Kinetics of Detoxification and Mineralization of Mono Azo Dyes in a Up-flow Anaerobic Fixed Film Reactors

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The study investigates the anaerobic treatability of azo dyes, namely, Remazol Red (RR), Remazol Blue (RB) and Golden Yellow (GY) in a three identical bench scale up-flow anaerobic fixed film reactors (UFAFF) R1, R2 and R3 followed by a semi-continuous aerobic activated sludge system. The effect of hydraulic retention time (HRT) on decolorization and degradation have been compared for three azo dyes. The kinetic studies have shown that the reactors can be operated at 2.59 – 8.3 kg m^{-3} d^{-1} COD for RR with removal of 65.72 – 76.00 % COD, 4.60 – 6.84 kg m^{-3} d^{-1} COD for RB with 74 – 87.11 % COD removal, 1.89 – 9.72 kg m^{-3} d^{-1} COD for GY with 56 – 79.6 % COD removal. HRT, as varied from 0.150 – 0.452 days for all the dyes and decolorization and degradation, are decreasing in fraction of HRT. COD removal for all the three azo dyes showed that a correlation coefficients of loadings are 0.9891, 0.7154 and 0.8652 for RR, RB, GY, respectively. But decolorization of azo dyes do not followed any correlation with loading.

Key words:
Azo dyes, decolorization, COD removal, loading rate, hydraulic retention time

Introduction

Reactive dyes are becoming more and more popular in the dying and textile industries. The textile industry accounts for two third of the total dye stuff market,[1] consuming a large reactive azo dyes, due to high demands of cotton fabrics with brilliant colors.[2] The reactive dyes are colored compounds capable of forming a covalent bond between the dye molecules and the fibers. However, they hydrolyze easily resulting in a high portion of unfixed dyes, which have to be washed off during the dyeing process. During production and usage of dyes an estimated amount of 10–15 % is released into environment mainly via wastewater.[3] Color is considered to be the first contaminant in textile wastewater and has to be removed before discharging into the receiving water body. The decolorization of textile wastewater is still a major environmental concern, because of the dyestuff is a kind of refractory organic matter, as they contain substituent nitro and /or sulpho group.[4] As a result, dye containing wastewater if not treated efficiently before discharge, have always been creating aesthetic problem to the environment, especially in developing countries. There is an urgent need of economical and effective biological treatment system. The traditional aerobic wastewater treatment systems do not substantially decrease the coloration of the wastewater.[5,6] The effectiveness of anaerobic decolorization has been reported in the literature.[7] Dye decolorization either by anaerobic or facultative microorganisms under anaerobic condition starts by reductive cleavage of the azo bond, with the formation of aromatic amines.[7,8] The initial step in the biodegradation of azo dyes is the reduction of the azo linkage, which results in the decolorization of the compound. It was also observed that the most of the bond reduction occurred during active bacterial growth.[7] Azo reduction is a ubiquitous process under anaerobic conditions if cosubstrate is present to donate electron.[5,6,9,10,11]

Fixed film treatment has shown to be more amenable to the removal of xenobiotics than suspended growth systems. Aerobic biofilm has a number of potential advantages for the treatment of xenobiotics in general, and azo dyes in particular. They offer the higher solid retention time necessary to prevent washout of adopted organisms and the film also provides a diffusion barrier against high inhibitory concentration of contaminants. In addition, they can provide, both, anaerobic and aerobic zones, which facilitates complete mineralization of the dyes.[11] *Luangdilok* and *Panswad*[12] investigated the color and COD removal efficiency by using anaerobic/aerobic SBR reactor for treatment of anthraquinone and diazo dyes. Total of 90 % COD and 45 % color removal efficiencies were obtained while acetic acid and glucose were used as carbon

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source. In order to investigate the anaerobic decolorization capability by UFAFF, three identical reactors treating dyes Remazol Red (RR), Remazol Blue (RB), Golden Yellow (GY), respectively, were studied. The efficiency in decolorization, COD removal of each dye was monitored and the decolorized effluents of UFAFF was fed to the aerobic activated sludge treatment.

Materials and methods

Experiment

A bench scale up-flow fixed bed anaerobic (UFAFF) reactors (R1, R2 and R3), with the dimensional details as per Table 1, were used for treatment of dyes Remazol Red (RR), Remazol Blue (RB), Golden Yellow (GY), respectively, and structures of which are given in Figure 1. The schematic of UFAFF reactor is given in Figure 2. The out let of reactor was connected to U tube for gas and liquid separation. The reactors were made in glass and maintained at room temperature (30 °C). Insulated beads of 2.5 mm diameter were used as immobilization support matrix as they are inert in nature. The packed column reactors were operated in a batch mode with a residence time of 24 h. Microorganisms were immobilized on the matrix by circulating treated sewage along with dyes (50 mg l^{-1}) with hydraulic retention times (HRT) of 0.405, 0.387 and 0.470 h for RR, RB and GY, respectively.

Table 1 – *Dimensional details of the reactors*

Dimensions of the reactor	Reactor 1	Reactor 2	Reactor 3
length, cm	49	47	49
radius, cm	2.3	2.35	2.3
void volume, ml	270	250	200
diameter of beads, mm	2	2	2
dye fed	remazol red	remazol blue	golden yellow

Basal Medium

The basal salt medium used in all batch experiments is formulated by *Tan* et al.[13] and contained (mg l^{-1}), $NaHCO_3$, 5000; NH_4Cl, 280; $CaCl_2$. $2H_2O$,10; K_2HPO_4,250; $MgSO_4$ $7H_2O$, 100; Yeast extract, 200; Trace element, 1ml l^{-1} along with glucose (100 mg l^{-1}).

Analysis

Color measurements in clarified samples of effluents from UFAFF reactors were performed in UV-visible spectrophotometer (Schimadzu 160A). Absorption of the samples was measured at the maximum (λ_{max}) wavelength 525 nm for RR, 580 nm for RB and 400 nm for GY. pH, Chemical Oxygen Demand (COD) and ammonia were determined according to Standard Methods.[14]

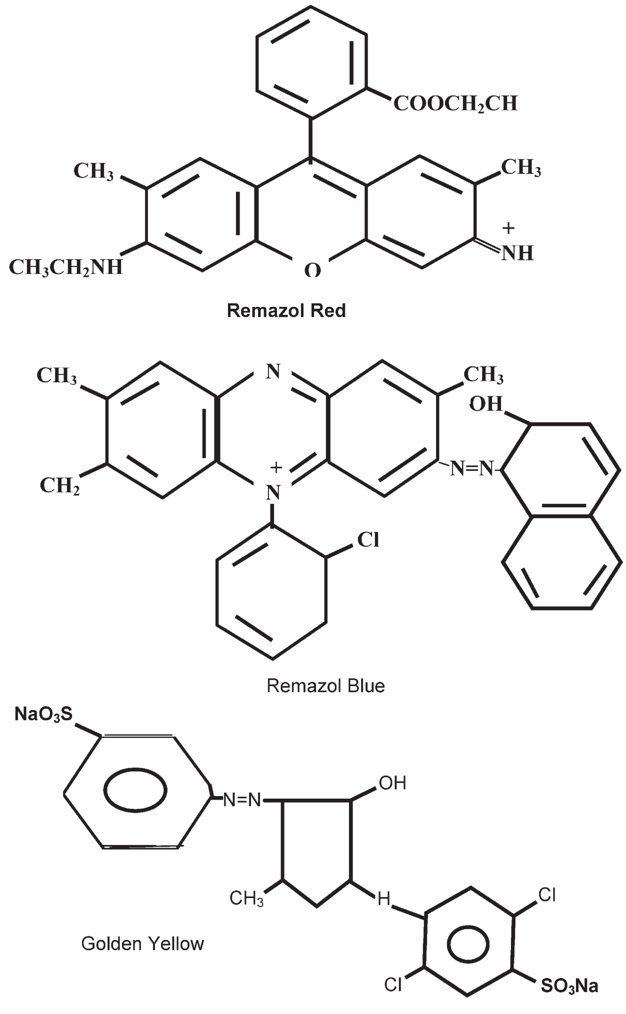

Fig. 1 – *Structure of azo dyes*

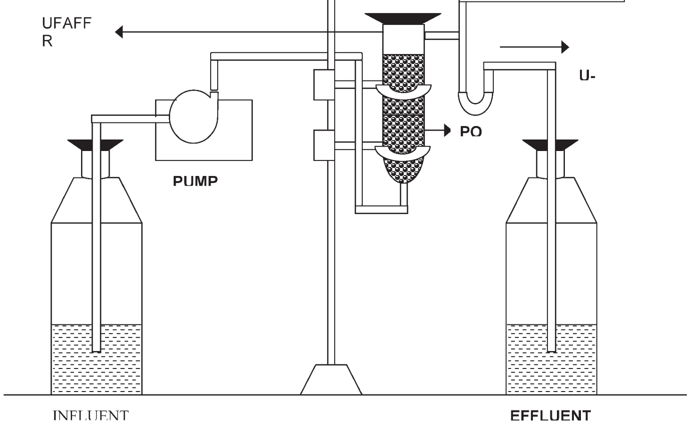

Fig. 2 – *Schematic diagram of UFAFF reactor*

Results and discussion

Operation of the packed bed reactors

Each bioreactor was operated as independent unit and was immobilized with bacterial cells. Each reactor was initially operated in batch mode with complete recycle till a bacterial fixed film was formed on support media. Once a static decolorization was achieved, the operation was changed to a continuous mode for about 110 days.

It appears, that, both the adsorption of dyes on the anaerobic sludge and degradation of dyes by microorganisms contribute to the removal of dyes from the synthetic wastewater. In a continuous flow system, adsorption may reach equilibrium in about 10 days. If no degradation occurs, the color removal rate will decrease along with the decrease of the adsorption capacity. Therefore, the high initial removal rates are mainly due to adsorption of dye to the sludge. After the adsorption equilibrium is reached, the study state color removal must have contributed through biological degradation.

The bioreactors were operated at different hydraulic retention time by varying flow rates stepwise during the experiments. At each flow rate, steady state was usually achieved within 72 h after the change of HRT, indicating easy adaptation to higher concentration. The performance efficiency for UFAFF reactors were evaluated at steady state conditions and the results are presented in Table 2, 3 and 4 for RR, RB and GY, respectively. The UFAFF reactor treating RR, had a maximum decolorization of 81.33 at 0.243 days HRT with 64.88 % for COD removal. RB had 93.66 % of decolorization at 0.348 days HRT with 82.76 % of COD removal. In case of GY, 84.17 % of decolorization at 0.411 days HRT with 74.38 % for COD removal, was observed. The efficiency of decolorization for RR was increasing with increase in loading of dye and maximum (81.33 %) was obtained at 2.019 kg m^{-3} d^{-1} COD loading. The efficiency of decolorization and COD removal for RB was decreasing with increase in loading of dye. In case of GY efficiency of decolorization increase with increase in substrate concentration up to 8.99

T a b l e 2 – *Decolorization and biodegradation of Remazol Red in UFAFF reactor*

Mean flow rate, Q / l d^{-1}	HRT t_{HRT} / d	Loading, COD Γ_{COD} / kg m^{-3} d^{-1}	γ_{COD} / mg l^{-1}			Decolorization, %	Final pH
			influent	effluent	removal, %		
1.162	0.384	2.74	673.93	234.30	68.19	73.0	7.8
2.019	0.243	7.61	1018.13	356.85	64.88	81.33	7.5
2.878	0.170	12.90	891.50	359.18	59.66	72.33	7.6

T a b l e 3 – *Decolorization and biodegradation of Remazol Blue in UFAFF reactor*

Mean flow rate, Q / l d^{-1}	HRT t_{HRT} / d	Loading, Γ_{COD} / kg m^{-3} d^{-1}	γ_{COD} / mg l^{-1}			Decolorization, %	Final pH
			influent	effluent	removal, %		
1.245	0.348	4.886	983.53	168.99	82.76	93.66	7.8
1.756	0.256	5.846	833.18	150.67	81.91	86.33	7.5
2.065	0.204	6.410	756.96	183.86	75.66	87.66	7.6

T a b l e 4 – *Decolorization and biodegradation of Golden Yellow in UFAFF reactor*

Mean flow rate, Q / l d^{-1}	HRT t_{HRT} / d	Loading COD Γ_{COD} / kg m^{-3} d^{-1}	γ_{COD} mg l^{-1}			Decolorization, %	Final pH
			influent	effluent	removal, %		
0.986	0.411	2.113	429.27	112.58	74.38	84.17	7.8
1.840	0.227	8.991	977.61	381.235	61.37	84.00	7.5
2.711	0.152	8.526	849.90	379.76	55.33	83.33	7.6

kg m^{-3} d^{-1} COD. But COD removal was reduced with increase in concentration. It could be observed that color removal did not correlate with COD removal. The decolorization and COD removal efficiencies for all the three reactors have also been plotted against the loading rate in Figure 3. Removal rate was maximum at lower loading rates for all the three dyes. But decolorization did not followed any correlation with loading as given in Figure 3. It seems that reducing environment prevailing in the bioreactor might have caused color removal. This is in agreement with the observation made by *Beydilli* et al.,[15] where reduction of dye took place under low redox condition. *Zee* et al.[16] have reported that longer HRT are required for decolorization of azo dyes, since the rate of decolorization are slow. *O Neill* et al.[17] demonstrated 68 and 86 % color and COD removal efficiencies respectively, in a up flow anaerobic sludge blanket / activated sludge sequential reactor system treating reactive azo dyes.

During the whole operation of the reactors, the variation in COD and decolorization for all the three dyes, with respect to time, are presented in Figure 4 for R1, R2 and R3, respectively. Figure 4

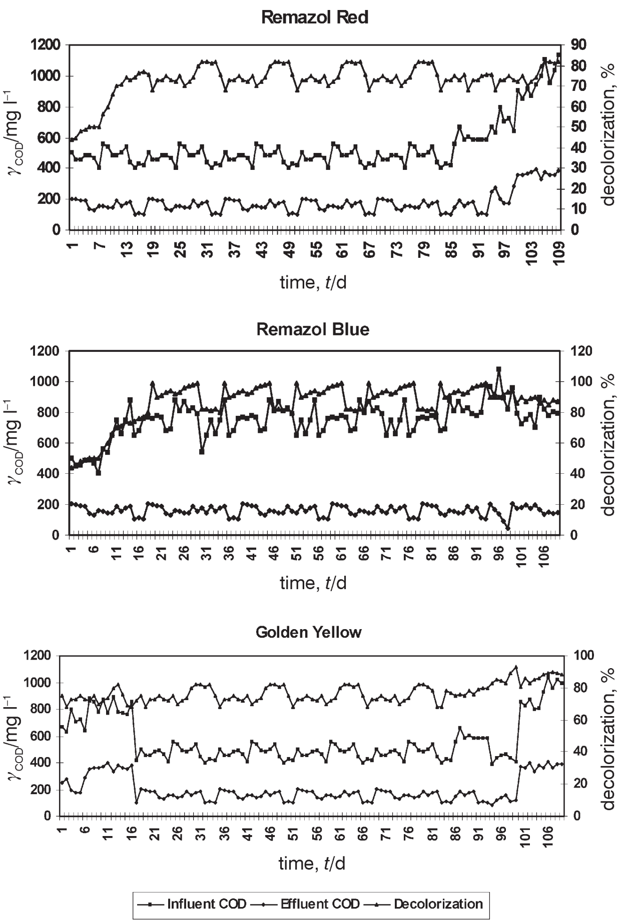

Fig. 3 – *Decolorization and biodegradation efficiency for azo dyes at various loadings*

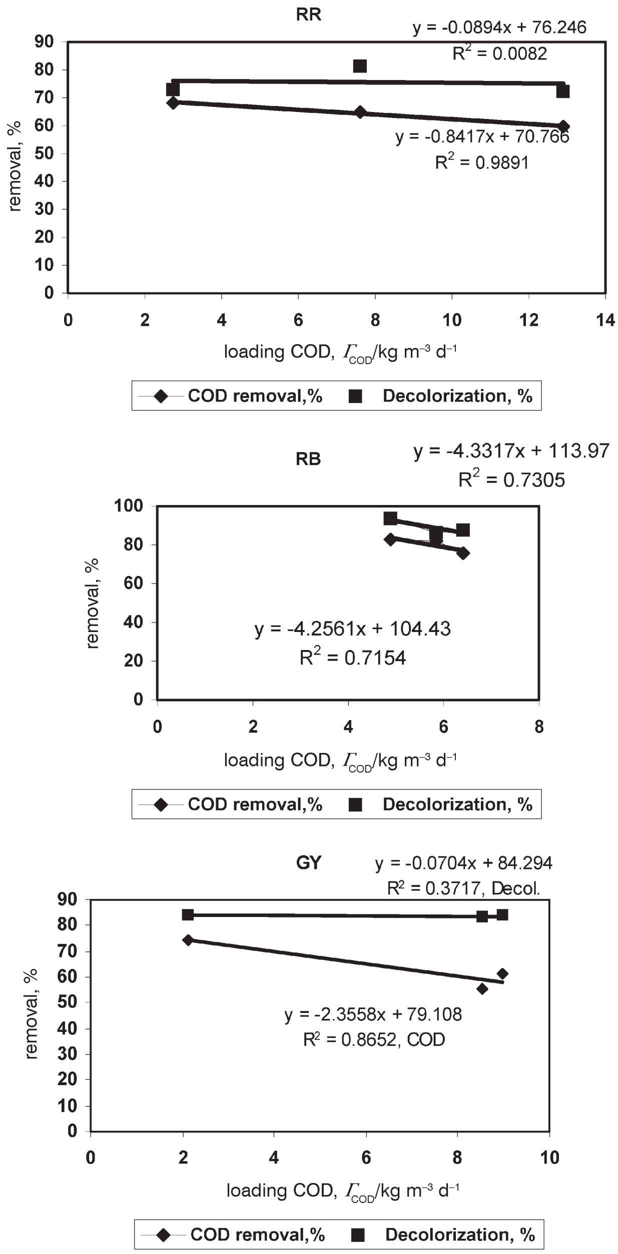

Fig. 4 – *Performance evaluation of R1, R2 and R3 reactors*

illustrates that the reactors have relatively stable effluent quality. COD content of effluents were 150 to 400 mg l^{-1} for RR, 50 to 200 mg l^{-1} for RB and 50 to 300 mg l^{-1} for GY, respectively. COD and decolorization rates increase gradually and then remain at steady state indicating acclimation of the microorganisms. *Shaul* et at.[18] reported that 15 out of 18 azo dyes passed through the activated sludge system substantially untreated even after 80 days of acclimation. The different dyes degradation efficiencies seem to be greatly influenced by molecular structure of the dye. *Oxspring* et al.[19] achieved more than 95 % color removal with Remazol Black B after 48 h retention time in an upflow anaerobic film reactor of 1.25 l total volume with initial dye mass concentration of 500 mg l^{-1}.

Performance of aerobic activated sludge reactor

The effluents from all the three reactors after decolorization were fed to aerobic activated sludge reactor operated in semi-continuous mode. The reactors R1, R2 and R3 were operated in UFAFF in a continuous way and aerobic phase in combined way in activated sludge reactor, and the COD removal at different loadings is given in Table 5. Anaerobically treated effluents have got very low COD in the range of 235.90 to 475.20 mg l^{-1} and because of which the effluents were treated in activated sludge system. One of the most reasonable explanations for COD removal in anaerobic-aerobic process is that anaerobic process apparently changed the molecular structure of the dyes into different fragments, which are readily degradable under aerobic conditions. *Razo-Florus* et al.[10] suggested that the dyes are degraded anaerobically to amines and which is further removed by means of activated sludge treatment, which is confirmed by increase in COD removal in aerobic activated sludge system.

Table 5 – *Aerobic degradation of combined effluent in an activated sludge system*

Effluent from anaerobic reactors at different dye loading rates Γ / kg m^{-3} d^{-1}	γ_{COD} / mg l^{-1}		
	influent	effluent	reduction, %
50	235.90	130.08	44.85
75	317.50	160.40	49.48
100	475.20	268.50	43.50

The data is an arithmetical average of eight readings

Conclusions

It can be concluded from the present investigation that:

Azo dyes RR, RB and GY were gratuitously decolorized under experimental conditions employed.

In all the three dyes, COD removal did not correlate with color removal, it seems that reducing environment prevailing in the bioreactor might have caused color removal.

The constant COD removal from influent is indicating that microbial activity is responsible for dye decolorization.

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