater for PCR-2 reactor at different HRT values

HRT (min)	Effluent	NO_2-N (mg/L)	NH_4-N (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	PO_4-P (mg/L)	Cond. (µS)	pH
0	Influent	0.30	21.54	18.55	400	22.01	8700	8.7
5	PCR-2	0.83	29.64	21.40	489	3.41	16670	12.4
15	PCR-2	0.66	24.27	19.70	465	1.30	16675	12.6
30	PCR-2	0.28	15.13	18.38	428	1.51	15000	12.6
45	PCR-2	0.14	10.28	15.30	450	0.74	16671	12.7

3.4. Color Treatment Performance of the System

Wastewater characteristics in terms of color are shown in Table 3, and the color removal efficiencies of the PCR-1, PCR-2 and the all system are also shown in Figure 4-6. According to color removal results of PCR-1, it was shown that percentage removal of color increased with increasing color concentration for Pt–Co (46.0-64.0%) up to dye concentration of 800 mg/L. However, this trend was observed for DFZ-436 nm (50.0–63.9%) up to 400 mg/L while, it was 200 mg/L for DFZ-525 nm (28.9-88.9%) and DFZ-620 nm (45.5-92.1%), respectively. Color removal efficiencies decreased again to 22.3%, 63.7% and 79.0% in the dye concentration of 800 mg/L for DFZ-436 nm, DFZ-525 nm and DFZ-620 nm, respectively. PCR-2 reactor was found very effective to remove color from wastewater by physicochemical treatment because of adsorption potential of ash bed. Color removal efficiency of the PCR-2 increased with increasing dye concentration for all color parameters.

Table 3. Wastewater characteristic of the all system in terms of color parameters

		Color			
Dye (mg/L)		**Pt-Co**	**DFZ–436 nm**	**DFZ–525 nm**	**DFZ–620 nm**
100	**Influent**	**426**	**0.36**	**1.06**	**2.76**
PCR-1 (24 h)	Effluent-PCR-1	230	0.18	0.75	1.50
PCR-2 (15 min)	Effluent-PCR-2	63	0.10	0.30	0.30
200	**Influent**	**940**	**0.79**	**2.44**	**6.33**
PCR-1 (24 h)	Effluent-PCR-1	385	0.32	0.27	0.50
PCR-2 (15 min)	Effluent-PCR-2	55	0.05	0.026	0.02
400	**Influent**	**1760**	**1.52**	**4.87**	**13.01**
PCR-1 (24 h)	Effluent-PCR-1	664	0.55	0.86	2.07
PCR-2 (15 min)	Effluent-PCR-2	104	0.09	0.04	0.02
800	**Influent**	**3730**	**3.09**	**9.92**	**26.3**
PCR-1 (24 h)	Effluent-PCR-1	1340	2.40	3.60	5.50
PCR-2 (15 min)	Effluent-PCR-2	134	0.11	0.05	0.04

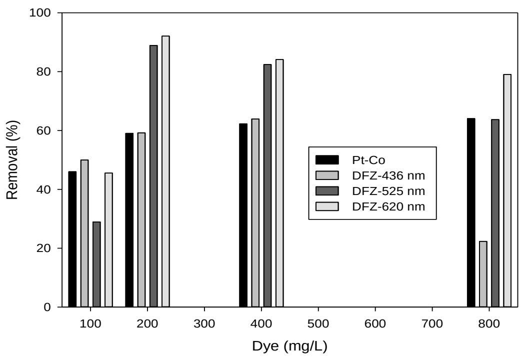

Figure 4. Color removal efficiency of PCR-1 (full aerobic biological system)

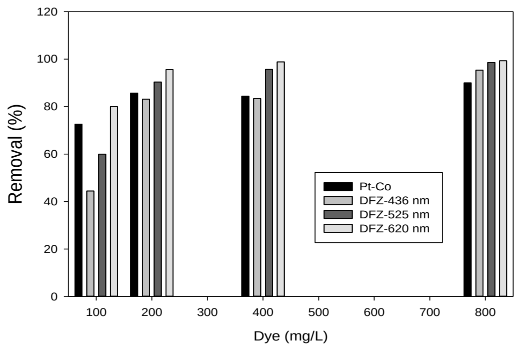

Figure 5. Color removal efficiency of PCR-2 (physicochemical system)

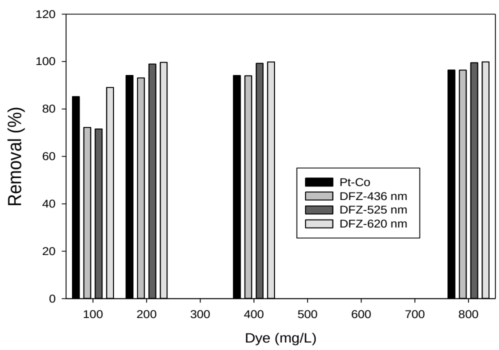

Figure 6. Color removal efficiency of the system (biological+physicochemical system)

4. Conclusions

In the present study, two biological/chemical sequencing up-flow submerged biofilm reactors packed with scoria and ash/lime mixture were used for treatment of simulated colored textile wastewater. It was indicated that scoria with porous structure was found to be suitable packing materials for biofilm formation and also microorganism propagation within the biofilter. In addition, scoria did not show any clogging problem in the experimental period because of its high porous structure, and it could be used repeatedly. If there is any clogging problem when this system is used in the pilot scale, there will be no problem in filling the reactor with a new bed because it has a same material with equal particle size. In addition, cleaning of the column could be made with backwashing. Ash/lime mixture was also other suitable packed material for phosphate and color removal from the system by adsorption and chemical reaction. It is concluded that up-flow sequencing packed bed biological-chemical column reactors can be effectively used in the treatment of textile wastewater for the removal of color, organics and nutrients (especially phosphates). Finally, the PCRs that have both of biological and chemical processes seems to be an efficient method for producing wastewater in direct dischargeable or reusable quality from textile industry. When analyzing the results in terms of nutrient removal efficiency, it was found that system reached high nutrient removal efficiencies at minimum HRT value of 2 h.

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