Removal of Direct red 12B Dye in an Integrated Fixed Film Activated Sludge Reactor (IFAS): Performance Evaluation and Kinetics Study

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Received: 24 Feb. 2017, Revised: 25 June 2017, Accepted: 07 July 2017

ABSTRACT

The application of biological treatment has been promising in recent years for the main advantage of biological treatment in COD and dye removal. The novelty of this study is capabilities of integrated fixed film system (IFAS) with a different arrangement of media to removal the dye and COD. The experiments were done with a survey of variables like SRT, MLSS/MLVSS, the initial concentration of dye and COD. In order to analyze data was used the first and second-order models. The result showed that the IFAS was effective even at high concentration of the dye (200mg L^{-1}). COD reduction and dye removal efficiency were higher than 70% and 88-95%, respectively. For the biological treatment, an increase in SRT to 48hr. increased the dye and COD concentration reduction. Kinetics of COD reduction and dye removal was fitted with the second-order reaction by coefficient correlation of 0.95 and 0.97, respectively. Finally, the integration of fixed film media into the biological reactors affected performances of the system for decolorization from colored wastewater.

Key words: Decolorization, Fixed-Film, Activated Sludge, Dye, Kinetic

INTRODUCTION

Direct Red 12B (Direct red 31) is known to be a carcinogenic and mutagenic that can highly harmful to the environment [1], so the presence of low dyes concentrations in water bodies, cause to unpleasant landscapes and indisputable as well as associated to problems like light penetration reduction and photosynthesis [2]. Accordingly to the annual statistics, more than 0.7 million tons dye is used in the world which is released from different industrial effluents [3]. Dye-containing effluents because of recalcitrant residues of dyes structure and high concentration are hardly treated by different methods treatment [4]. Therefore, using of methods for removal of dye (Direct Red 12B) before discharge in the environment is inevitable [5]. Several methods like: physicochemical techniques, membrane adsorption, Electrocoagulation and etc. have been used for the removal of dye. The mentions methods are difficult, expensive and produce large sludge or toxic substances as well as fouling of the membrane [6]. With respect to other techniques, microbial biodegradation of dye is taken into consideration, recently [7]. Due to environmental implications, microbial biodegradation as ecofriendly technique with operation easy and cost-effective have been widely used in water and wastewater treatment [8]. Dye removal from wastewater by conventional methods such as activated sludge treatment because of toxicity to microorganisms due to commercial dyes is not used. Indeed, the application of IFAS has become known and taken a place as one of the most effective techniques for the removal of different effluents containing organic and inorganic matter [9]. Other methods for example adsorption due to exceeded the discharge standards concerning the quality of the textile effluent treated is limited. In order to overcome problems such as bulking, reduction in COD removal and poor sedimentation of suspended solids has been carried different configurations. So, among different activated sludge configuration, integrated fixed film activated sludge (IFAS) system because of the co-existence of suspended and attached sludge in reactor is noteworthy [2]. This possibility as an attractive option allows to diverse solids retention times and higher biomass concentration for increasing volumetric treatment capacity [10]. The dye removal by IFAS is of interest because it allows a biofilm production, reduction of carbon and resistance to organic and hydraulic shock loads that result to improving the removal effectiveness [11]. The importance of this issue to the extent that Gu *et al.* reported regard to municipal wastewater treatment which is dependent on the COD input concentration[9]. The main purpose of this study is removal of color of textile Direct Red 12B dye and COD by different configuration of integrated fixed film activated sludge (IFAS) system, arrangement of media and evaluation of factors affected on removal efficiency by biological process.

MATERIALS AND METHODS

Materials and reagents

For experiments, Direct Red 12B (DR12B - C32H21N5Na2O8S2) with 98% purity – (ALVAN SABET) was used to prepare the stock solution, with the DR12B chemical structure shown in Fig. 1. Other materials and reagents were ordered from Merck Company, Germany and used as received.

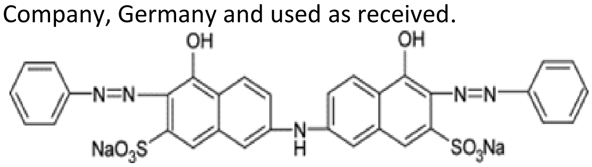

Fig. 1: Anionic direct Red 12B chemical structure. (Molecular Weight: 713.65 gr mol^{-1}, Solubility: 45 g L^{-1} in 80 0C and Maximum Wavelength=523 nm)

IFAS Design

IFAS reactor was made of Plexiglas, with dimensions of 51.7 (height), 47.1 (length) and 31 (width) cm and volume of 0.0784m^3. The reactor included three parts; down-flow aerobic part, up-flow aerobic part (volume of the IFAS is 0.061 m^3) and sedimentation tank (volume of 0.03m^3). Specifications of the reactor are shown in Fig. 2. The support material used for immobilization of the biomass consists of pieces of P.V.C (number of 21, ENEXIO water technologies GmbH, Germany) that was placed in the reactor with media to 30% of the working volume. The media in the reactor was arranged in 2 rows of 10. Also, height, length, and width of each media were 12.5, 28 and 20.75, respectively with total volume of 6100.5cm^3. Specific surface area of the media was 81.34 m^2 m^{-3} to support beds with many holes for higher biomass accumulation and enhancement of them [2].

Design of experiments

Activated sludge flows were inoculated from a sewage treatment plant situated in West Town, Tehran. Synthetic wastewater was fed to the reactor with the composition: Sucrose ($C_{12}H_{22}O_{11}$-600mgL^{-1}) as the carbon source with COD of 530 ± 0.89mg L^{-1}, NH_4Cl as the nitrogen source and $NaH_2PO_4.2H_2O$ as the phosphorus sources. Trace elements for addition into the feeding solution was provided following: 1ml L^{-1} of a stock solution (Ethylene diamine tetra acetic acid (EDTA) [10ml L^{-1}], $ZnSO_4.7H_2O$ [2.3ml L^{-1}], $MgSO_4$ [60ml L^{-1}], $CoCl_2.6H_2O$ [3.2ml L^{-1}], $MnCl_2.4H_2O$ [1.04ml L^{-1}], $CuSO_4.5H_2O$ [0.25mlL^{-1}], $(NH_4)6Mo_7O_{24}\cdot4H_2O$ [2.4mlL^{-1}], $CaCl_2.2H_2O$ [1.2ml L^{-1}], $FeSO_4.7H_2O$ [1.02 ml L^{-1}], H_3BO_3 [0.33ml L^{-1}] and $NiSO_4.6H_2O_{10}$ ml L^{-1}). For the operation of IFAS system, influent wastewater primary from feed tank was pumped with the flow rate of 0.12m^3 d^{-1} in the reactor. The reactors were aerated at room temperature during the whole experiment, in order to avoid microbial growth. pH in the reactor was monitored daily to ensure between 6 and 8. Experiments were performed with controllable factors namely the initial concentration of dye (C0), hydraulic retention time (HRT) and solid retention time (SRT). The levels of factors have been adjusted based on dye concentration (0.1, 1, 5, 10, 25, 50, 100, 150 and 200mg L^{-1}), HRT (6, 8, and 10 hours) and SRT (24, 48 and 72 hours) and responses were dye removal, COD reduction, and pH variations. In the first phase of the study, the reactor was operated with a suspended biomass solids retention time of 7 days. After approximately 3 months of steady state operation by adjusting the amount of sludge wasted daily, the suspended phase SRT was changed to 24hr. for the second phase of the study. After acclimation for the second phase, the desired concentration of DR12B solution from stock solution by successive dilutions was prepared.

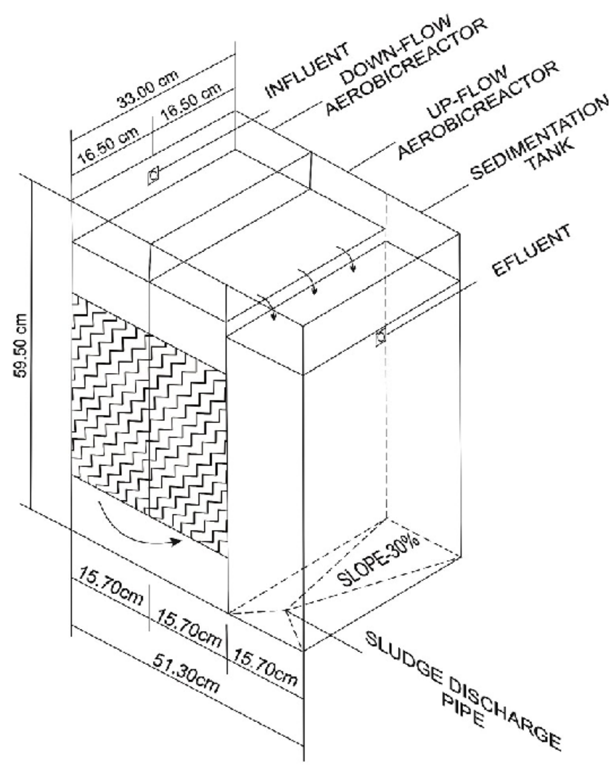

Fig. 2: Schematic diagrams of the IFAS system

Analytical methods

MLSS/VSS measured in accordance with methods 4318E and 5220B in standard methods for water and wastewater examination [12]. Dye removal and COD reduction were measured in accordance 4318E and

5220B method with a spectrophotometer (HACH DR 5000™ UV-Vis Spectrophotometer). Determination of dye concentration was based on the Lambert-Beer law, so that by the calibration curve, i.e. the graph of a solution of a known in λ=582 nm versus absorbance by spectrophotometer [9].

RESULTS AND DISCUSSION

The whole experimental period based on process performance of IFAS system was divided into two periods (acclimation and operation stability of reactor periods).

Acclimation period

The acclimation of the reactors was subjected to the growth and adaptation of the microbial community, and the effects of the IFAS process on the COD removal were examined. Acclimation of bacteria using organic carbon source (sucrose) was performed in this study. To start up, the reactors with $4gL^{-1}$ MLSS and $3.3gL^{-1}$ MLVSS were inoculated, which by return-back biomass or take-out sludge were maintained for achieving an SRT = 24 days. Adequate time was provided to the bacteria community for the removal of input COD and adaptation, at the first stage of experimental works [13]. COD utilization trends with mean of 530 ± 0.89 mg L^{-1} was observed as shown in Fig. 3. Fig. 3 also indicate the results of the MLSS/MLVSS ratios variation during acclimation period, in which the bacteria used COD preferentially. Sufficient time resulted in increased MLVSS rate of approximately 10000mg L^{-1}. The results demonstrate that COD removal from 13% by correct operation improved the performance of the IFAS, and high removal efficiency occurred with time to 93.5% in steady state mode. These results regard to biomass rate in IFAS reactor were corresponded with other research [14, 15].

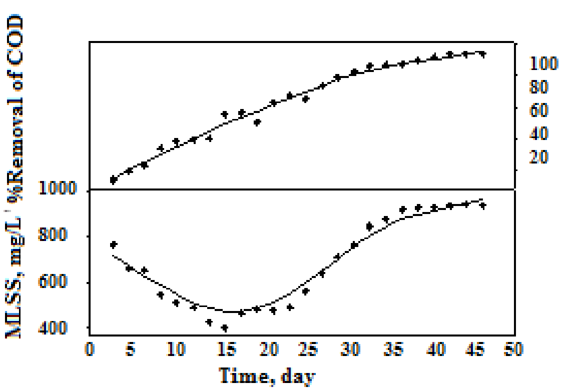

Fig. 3: COD reduction and MLSS variation versus time during acclimation of IFAS system

Operation stability of reactor

Removal efficiency of COD and dye in IFSA system

Biomass re-distributions in the IFAS lead to biomass growth in the reactor. Indeed, IFAS reactor affected both the concentrations and amounts of biomass in the reactor and the total amounts of biomass maintained in the system. Integration of fixed film media in the IFAS system increased biomass maintained in the system. The COD and dye concentrations in the reactor, including its removal efficiencies observed at steady state during the experimental phases, are shown in Fig. 4. The results show that the experimental operating conditions had appropriate effect on the stimulation COD and dye removal efficiencies, and high effects on the dye removal efficiencies. The total system dye removal efficiencies were approximately 88% when they were operated at 48hr MCRT, regardless of influent flow split and IFAS media installation. The COD removal decreased in the system when the mean cellular retention time (MCRT) was decreased to 24hr, i.e. to about 82% in SRT 72hr., 88% in SRT 48hr., and 62% in SRT 24 hr. Dye removals improved slightly when the system was operated at the much higher SRT, but less than expected. As shown in Fig. 4, after the retention time was increased from 24hr. to 48hr. in the reactor, average removal of dye and COD significantly increased in IFAS system ($p<0.04$). So that, The dye removal for initial dye concentrations of 0.1, 25 and $200mgL^{-1}$, where the formation of intermediates in the SRT of 24hr. results to lower dye removal percentage (Fig. 4-A). However, with a longer SRT there is a greater reduction in the COD and dye concentration through biological treatment. It was obtained concerning the dye removal for longer SRTs (48hr. rather than 72hr. for COD of 800mg L^{-1} and dye concentration of 50mg L^{-1}); effluent COD concentration was lower than $100mgL^{-1}$, while for a shorter SRTs concentrations reached to $300mgL^{-1}$. It can be verified that SRT rising to 48hr. can increases the dye removal efficiency, and in higher SRT (e.g.72hr.) because of microorganisms entry to decay phase, dye removal efficiencies decreases. These increases in removal efficiency were consistent with increases in biomass content production after the retention time change (Fig. 4). Increases in biomass content with the time change (SRT) were significant for the system ($p<0.04$), similar to the trends in biomass content. Increasing biomass content with increasing SRT is expected; because of lower SRTs are correlated lower reactor biomass concentrations, since the loading of influent dye for removal was unchanged and existence fixed film in the reactor as warp and woof taken for maintain and increase biomass concentration (Fig. 4). Malovanyy *et al.* (2015) reveals that IFAS installation could improve wastewater treatment caused by the fact that it allows for a short SRT in the suspended growth, which favors for biomass accumulation [16]. While dye concentration in the reactor increased after the SRT was decreased, effluent COD concentrations increased, (Fig. 4). This may have been caused by this fact that a greater capacity to withstand the presence of more toxic materials than the former. Increases in dye concentration; that is, approaching maximum COD rate in reactor may have limited dye removal percentage, which could have deteriorated IFAS performance.

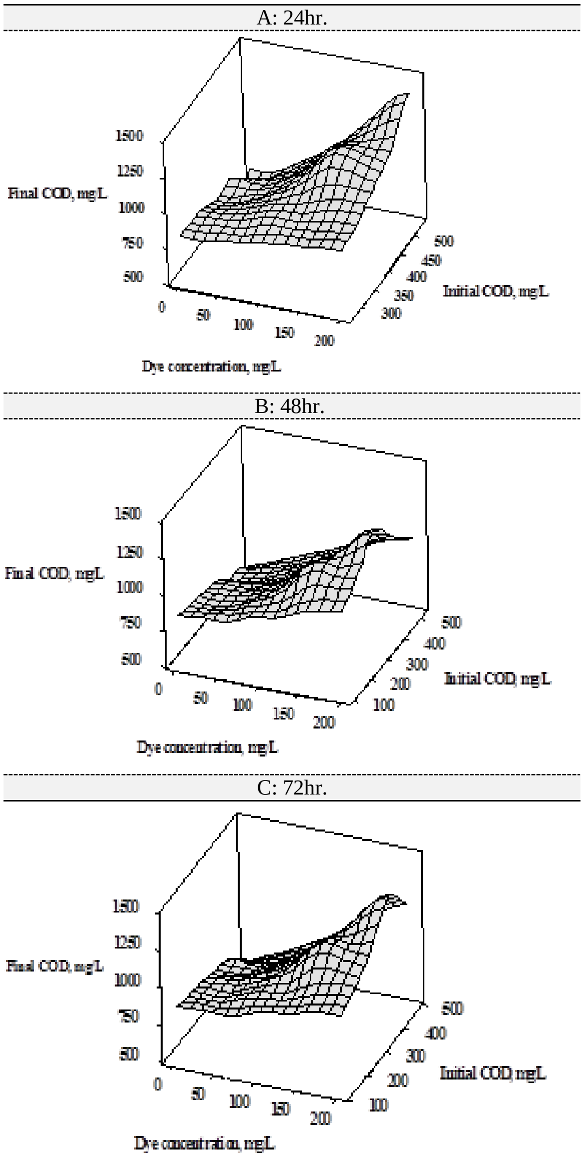

Fig. 4: Surface plot of remaining COD and final dye in different concentrations (A: 24hr., B: 48hr. and C: 72hr.)

This performance in IFAS systems was also reported by Sriwiriyarat, who evaluated the performance of IFAS systems at high mean cell residence time and low temperature [17]. Also, the result sets at the 72hr and 24hr SRTs indicated a more or less continuous linear relationship between MLSS/MLVSS and density (Fig. 5), as well as the MLSS/MLVSS rate versus relationships at these SRTS, were nearly parallel.

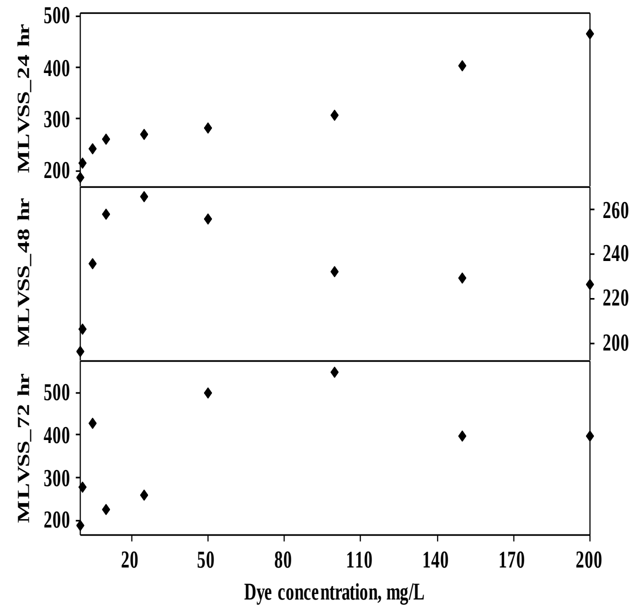

Fig. 5: Matrix Plot of MLVSS variations in different SRT and dye concentration

Changes in MLVSS variations with the SRT increase dominated effects on MLVSS density, while changes in MLVSS resulting to other SRT-influenced factors, like VSS endogenous decay, had less of an effect on MLVSS rate. This may be attributed to the fact that the effects of IFAS on settling biomass that several authors have yielded mixed results Stricker *et al.* (2007); Sriwiriyar *et al.* (2008); Sriwiriyarat *et al.* (2005) [18-20]. On the contrary, increase in SVI value in this system is small but significant. Furthermore, previous studies have mentioned that change in the SRT in IFAS system can be approximately reduced solids loading rate to the secondary clarifiers of about 33% [21]. Indeed, any improvements in dye removal may have been counteracted due to the lower density of the biomass in the IFAS. Regardless, the maximum removal rate of dye and COD were between 88-95% and 72%, respectively. So, by analyzing data obtained in the IFAS systems, removal percentage of dye was good in all samples in this study.

Kinetics study of direct red 12Band COD removal

The behavior of the IFAS system was modeled by the two models namely first order and second order kinetic equation [22]. The constants value (K_1 and K_2) corresponding Direct Red 12 B removal is given in Table 1. From the results, it was observed that the dye removal better fitted to second-order kinetic model by R^2=0.95. This indicates that Direct Red 12 B removal is controlled by co-metabolic reactions. So that in a co-metabolic reaction, a compound transforms by microorganism enzymatically which it cannot utilize as an energy source or of one of the constituent elements in the substrates. The same behavior for dye removal was reported by McKay *et al.* and Huwang [23, 24]. In addition, Table 1 demonstrates that K_2 (13.7) is high for dye removal in an IFAS reactor. In other hands, regarding COD removal by IFAS system, data fitted to a second-orderkinetic model (R^2=0.97) as well as the corresponding constants tabulated in Table 1. The results indicated that the metabolic reactions corresponded for COD removal with the highest COD removal, K=2.1. Increases in COD constants relate to increasing MLSS concentration due to presences of fixed film in the reactor and arrangement of them toward SRT. Based on the above results, SRT equal 48hr was suitable option to achieve the highest efficiency in COD and dye removal.

Table 1: Kinetic models (First and second order equations)

	Constants			
	First-Order		Second- Order	
	K_1 (h^{-1})	R^2	K_2 (L $mg^{-1}.h^{-1}$)	R^2
Decolorization	0.15	0.67	13.7	0.95
COD removal	0.66	0.54	2.1	0.97

The results show that the higher rate constants, k_2, for the decolorization rate could be explained the fact that relatively short-term SRT contact of mixed bacterial culture during the experiment period, indicate that the raising reaction of the DR 12B as catalyzed intracellular process by enzymes produced in the bacterial community. Also the high concentration of COD is unlikely to optimize reduction and so lead to the reduction K_1 for COD removal.

CONCLUSION

Treatment of colored wastewater in an integrated fixed-film activated sludge reactor (IFAS)using different bacterial community was an economic and suitable process that is capable of removing a high percentage of COD (higher than 70%) and color between 88-95%. IFAS with a biofilm leads to increases in biomass content, because of correlated higher reactor biomass concentrations, since existence fixed film in the reactor as warp and woof took for maintaining and increase biomass concentration maintains because of preventing biomass washing. Although biological treatment was as curtained as a suitable process for decolonization, it is also necessary to combine methods for enhanced COD reduction and dye removal from wastewater containing Direct Red 12B. This work suggests that inhibitors' factors system should be taken into consideration for performance evaluation of IFAS system. Also, the analysis of toxicity for determination compounds in effluent should be the subject of future study.

ETHICAL ISSUES

The ethical issues were considered during the conduct of this study.

CONFLICT OF INTEREST

We affirm that this article is the original work of the authors and have no conflict of interest to declare.

AUTHORS' CONTRIBUTION

All authors participated in all stages of the research.

FUNDING/ SUPPORTS

The authors would like to thank the facility supported by Islamic Azad University, Science and Research Branch.

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