RUHUNA JOURNAL OF SCIENCE
Vol. 2, September 2007, pp. 96-110
http://www.ruh.ac.lk/rjs/rjs.html
ISSN 1800-279X

Removal Mechanisms of Acid Dyes of Different Chemical Groups under Anaerobic Mixed Culture

S. Wijetunga[1], L. Xiufen, R. Wenquan, J. Chen

[1]Department of Agricultural Engineering, Faculty of Agriculture, University of Ruhuna, Kamburupitita, SRI LANKA.
Laboratory of Environmental Biotechnology, School of Biotechnology, Southern Yangtze University, No 170, Huihe Road, Wuxi 214036, PR China
Correspondence: : [1] swije@ageng.ruh.ac.lk, swije2001@yahoo.com

AbstractS Removal mechanisms of Acid Red 131, Acid Yellow 79 and Acid Blue 204 dyes with different chemical groups under anaerobic process using mixed anaerobic granular sludge were studied. The UV-visible spectrum obtained and dissolved residual chemical oxygen demand measured at the end of incubation suggest that Acid Red 131 and Acid Yellow 79 were biodegraded and no further degradation of dye metabolites have occurred. Acid Red 131 and Acid Yellow 79 were decolourized by biodegradation achieving 81% and 97% of colour removal at 300 mgl-1 dye concentrations, respectively. Acid Red 131 biodegradation followed the first order kinetic model with respect to dye concentration while Acid Yellow 79 biodegradation followed the second order kinetic model. Although over 90% of colour was removed in Acid Blue 204 dye, no biodegradation was noticed. It is clear that different dyes can be decolourized under anaerobic condition even though mechanism of decolourization is not same.

Keywords: acid dyes; anaerobic; biodegradation; decolourization; kinetics; textile wastewater;

1. Introduction

Wastewater generated from various industries creates severe detrimental effects to the environment leading to bio-systems imbalance. The textile industry, which is one of the largest water consumers in the world, produces wastewater composed of various recalcitrant agents such as dye, sizing agents, and dyeing aids, that should be of concern in releasing into the environment. The removal of colour is needed to be considered in the disposal of textile wastewater due to aesthetic deterioration as well as the obstruction of penetration of dissolved oxygen and sunlight into water bodies, which seriously affects aquatic life. Besides, the dye precursors and degradation products are proven carcinogenic and mutagenic in nature (Kalyuzhnyi and Sklyar, 2000). It is estimated that 10-20% of dye produced is lost into wastewater during textile dyeing process (Graça *et al*., 2001).The largest class of dyes used at present is referred to as acid dyes, which are anionic compounds mainly used for dyeing nitrogen containing fabrics like wool, polyamine and silk. Out of 12 classes of different chromogenic groups of dyes, most common group is azo group, which contributes up to 70% of all textile dyes produced, followed by anthraquinone group (Vandevivere *et al*., 1998). Azo dyes, characterized by their typical azo bond (R_1-N=N-R_2), which is responsible for colour, are a more popular dye group used in the textile industry and due to their poor exhaustion properties, as

much as 30% of initial dye applied remain unfixed and end up in effluents (Manu and Sanjeev, 2003). Anthraquinone dye chromophore is characterized by its carbonyl group, and it may be present once or repeated times. The colour of anthraquinone dyes is partially associated with the anthraquinone nucleus and is modified by the type, number, and position of the substitutes. The colour of wastewater decreases when the cleavage of -N=N-, -C=C- bonds and heterocyclic and aromatic rings occurs. Then, absorption of light by the associated molecules shifts from visible to UV or infrared region of the electromagnetic spectrum (Slokar *et al*., 1998).

Even though there are various physical and chemical wastewater treatment methods that can be applied for textile wastewater treatment, the applicability of those methods are limited due to various limitations.

Advanced oxidation process such as Fenton's regent (H_2O_2 and Fe^{2+}), H_2O_2, and Ozonation are costly in terms of operational costs (Stanislaw and Monika, 1999). Coagulation and flocculation with lime, alum, polyelectrolyte, and ferrous salts produce large amount of sludge, which impose handling and disposal problems (Huseyin, 2005; Georgiou *et al*., 2003; Daneshvar *et al*., 2003). The adsorption of dyes using activated carbon and various other absorbents are also costly (Zhemin *et al*., 2001). The photochemical oxidation of dyes using UV and sunlight with oxidation agents like catalyses, H_2O_2 are also not economically viable (Muruganandham and Swaminathan, 2004).

Most of the studies with respect to decolourization of textile wastewater containing dyes have been focused on azo dyes and have shown that they could be effectively decolourized by biological means, such as anaerobic and combined anaerobic/aerobic processes (Frank *et al*., 2001; Manu and Sanjeev, 2003; Méndez-Paz *et al*., 2005; André *et al*., 2004; Georgiou *et al*., 2004; Rui *et al*., 2001; Pearce *et al*., 2003).

The information on decolourization and biodegradation of dyes having different chemical groups under anaerobic process are inadequately reported. Therefore, the objectives of this study were to find removal mechanisms of different acid dyes performed by mixed anaerobic consortia and compare them with respect to each dye, and monitor the inhibition caused to microorganisms by acid dyes widely used in the textile industry. Furthermore, the dye removal kinetics was also evaluated.

2. Materials and methods

2.1 Laboratory Scale Batch Reactors and Inocula

The anaerobic batch reactors, glass vessels of 500 ml capacity having sample ports for withdrawing samples for the analysis of colour and chemical oxygen demand (COD), were used in the study. The reactors were seeded by anaerobic granular sludge obtained from a laboratory scale Upflow Anaerobic Sludge Blanket (UASB) reactor, which had been steadily operated for six months in synthetic wastewater. The total suspended solids (TSS) and the total volatile suspended solid (TVSS) of granules were 104.74 gl^{-1} and 84.90 gl^{-1}, respectively.

2.2 Incubation Medium

The incubation medium was prepared according to Ergüder and co-workers (2003) with minor modifications. The composition of medium consisted of following inorganic compounds (mgl^{-1}): NH_4Cl, 1200; $MgSO_4.7H_2O$, 400; KCl, 400; $CaCl_2.4H_2O$, 50; $(NH)_2HPO_4$, 170; $FeCl_2.4H_2O$, 40; $CoCl_2.6H_2O$, 10; KI, 10; $MnCl_2.4H_2O$, 0.5; $CuCl_2.2H_2O$, 0.5; $ZnCl_2$, 0.5; $AlCl_3.6H_2O$, 0.5; $Na_2MoO_4.2H_2O$, 0.5; H_3PO_3, 0.5; $NiCl_2.6H_2O$, 0.5; $NaWO_4.2H_2O$, 0.5; and Na_2SeO_3, 0.5. The sufficient buffering capacity in reactors was maintained by $NaHCO_3$ 4500 mgl^{-1}. Glucose concentration of 2500 mgl^{-1} as COD was used as the carbon source as well as to provide reducing equivalents required to breakdown the azo bond in the case of azo dyes (Georgiou *et al*., 2004).

2.3 Chemicals Used

All chemicals used in this study were of analytical grade (AR), except for gas chromatography (GC), where GC grade chemicals were used. The dyes; C.I. Acid Red 131 (Telon Red M-3B belongs to azo dye group), C.I Acid Blue 204 (Telon Blue M-RLW belongs to anthraquinone dye group) and C.I Acid Yellow 79 (Telon Yellow M-4GL, of which the chemical group of dye has not been defined) were of commercial grade and used for this study without further purification.

2.4 Experimental Procedure

Four levels of dye concentration of 50, 100, 150 and 300 mgl^{-1} of each dye were studied under anaerobic condition at 37 °C in a dark incubator and a control reactor without dye was also incubated to find out the effect of dye on anaerobic microorganisms. The reactors were seeded with 5.1 g anaerobic granules in TVSS and other macro, micro, buffering agent, and a carbon source was added in aforementioned concentrations. Before keeping in the incubator, headspace of the reactors was flushed with Nitrogen gas for 5 minutes. Abiotic assays using autoclaved biomass were also done in order to determine the dye removal by non-biological processes.

2.5 Analytical Procedure

Total alkalinity, pH, TSS and TVSS were determined according to the procedure outlined in standard methods (APHA, 1985). Chemical oxygen demand was determined spectrometrically by digestion in 5B-1 Quick COD analyzer (The LianHua Environmental Instrument Institute, Langzhou, PR China). Volatile Fatty Acids (VFA) at the end of the incubation were determined by Shimadzu GC-14A gas chromatography with PEG-20M capillary column (SGE International, Australia), 30 m length and internal diameter 0.53 mm. Prior to injection, samples were acidified with 1 M H_2SO_4, centrifuged for 15 minutes at 13000 rpm, and filtered through 0.22 μm filter (Tahar and Sami, 2005). The column temperature was initially set at 100 °C for 1 minute and then increased at a rate of 5 °C per minute up to 240 °C and held for 20 minutes. The injector and detector temperature

were set at 240 °C and 250 °C, respectively. Nitrogen was used as the carrier gas at a flow rate of 1.5 ml min^{-1}. The colour of the samples was measured spectrometrically using the maximum absorbance of each dye by UV-visible spectrometer (Shimadzu UV-2450). The samples were filtered through microfiber filter and centrifuged at 7000 rpm for 10 minutes prior to absorbance measurements. The residual dyes after incubation were quantified by standard curves based on the maximum absorbance of respective dyes. Colour removal was determined according to Eq. (1).

$$\frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

Where A_0 is absorbance at the beginning of incubation and A_t is absorbance at selected time. The values given are the mean values of independent replicates and error bars show standard deviation.

3. Results and Discussion

3.1 Primary Removal Mechanism of C.I. Acid Red 131 by Anaerobic Consortia

The maximum absorbance wavelength and UV-visible spectrum were scanned at the beginning and end of incubation (where more than 90% of colour was removed and no more changes of UV spectrum were observed after this period) to find out whether the colour removal is merely physical adsorption of dyes onto granules or biodegradation by microbial granules. The UV-visible spectrum of C.I. Acid Red 131 (AR131) dye containing medium before and after incubation of 45 hours are shown in Fig.1. The remarkable changes of UV-visible spectra could be seen in the samples obtained after incubation and explained by the structural modifications of the dye molecules performed by anaerobic microorganism. Changes in the spectrum especially in UV region provide the evidences of degradation of dye molecules (Manu and Sanjeev, 2003; Rui *et al*., 2001; Pinheiro *et al*., 2004; Robert and Sanjeev, 2005).

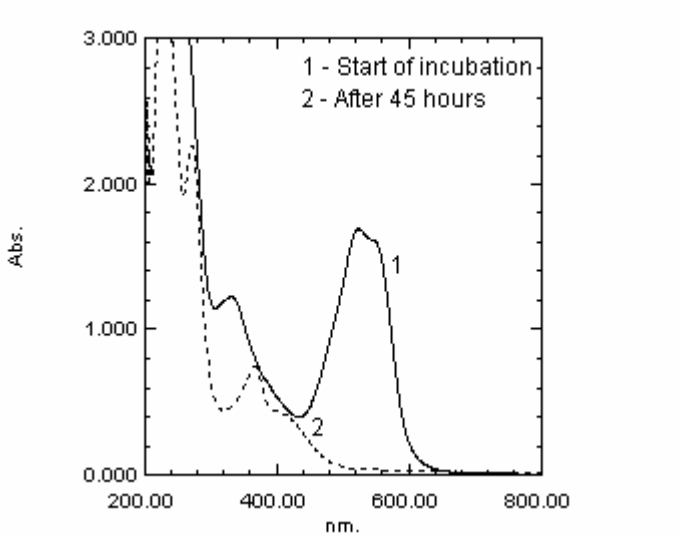

Figure.1 UV-visible spectrum obtained before and after incubation (300mg l-1) AR131

Acid Red 131 showed its maximum absorbance in visible region (400-800 nm) at 548 nm before incubation. However, after incubation for 45 hours, the maximum absorbance peak disappeared and a new peak appeared in UV region at 366 nm, thereby confirming biodegradation of the dye. At the same time, red colour of the dye disappeared and a strong straw colour appeared indicating biodegradation of AR131 after the anaerobic incubation. The previous studies showed that anaerobic digestion of several azo dyes produce relevant amines (or aromatic amines) by cleavage of azo bond (André *et al*., 2004; Georgiou *et al*., 2004). According to Pinheiro and co-workers (2004), the peak resulted at 270 nm after incubation is probably due to aromatic amines produced after biodegradation of AR131 by anaerobic consortia. The emergence of the new colour might be due to partial break down of azo bond or breakdown products. Similar observations have been noted by Frank *et al*. (2001) in their study of Reactive Red 2 and Reactive Red 4, azo dyes, under anaerobic process. The colour of these dyes had been shifted to yellow under anaerobic process.

The aromatic amines produced are not generally mineralized to CO_2 and CH_4 by anaerobic process, with the exceptions of a few aromatic amines characterized by the presence of hydroxyl and or carboxyl groups (Elías *et al*., 1996; Razo-Flores *et al*, 1997). Consequently, AR131 was probably not mineralized and it was confirmed by UV-visible spectra and COD obtained after incubation.

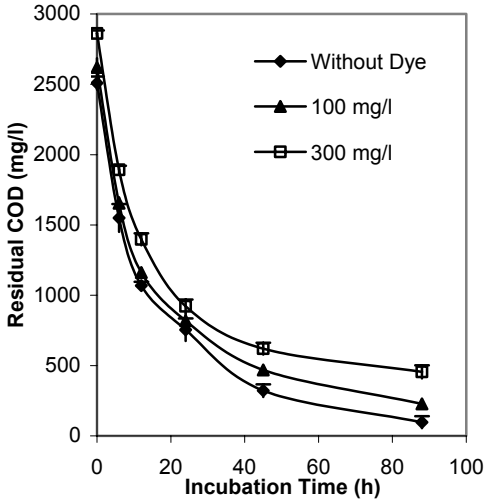

Figure.2 Residual dissolved COD at different AR131 dye concentrations

The residual dissolved COD in the reactors containing AR131 under 0 mgl^{-1}, 100 mgl^{-1} and 300 mgl^{-1} dye concentration with respect to time are shown in Fig. 2. It could be seen that more than 90% of COD was removed in all reactors after 88 hours of incubation, except 300 mgl^{-1} dye concentrations, where ca. 84% COD was removed. It appears that COD removal declined as dye concentration increased. Chemical oxygen demand in controlled reactor was ca. 95 mgl^{-1} while it was 450 mgl^{-1} at 300 mgl^{-1} of dye concentration. This indicates that substrate was degraded faster without AR131 or with its low concentrations. It was also confirmed by substrate removal kinetics. The substrate removal seems to be followed first order kinetics and the first order kinetic constants decreased from 0.0353 h^{-1} in dye free reactor to 0.0193 h^{-1} in reactors supplemented with 300 mgl^{-1} of dye, suggesting a slight inhibition on substrate removal. The dye contribution to feed COD was ca.1200 mg COD per gram of AR131 dye, so the measured residual COD indicates that the dye metabolites seem to contribute same COD as the initial dye. It means that considerable mineralization of dye metabolites have not taken place. Similar observations have reported by Mustafa and Delia (2005) and Méndez-Paz and co-workers (2005) with regard to azo dye degradation under anaerobic conditions.

3.2 Primary Removal Mechanism of C.I. Acid Yellow 79 by Anaerobic Consortia

The maximum absorbance of C.I Acid Yellow 79 (AY79) before incubation was observed at 400 nm, while it disappeared after incubation leading to decolourization (Fig.3). The substantial changes of UV-visible spectrum can be seen after incubation. The new peak at about 336 nm emerged and it might be due to degraded products of AY79. At the same time, it can be concluded that AY79 could be biodegraded under anaerobic condition by mixed anaerobic consortia. No new

colour developments were observed in AY79 containing effluents. The effluents were colourless.

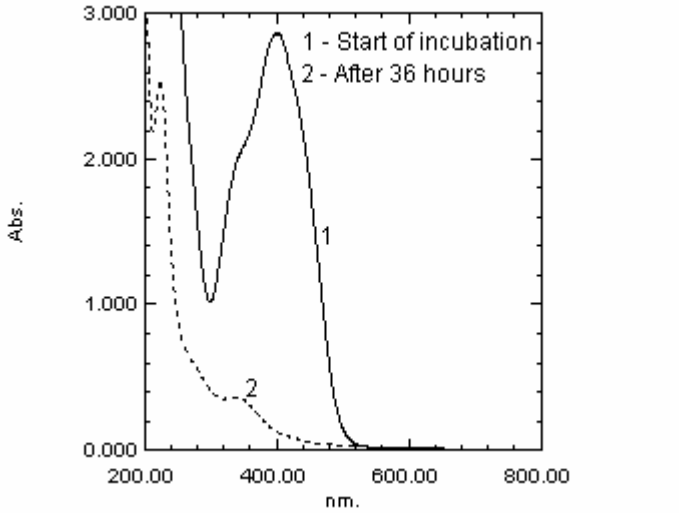

Figure.3 UV-visible spectrum obtained before and after incubation of AY79 (300mg l^{-1}) with anaerobic consortium

More than 90% of COD removal was achieved in all batch reactors except in 300 mgl^{-1} concentration, where 87% COD was removed indicating COD removals tend to decrease as increasing dye concentration in influent (Fig. 4). COD in controlled reactor was ca.111 mgl^{-1} and it was 345 mgl^{-1} in reactors containing 300 mgl^{-1} dye. COD were not considerably decreased after 72 hours indicating almost all co-substrate COD provided by glucose was exhausted. COD removal was high in reactors with low or without dye, exhibiting higher dye concentrations inhibited COD degradation. The substrate removal followed the first order kinetic model and kinetic constant was decreased from 0.0393 h^{-1} to 0.0266 h^{-1} in 0 to 300 mgl^{-1} dye concentrations, respectively, confirming the little inhibition on substrate removal. The dye itself contributed ca. 848 mg COD per gram of AY79 dye, so the most dissolved COD at the end of the study was provided by the dye metabolites suggesting that the dye was not completely degraded by anaerobic microorganisms.

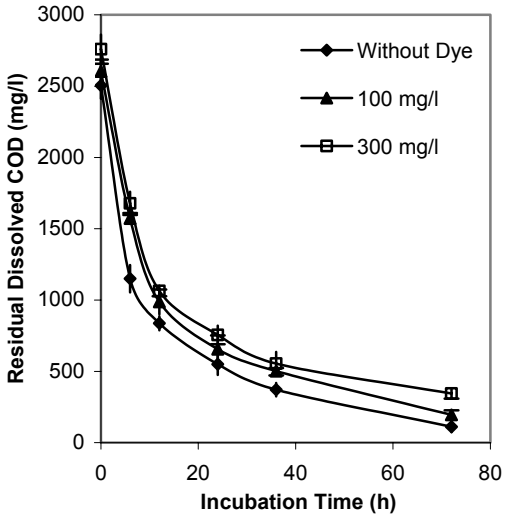

Fig.4 Residual dissolved COD at different AY79 dye concentrations

3.3 Primary Removal Mechanism of C.I. Acid Blue 204 by Anaerobic Consortia

The dye C.I. Acid Blue 204 (AB204) seems to be resistant to biodegradation by anaerobic consortia and UV-visible spectrum obtained reveals that the colour removal observed was a result of physical adsorption (Fig. 5).

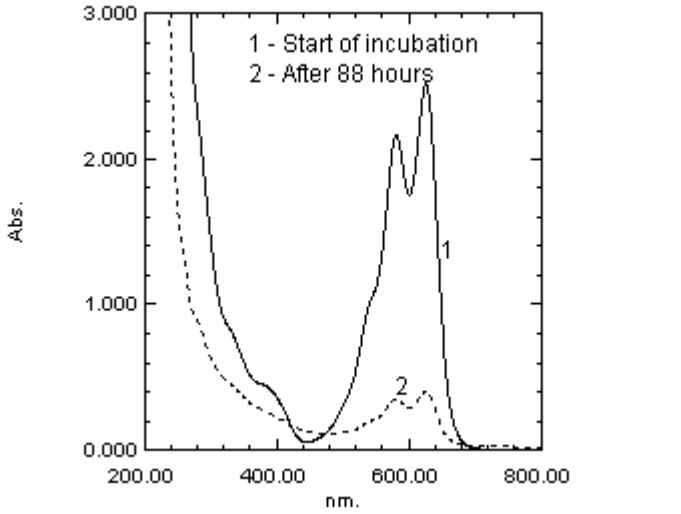

Figure.5 UV-visible spectrum obtained before and after incubation of AB204 (300mg l^{-1}) with anaerobic consortium

Decolourization of dyes by microbes occurs by biodegradation or adsorption to microbial cells or both. In adsorption, examination of UV-visible spectrum will

reveal that all peaks decrease approximately in proportion to each other. If dye removal is attributed to biodegradation, either the major visible light absorbance peak will completely disappear or a new peak will appear (Kuo-chen *et al*., 2003). The prominent peaks that contributed to the colour of AB204 can be seen at 625 and 580 nm, and these peaks can be seen in both media before and after incubation, suggesting that decolourization is due to physical adsorption onto microbial granules. This was confirmed by observation of microbial granules after incubation. The granules were dark in colour and when they were washed slightly, colour became visible in water. It seems that a greater removal of colour of AB204 was by adsorption onto microbial granules. Several authors have reported that most anthraquinone dyes studied under anaerobic process are quite resistant to biodegradation. Thongchai and Worrawit (2000) have reported that anthraquinone dye, Reactive Blue 5 and Reactive Blue 19 were not biodegraded under anaerobic processes but the decolourization of these dyes was observed. It was merely as a result of adsorption on to bacterial floc materials. Anthraquinone dyes, Brillant Red Resolin BLS, C.I. Acid Blue 40 and Tectilon Blue 4R-01 have been examined under anaerobic conditions and reported that except Tectilon Blue 4R-01, where single microbial strains were used, other dyes are resistant to biodegradation and colour removal observed only by adsorption (Malpei *et al*., 1998; Stanislaw *et al*., 2001; Walker *et al*., 2000).

In this study, AB204 was not biodegraded but considerable colour removal was observed and the slight disintegration of granules after incubation with this dye was also noticed.

The decolourization or removal mechanisms of different dyes under anaerobic process are different. Therefore, this study shows the possibility of the use of anaerobic process for the treatment of textile wastewater containing different types of dyes with different chemical groups. It has to be realized that some dyes, such as anthraquinone dye AB204 could not be biodegraded although high colour removal can be achieved.

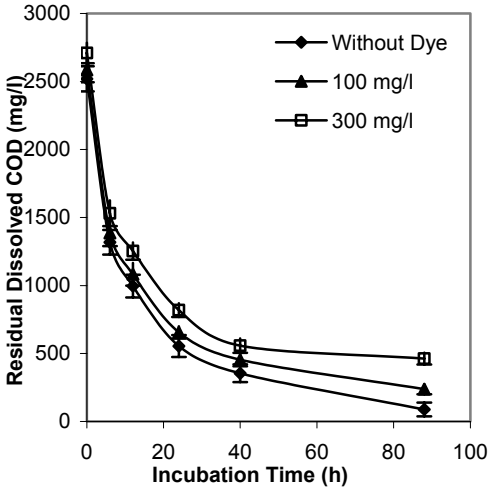

Figure.6 Residual dissolved COD at different AB204 dye concentrations

Over 90% of COD removal was observed in 100 mgl^{-1} of AB204 dye concentration (Fig.6). Chemical oxygen demand concentrations at the end of the incubation were 89 and 420 mgl^{-1} in reactors without dye and with 300 mgl^{-1} dye, respectively. Since, dye contribution for dissolved COD is ca. 657 mg COD per gram of AB204 dye, the residual dissolved at the end of the study was primarily supplied by the dye. The rate of low COD depletion at later stage of incubation with AB204 dye might be owing to the toxic effects of dye on anaerobic consortia. The probable reason for toxicity could be that the active sites of enzymes involved in co-substrate degradation is occupied by anthraquinone AB204 dye molecules, thus, blocking the binding of substrate and cofactors (Prestera *et al*., 1992). Another proposed inhibition mechanism is the uncoupling of electron transfer from ATP synthesis via an anthraquinone-mediated electron transfer reaction (Cooling III *et al*., 1996). However, from this study, it cannot be justified that the above one or both mechanisms are involved in the inhibition process till the end of incubation, since COD at the end of study was not high in comparison to controlled reactor, suggesting that no high accumulation of glucose or VFA in reactors. Therefore, inhibition extended by AB204 only caused to slow down the COD depletion process but it does not affect long-term inhibition.

3.4 Decolourization Kinetics of AR131, AY79 and AB204 Dyeing Wastewater

Decolourization rate constants, k_0, k_1 and k_2 for zero, first and second order kinetic models were determined by fitting the data obtained during study period to Eq. (2), (3) and (4), respectively.

$$D_t = D_0 - k_0 t \qquad (2)$$

$$D_t = D_0 e^{-k_1 t} \qquad (3)$$

$$\frac{1}{D_t} = \frac{1}{D_0} + k_2 t \qquad (4)$$

where D_t is the dye concentration in the medium at a given time; D_0 the dye concentration at time 0; k_0 zero order rate constant; k_1 first order rate constant; k_2 second order rate constant and t is the time. Rate constants determined and R^2 values are given in Table 1.

Table 1. Decolourization rate constants for AR131 and AY79

Dyes	Constant	50 mgl^{-1}	100 mgl^{-2}	150 mgl^{-3}	300 mgl^{-1}
AR131	k_0 ($mgl^{-1}h^{-1}$)	0.8788	1.8111	2.7372	5.2168
	R^2	0.79	0.78	0.80	0.75
	k_1 (h^{-1})	0.0497	0.0560	0.0559	0.0517
	R^2	0.97	0.97	0.98	0.97
	k_2 ($lmg^{-1}h^{-1}$)	0.0040	0.0026	0.0017	0.0008
	R^2	0.96	0.95	0.90	0.95
AY79	k_0 ($mgl^{-1}h^{-1}$)	0.9055	1.9829	3.0247	6.3753
	R^2	0.52	0.59	0.60	0.65
	k_1 (h^{-1})	0.0543	0.0735	0.0792	0.0932

	R^2	0.74	0.88	0.90	0.96
	k_2 ($lmg^{-1}h^{-1}$)	0.0050	0.0049	0.0039	0.0030
	R^2	0.93	0.99	0.99	0.94

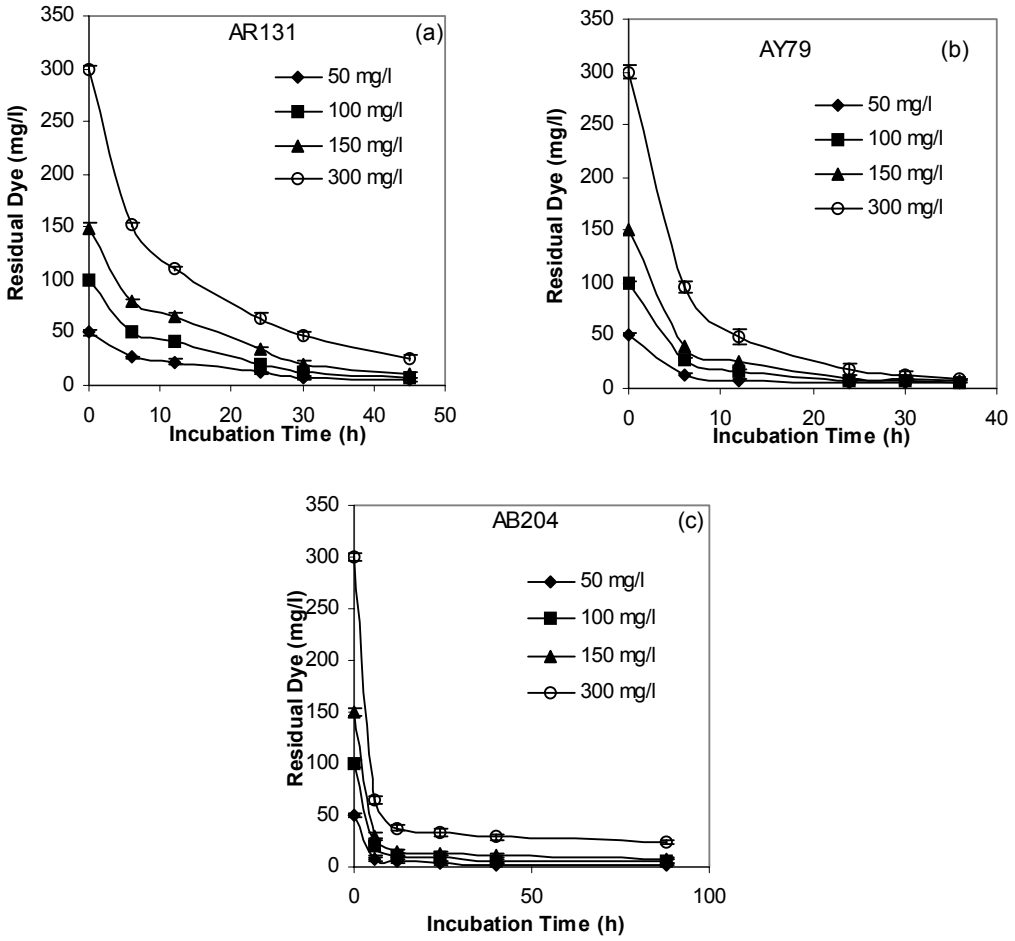

Figure.7 Variation of residual dye levels of (a) AR131, (b) AY79 and (c) AB204 during incubation period

The residual dyes of different reactors having different dyes after incubation are shown in Fig. 7. As it can be seen, all levels of AR131 dye concentrations reduced to ca.10 mgl^{-1} except in 300 mgl^{-1} dye concentration (Fig. 7(a)). The color removals were almost 90% in all reactors excluding 50 mgl^{-1} dye where comparatively lower removal was noticed with 87%. It seems that the removal mechanism of different dyes under anaerobic process is the physical adsorption followed by biodegradation. At the lower dye concentrations, dye adsorbed onto microbial granules appears to be lower than high dye concentrations providing less opportunity for biodegradation and removal. The residual dye estimated in the reactors of 300 mgl^{-1} of AR131 dye concentration is ca. 25 mgl^{-1} after 45 hours of incubation. Even after 300 hours of incubation (not shown), no further reduction of residual dye was observed

suggesting that the long incubation period does not bring additional decolourization. Abiotic test performed with autoclaved anaerobic granules removed 10-14% of colour and it probably is as a result of adsorption.

This implies that physical adsorption of dyes onto anaerobic granules is not the primary mechanism of colour removal of AR131 dye.

The R^2 values (>0.95) indicated that colour of AR131 was removed according to first order kinetic model. The highest first order rate constant, 0.0560 h^{-1} was observed at 100 mgl^{-1} of AR131 dye concentration, whereas it was 0.0559 and 0.0517 h^{-1} at 150 and 300 mgl^{-1} dye concentrations, respectively (Table 1). Decolourization rate seems to be decreased slightly with increased dye concentrations. First order kinetics of degradation by anaerobic granules with respect to dye concentration from 60 mgl^{-1} to 3200 mgl^{-1} with different azo dyes has been reported by several researchers (Mustafa and Delia, 2004; Frank *et al*., 2001; Méndez-Paz *et al*., 2005; Robert and Sanjeev, 2005; Pearce *et al*, 2003). André and co-workers (2004) have stated that Mordant yellow 10 followed zero order models. It appears that different azo dyes may follow different degradation rates with regard to dye concentration. The rate and the amount of decolourization of azo dyes depend on their molecular structure, molecular weight, substitution groups of the dye molecule and the intermolecular hydrogen bond between azo and hydroxyl groups (Nuttapum *et al*., 2004).

Acid Yellow 79 was incubated up to 36 hours where almost total decolourization was achieved with more than 95% of colour removal, except in 50 mgl^{-1} dye concentration, where only 90% removal was attained (Fig.7(b)). The residual dye concentration for each initial concentration was less than 10 mgl^{-1} at the end of incubation. Biodegradation rate constants, determined based on the data obtained during the study, are also shown in Table 1. Acid Yellow 79 biodegradation with respect to time, seems to follow the second order reaction kinetic model, where R^2 is higher than that of zero and first order kinetics. The initial biodegradation was very high; more than 70% of colour was removed after 6 hours of incubation, except 300 mgl^{-1} dye concentration, where 60% was removed. After 6 hours of incubation, colour removal rate appears to have declined. It may be due to the less availability of dye in the medium due to being adsorbed into microbial granules for further biodegradation. Therefore, the remaining dye dissolved in the supernatant could probably be degraded by microbes present there and not by the anaerobic granules.

As aforementioned, no biodegradation of AB204 was observed during 88 hours of incubation period but more than 90% decolourization was observed (Fig.7(c)). The residual dyes in reactors are almost constant after 12 h of incubation, indicating that the adsorption of AB204 dye onto anaerobic granules reaches equilibrium within 12h. Although the main mechanism of colour removal of AB204 appears to be physical adsorption, abiotic study conducted using autoclaved granules yielded only ca. 16% removal of color in all reactors. Reasons for these phenomena might be the dense structure of live anaerobic granules that can absorb more dye into cell mass, and dye precipitation by the actions of granules. On autoclaving, the structure of

granules is destroyed and it appears loose, causing poor adsorption. The similar results have been observed by Stanislaw *et al*. (2001) and reported that viable cells of activated sludge can remove more colour than dead cell mass in anthraquinone dye (C.I. Acid Blue 40) but they did not find any biodegradation. They noticed that adsorption and dye precipitation were the main mechanism of colour removal.

4. Conclusions

The UV-visible spectrum obtained and dissolved residual COD measured at the end of incubation suggest that AR131 and AY79 could be biodegraded and no further degradation of dye metabolites occurred. However, both dyes were decolourized by anaerobic consortia achieving 81% and 97% of colour removal at 300 mgl^{-1} dye concentrations, respectively. The AR131 biodegradation followed first order kinetic model with respect to dye concentration while AY79 biodegradation process approximates to second order kinetic model. No evidences were found for biodegradation of AB204 by anaerobic process under examined conditions. However, almost 90% of colour caused by AB204 dye was removed by adsorption. Since real textile wastewater contains many kinds of auxiliary chemicals except dyes; further studies are needed to find out the overall effect of these chemicals on decolourization and degradation of dyes by anaerobic process before application.

References

APHA, Standard Methods for the Examination of Water and Wastewater. 16th Edn. APHA-AWWA and WPCF, Washington DC; 1985

André, B.D.S.; Iemke, A.E.B.; Francisco, J.C.; Jules, B.V.L. Effects of different redox mediators during thermophilic azo dye reduction by anaerobic granular sludge and comparative study between mesophilic (30°C) and thermophilic (55°) treatments for decolourisation of textile wastewaters. Chemosphere 55: 1149-1157; 2004

Cooling III, F.B.; Maloney, C.L.; Tabinowski, J.; Odom, J.M. Inhibition of sulfate respiration by 1,8-dihydroxyanthraquinone and other anthraquinone derivatives. Appl. Environ. Microbiol. 62: 2999-3004; 1996

Daneshvar, N.; Ashassi, S.H.; Tizpar, A. Decolorization of Orange II by electrocoagulation method. Seperation and Purification Technology 31(2): 153-162; 2003

Elías, R.F.; Brian, D.; Jim, F.; Gatze, L. Biodegradation of N-substituted aromatics and alkyl phenols under methanogenic conditions using granular sludge. Wat. Sci. Tech. 33(3): 47-57; 1996

Ergüder, T.H.; Guven, E.; Demirer, G.N. Inhibitory effects of lindane in batch and upflow anaerobic sludge blanket reactors. Chemosphere 50: 165-169; 2003

Frank, P.V.Z.; Lettinga, G.; Field, J.A. Azo dye decolourization by anaerobic granular sludge. Chemosphere 44: 1169-1176; 2001

Georgiou, D.; Aivazidis, A.; Hatiras, J.; Gimouhopoulos, K. Treatment of cotton textile wastewater using linme and ferrous sulfate. Wat. Res. 37: 2248-2250; 2003

Georgiou, D.; Metallinou, C.; Aivasidis, A.; Voudrias, E.; Gimouhopoulos, K. Decolorization of azo-reactive dyes and cotton-textile wastewater using anaerobic digestion and acetate-consuming bacteria. Biochem. Eng. J. 19: 75-79; 2004

Graça, M.B.S.; Maria, C.F.; Pessoa, D.A.M.T. Decolorization of an anthraquinone-type dye using a laccase formulation. Bioresource Technol. 79: 171-177; 2001

Huseyin, S. Decolorization and detoxification of textile wastewater by Ozonation and coagulation. Dyes Pigments 64: 217-222; 2005

Kalyuzhnyi, S.; Sklyar, V. Biomineralization of azo dyes and their breakdown products in anaerobic-aerobic hybrid and UASB reactors. Wat. Sci. Technol. 41(12): 23-30; 2000

Kuo-chen, C.; Jane-Yii, W.; Dar-Jen, L.; Sz-Chwun, J.H. Decolorization of the textile dyes by newly isolated bacterial strains. J. Biotechnol. 101: 57-68; 2003

Malpei, F.; Andreoni, V.; Daffonchio, D.; Rozzi, A. Anaerobic digestion of print paste: A preliminary screening of inhibition by dyes and biodegradability of thickeners. Bioresource Technol. 63: 49-56; 1998

Manu, B.; Sanjeev, C. Decolorization of indigo and azo dyes in semicontinuous reactors with long hydraulic retention time. Process Biochem. 38: 1213-1221; 2003

Méndez-Paz, D.; Omil, F.; Lema, J.M. Anaerobic treatment azo dye Acid Orange 7 under batch conditions. Enzyme Microb. Tech. 36: 264-272; 2005

Muruganandham, M.; Swaminathan, M. Photochemical oxidation of reactive azo dye with UV-H2O2 process. Dyes Pigments 62(3): 269-275; 2004

Mustafa, I.; Delia, T.S. A batch kinetic study on decolorization and inhibition of Reactive Black 5 and Direct Brown 2 in an anaerobic mixed culture. Chemosphere 55: 119-128; 2004

Mustafa, I.; Delia, T.S. A batch study for assessing the inhibition effect of Direct Yellow 12 in a mixed methanogenic culture. Process Biochem. 40: 1053-1062; 2005

Nuttapum, S.; Kanchana, J.; Somsak, D.; Marie-Line, D.; Pierre, S. Microbial decolorization of reactive azo dyes in a sequential anaerobic-aerobic system. Chem. Eng. J. 99: 169-176; 2004

Pearce, C.I.; Lloyd, J.R.; Guthrie, J.T. The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes Pigments 58: 179-196; 2003

Pinheiro, H.M.; Touraud, E.; Thomas, O. Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrometric detection in textile industry wastewaters. Dyes Pigments 61: 121-139; 2004

Prestera, T.; Prochaska, J.; Talalay, P. Inhibition of NAD(P)H: (Quinone-acceptor) oxireductase by Cibracon Blue and related anthraquinone dyes: a structure-activity study. Biochemistry 31: 824-833; 1992

Razo-Flores, E.; Luijten, M.; Dolon, B.A.; Lettinga, G.; Field, J.A. Complete biodegradation azo dye Azodisalicylate under anaerobic conditions. Environ. Sci. Technol. 31:2098-2103; 1997

Robert, M.; Sanjeev, C. Adsorption and biological decolourisation of azo dye Reactive Red 2 in semicontinuous anaerobic reactors. Process Biochem. 40: 699-705; 2005

Rui, B.; Isabel, M.A.F.; Helena, M.P.; Isolina, C.G. Batch tests for assessing decolurisation of azo dyes by methanogenic and mixed cultures. J. Biotechnol. 89: 155-162; 2001

Slokar, Y.M.; Majcen, A.L.M. Methods of decolourisation of textile wastewaters. Dyes Pigments 37(4): 335-356; 1998

Stanislaw, L.; Monika, S.; Renata, Z. Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation process. J. Biotechnol. 89: 175-184; 2001

Stanislaw, L.; Monika, G. Optimization of oxidants dose for combined chemical and biological treatment of textile wastewater, Wat. Res. 33(11): 2511-2516; 1999

Tahar, M.; Sami, S. Evaluating process imbalance of anaerobic digestion of olive mill wastewaters. Process biochem. 40(1): 139-145; 2005

Thongchai, P.; Worrawit, L. Decolorization of Reactive dyes with different molecular structures under different environmental conditions. Wat. Res. 34(17): 4177-4184; 2000

Vandevivere, P.C.; Bianchi, R.; Verstraete, W. Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. J. Chem. Technol. Biotechnol. 72: 289-302; 1998

Walker, G.M.; Weatherley, L.R. Biodegradation and biosorption of acid anthraquinone dye. Environ. Pollut. 108: 219-223; 2000

Zhemin, S.; Wenhua, W.; Jinping, J.; Jianchang, Y.; Xue, F.; An, P. Degradation of dye solution by an activated carbon fiber electrode electrolysis system, J. Hazard. Mater. 84(1): 107:116; 2001