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Dye Decolorization and Organic Compounds Removal of Synthetic Textile Effluent (STE) by Anaerobic-aerobic Magnetic Activated Sludge (A_2-MAS) Reactor

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Abstract

The developed anaerobic-aerobic magnetic activated sludge (A_2-MAS) reactor was found to be suitable for the textile effluent management. An azo dye (Orange II) and an anthraquinone dye (Remazol brilliant blue R) were used in the synthetic effluent (STE) for dye decolorization. The A_2-MAS reactor consisted of an anaerobic tank (8.0 L) sequenced with an aerobic tank (4.0 L) for simultaneous dye decolorization and organic compounds removal. The anaerobic tank was operated at 35 ± 1°C while the aerobic part was maintained at room temperature. The magnetic separation technique in both aerobic and anaerobic condition of A_2-MAS reactor was found effective and it is completely new to anaerobic operation. The sequential A_2-MAS reactor attained well with 99.6% dye decolorization and 90.7% COD_{Cr} removal with the initial loading of 34.2 mg/l dye compounds and 365 mg/l COD_{Cr}, respectively. Anaerobic treatment played the major role for both dye decolorization (96.8%) and COD_{Cr} removal (78.4%) for the period of 100 day. Interestingly, sludge emission was zero all throughout the treatment.

Introduction

Various dye compounds are used in a wide number of industries to color their finished products. It is not surprising that these dye compounds have become a major environmental concern. There is a continual demand to develop longer lasting and more applicable dyes for textile industries. The development of synthetic fabrics such as nylon, rayon and polyester has required the production of new dyes that can effectively bond

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with the fabrics. Brighter and longer lasting dyes are often necessary to satisfy the demand. The dyes are released into the environment through industrial effluents and are highly visible even at low concentrations (<1.0 mg/l) (Bell and Buckley 2003). The treatment of textile dyeing industries effluent is important due to their toxic effects and aesthetic impacts on receiving water. Various types of the treatment technologies can be applied for the textile dyeing effluents. Chemical and physical treatment systems mostly are not cost effective. Biological treatment may be a good alternative as the operational cost is relatively low in compared to physical/chemical treatments (Frijters et al. 2006).

Textile and dyestuff industries are the major contributors of industrial pollutants containing dyes. Effective and economic treatment is a need for dye containing effluents. Acid Orange 7 (Orange II) is a popular water soluble dye that is used for dyeing a variety of materials such as nylon, wool and silk. Like most other azo dyes, it tends to be disposed in industrial wastewater and poses a severe health threat to humans (Banat et al. 1996, Clark and Anlikar 1980). On the other hand, remazol brilliant blue R has been widely used as a model compound in degradation studies. It is the raw material in the production of polymeric dyes and as a derivative of anthracene, represents an important member of toxic and recalcitrant organo-pollutants (Machado and Matheus 2006).

Conventional activated sludge treatment of wastewater is an effective and highly economic system for reducing organic pollutants in wastewater. A very few researches have been conducted assessing the viability of using activated sludge to treat textile effluents (Pagga and Brown 1986, Shaul et al. 1991, Zissi et al. 1997). Fewson (1988) reported that textile dye compounds are usually difficult to decolorize by aerobic treatment. Anaerobic reduction of azo dyes using microbial sludge could be effective and economic treatment process. Chinwetkitvanich et al. (2000) performed anaerobic decolorization of reactive dye bath effluents by a two-stage UASB system with tapioca as a co-substrate. Seshadri et al. (1994) investigated the fate of some selected azo dyes in an anaerobic/aerobic sequential step treatment system. Field et al. (1995) showed that the aerobic stage of combined anaerobic-aerobic treatment of dye wastes could eliminate the additional chemical oxygen demand (COD), attributed to the removal of aromatic amines, which are anaerobically recalcitrant. Sequential anaerobic and aerobic processes are necessary for keeping anaerobic organisms active in anaerobic condition and aerobic organisms in aerobic condition since the textile effluents containing various types of compounds for treatment. The conventional activated sludge process was found to be difficult to carry out sequentially anaerobic and aerobic treatment.

Magnetic activated sludge (MAS) and magnetic separation technique were found to be useful in wastewater treatment (Sakai et al. 1991, 1992, 1994, 1997, 2022). The potential application of magnetic activated sludge in different kinds of wastewater has been the target due to its effective separation of sludge from the treated water. In addition, magnetic activated sludge could maintain zero emission excess sludge and the longer sludge retention might help in the proliferation of the important microbial consortia to degrade recalcitrant toxic compounds. Therefore, the present study was undertaken with

the following objectives: (1) development of anaerobic-aerobic magnetic activated sludge (A_2-MAS) reactor for the dye and other compounds present in the textile effluent, (2) introduction of magnetic separation in the anaerobic part of the A_2-MAS reactor, (3) evaluation of zero emission sludge by the A_2-MAS reactor operation in the textile effluent treatment.

Materials and Methods

An azo dye, orange II (Kanto Chemical Co., Inc, Japan) and an anthraquinone dye, remazol brilliant blue R (RBBR) (Acros organics, New Jersey, USA) were used for the synthetic textile effluent (STE) all throughout the fed-batch experiment. In the fed-batch treatment, remazol brilliant blue R (RBBR) and orange II (OII) were used separately for the decolorization test. Starch was hydrolyzed with NaOH (0.116 mg/l) at room temperature overnight to make the starch usually found in the industrial effluent. The synthetic textile effluent STE used in the experiment is a modification of O'Neill et al. (2000). Both fed-batch and continuous process were done using the modified STE. The STE of fed-batch contains (mg/l): Dye (OII/RBBR) 50, starch 290, NaCl 15, CH_3COOH 53, $NaHCO_3$ 200, all other ingredients was same to O'Neill et al. (2000). Fed-batch treatment was carried out by fill and draw method. For this 50% (volume) supernatant of treated STE was taken out from the reactor and equal amount of fresh STE was added in each time to keep same working volume.

For aerobic treatment, a tank was made from transparent acrylic resin while Erlenmeyer flask (3.0 L) was used for the anaerobic treatment. Working volume of both cases were 2.0 L. Aerobic treatment was done by magnetic activated sludge (MAS), a modified form of activated sludge (AS). The MAS was made by mixing with the AS suspension at the ratio of 1:1 (W/W, AS in terms of MLVSS,). Anaerobic process was conducted with anaerobic sludge and without modification of the flask. Anaerobic condition was maintained by purging with oxygen-free nitrogen gas through the vinyl tube and rubber stopper. Both aerobic and anaerobic decolorization tests were carried out at room temperature.

A schematic diagram of the anaerobic-aerobic magnetic activated sludge (A_2-MAS) reactor for sequential anaerobic-aerobic STE treatment process was presented in Fig. 1. The A_2-MAS reactor consisted of main tank and magnetic separator for each anaerobic and aerobic part. In case of aerobic part the magnetic separator was one while anaerobic part was provided with two magnetic separators and placed in two different heights. Both the anaerobic and aerobic tanks of the A_2-MAS reactor were made of transparent acrylic resin. The contents of the anaerobic reactor were mixed gently by the polyacrylamide impeller. The magnetic separation unit was consisted of a tank of transparent acrylic resin with a magnetic drum made of polyvinyl chloride and covered with a plastic magnetic sheet (MagX Co. NT-5M, 3 mm thick). A rubber scraper was used to scrap out the attracted MAS of the magnetic drum to the main tank. The strongest

magnetic flux on the surface of the magnetic drum was about 700 G, which was determined by a gauss meter (F. W. Bell, Model 5080, Yokogawa Co. Type 3251, Japan). The drum was rotated by a stainless steel axle connected to an AC servomotor.

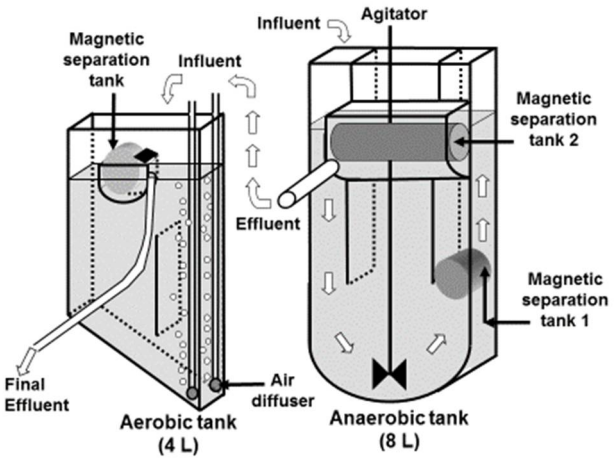

Fig. 1. Schematic diagram of the anaerobic-aerobic magnetic activated sludge (A_2-MAS) reactor.

The anaerobic set-up was placed in a water bath at the temperature of 35 ± 1°C. The STE was continuously treated by the A_2-MAS reactor. The anaerobic reactor part of the A_2-MAS reactor was initially filled with anaerobic MAS. Operation conditions were set to as: working volume 8.0 L, flow rate of 333 ml/h (HRT 24 h), agitation speed 120-200 rpm, pH 7.95. To make the reactor anaerobic condition, nitrogen gas was supplied to the anaerobic tank. The STE was fed continuously by peristaltic pump (Tokyo Rikakikai Co. LTD., MP3). During reactor operation MAS was continuously attracted by the magnetic drum and separated by the scraper through the rotation of the drum of the magnetic separation unit. This magnetic separation technique kept the anaerobic sludge in the anaerobic reactor leaving sludge free treated water through the reactor outlet. The anaerobic reactor outlet was connected with the aerobic reactor inlet.

The aerobic reactor unit of the A_2-MAS reactor received the effluent from the anaerobic reactor for final treatment and was maintained at room temperature. The aerobic tank consisted of an oxidation tank and a magnetic separation unit. The preparation of the aerobic oxidation tank and a magnetic separator was same to that anaerobic one. Like anaerobic tank, aerobic tank was filled with aerobic sludge. Operation conditions of the aerobic tank were as: working volume 4.0 L, flow rate of 333 ml/h (HRT 12 h) of the influent received from the anaerobic tank. The aeration was carried out by the two glass ball diffuser at the rate of 1.0 L/min.

During this study fresh aerobic and anaerobic sludge materials were obtained from the aeration tank and the anaerobic digester, respectively of Kawada municipal sewage treatment plant, Utsunomiya, Japan. Both the sludge materials were modified into aerobic and anaerobic MAS by seeding with Fe_3O_4 (as mentioned in batch process). The concentrations of anaerobic and aerobic MAS were 6400 mg/l and 3000 mg/l MLVSS and Fe_3O_4, respectively. Both dye compounds, RBBR and OII (25 mg/l each) were used in the STE preparation for continuous experiment. All other ingredients of the STE were same as batch experiment. The feed was stored in a refrigerator as 15-fold concentrate, and diluted at point of feeding with tap water.

The STE treated water samples were collected from both anaerobic and aerobic outlet at a regular interval. The collected samples were analyzed for pH, residual dye, COD_{Cr}, concentration; while temperature, dissolved oxygen (DO), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS) and mixed liquor inorganic volatile suspended solids (MLIVSS) were measured from the reactors. For soluble COD measurement, a portion of collected samples were filtered by glass fiber filter (GB140, Advantec, Japan). Both the filtered and non-filtered water samples were analyzed for COD_{Cr} followed by the Japan Industrial Standard (JIS 2003). The true color, and hence color removal was determined by measuring the optical density of the filtered sample by a UV-VIS recording spectrophotometer (Shimadzu UV-2400, Japan).

Results and Discussion

Two dye compounds, OII and RBBR were individually tested for both in anaerobic and aerobic condition. The results was presented in the Fig. 2. Anaerobic process was found to be effective for both OII and RBBR decolorization. Moreover, RBBR was found to degrade better. OII was found to be very difficult to decolorize in the aerobic process. Very little change in OII decolrization was observed in the successive cycles in the aerobic treatment and it could be explained as the adsorption instead of degradation. There is a finite capacity for the biomass to adsorb dye and this will be limited the generation of new cells (Bell and Buckley 2003). The increased concentration of OII with the following fed-batches might be due to over saturation of the sludge. The result indicated that azo dye (OII) was more resistant to decolorize than anthraquinone (RBBR) especially in the aerobic system. Fewson (1988) mentioned that the approximately 80% of the acid and reactive dyes are azo compounds, which generally resist aerobic degradation due to electron-withdrawing nature of the azo (N=N) linkages. Batch experiment revealed that sequential anaerobic and aerobic stages are required to decolorize dye compounds present in the textile effluent.

The magnetic separation for both aerobic and anaerobic sludge separations in the A_2-MAS reactor was found to be effective and the magnetic separation could be new to anaerobic wastewater treatment. The two magnetic separators were found to be successful in the effective anaerobic MAS separation. Although anaerobic sludge

characteristic is very much different from that of AS but interestingly similar performance was observed. Through magnetic separation only treated water from anaerobic tank entering in the aerobic tank for final treatment. The aerobic and anaerobic part of the A_2-MAS reactor might help in the adaptation of the beneficial organisms since it had no sludge washout effect at all. The magnetic separation process as a whole performs smoothly without any inter-microbial community interference of the two reactor sub-units.

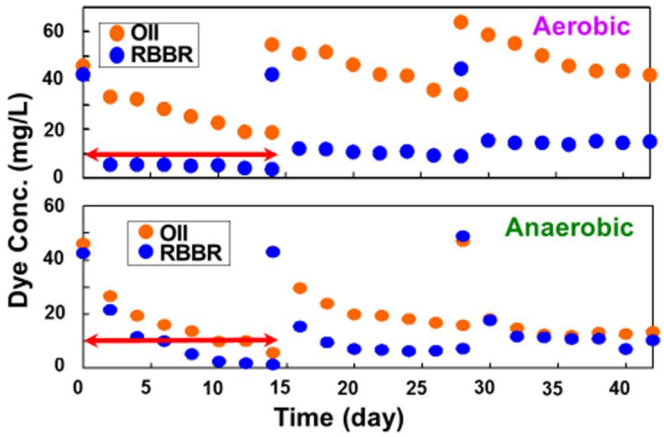

Fig. 2. Aerobic and anaerobic dye decolorization by fed-batch method.

The result of dye decolorization by the A_2-MAS reactor was presented in the Fig. 3. The loaded soluble dye concentration of the STE was 34.2 mg/l. The residual dye concentration of the anaerobic and aerobic treated effluent ranged in between 1.0-2.0 mg/l and 0.1-0.5 mg/l, respectively. It clearly showed that anaerobic MAS played the major role in the dye decolorization of the STE in the sequential anaerobic-aerobic process. With the available known information on anaerobic-aerobic degradation of dyes, it could be mentioned that the dye was not simply adsorbed to biomass but was actually degraded anaerobically to amines that were then removed by means aerobic sludge (O'Neill et al. 2000). Therefore, simultaneous anaerobic-aerobic treatment is very important for complete decolorization and detoxification of textile dyeing wastewater. Frijters et al. (2006) also mentioned that anaerobic system played a significant role in decolorizing and detoxifying the textile wastewater in the sequential anaerobic/aerobic system. The present study showed that the dye decolorization of STE was stable all throughout the treatment period in both anaerobic and aerobic stages. The overall dye decolorization percentage was presented in the Fig. 4. The results indicated that about 99% of dye decolorization had been achieved for 100 day period.

The COD_{Cr} removal performances of STE by A_2-MAS reactor was presented in the Fig. 5. The COD_{Cr} concentration of STE was in the range of 300-400 mg/l. The soluble

COD_{Cr} concentration of the anaerobically treated effluent was below 100 mg/l. The result reflected that the anaerobic process of the A_2-MAS reactor could remove a major amount of COD. O'Neill et al. (2000) reported that majority of the COD and BOD removal occurred in anaerobic treatment. The aerobic part of the A_2-MAS reactor is receiving anaerobically treated effluent with low concentration of COD_{Cr} for final treatment. Therefore, the HRT of the aerobic process was set half to that of anaerobic treatment. The soluble COD_{Cr} concentration of the aerobically treated water was found to be below 50 mg/l. A little higher total COD_{Cr} concentration was noticed on 30th day and it might be due to higher suspended solid of the effluent (data not shown). Frijters et al. (2006) mentioned that the overall COD removal efficiency of the anaerobic/aerobic treatment was 80-90%. The present A_2-MAS process could remove about 90% COD from the STE.

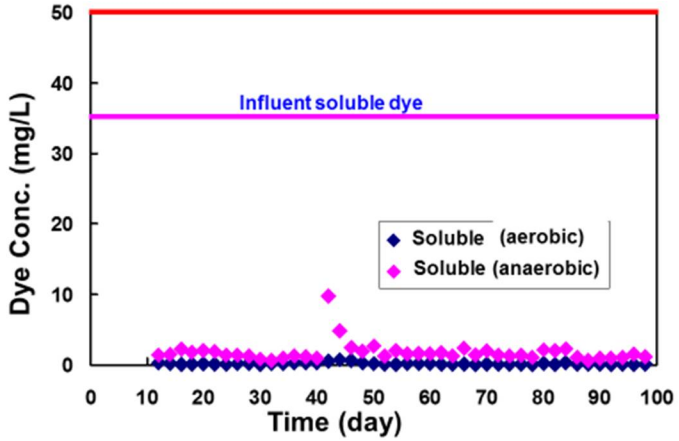

Fig. 3. Residual dye concentration of the treated synthetic textile effluent (STE).

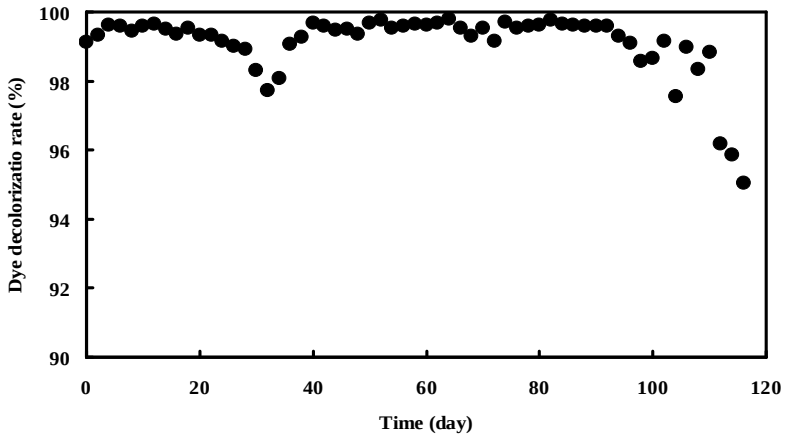

Fig. 4. Overall dye decolorization rate of the treated STE.

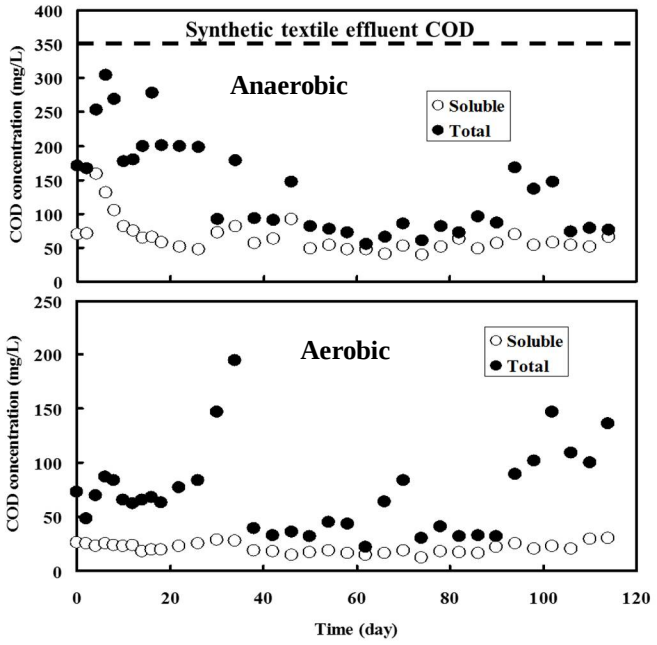

Fig. 5. Sequential anaerobic-aerobic COD removal by A_2-MAS reactor.

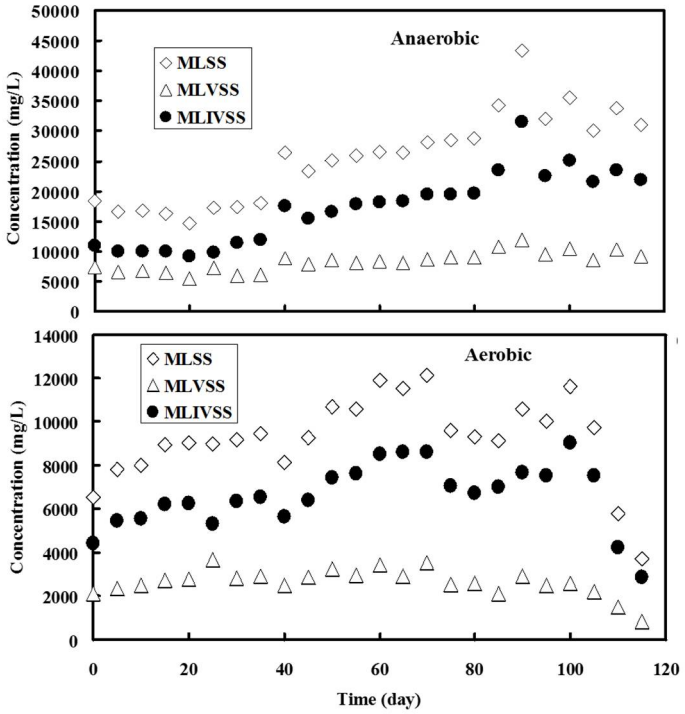

Fig. 6. Sludge concentration in the sequential A_2-MAS reactor.

Mixed liquor suspended solids of both anaerobic and aerobic units were found to be stable all throughout the treatment (Fig. 6) and sludge was never been withdrawn. A little increased concentration of MLSS and MLIVSS were noticed. This increased concentration could be due to the accumulation of the inorganic components such as sulfur, which might release during the decolorization process of the dye compounds used in STE. The stable concentration of MLVSS of the A_2-MAS reactor could support the zero emission sludge. Moreover, the longer sludge retention might help in the proliferation of the important microbial groups and their activities towards the degradation of toxic pollutants present in the industrial effluent.

The average dye concentration and COD_{Cr} value in between days 74 and 86 of the A_2-MAS treated STE effluent were shown in Table 1. The result showed that about 99.6% of the soluble dye and 90.7% soluble COD_{Cr} removal were achieved. Anaerobic process was found to be more effective in which 96.8% dye compounds and 78.4% COD_{Cr} removal were achieved. The present findings were found to be similar to the report on the azo-dye

Table 1. Dye decolorization and COD removal efficiency of the anaerobic-aerobic A_2-MAS reactor.

Parameter	Synthetic effluent	Anaerobic effluent	Aerobic effluent	Anaerobic reduction (%)	Aerobic reduction (%)	Overall reduction (%)
Dye (mg/l)	34.2	1.1	0.1	96.8	2.8	99.6
COD_{Cr} (mg/l)	366	79.1	33.9	78.4	12.3	90.7

degradation in an anaerobic-aerobic treatment system operating on simulated textile effluent by O'Neill et al. (2000). In another experiment, Frijters et al. (2006) observed that 80-90% color removal was achieved, of which the larger part was removed in the anaerobic reactor. Bell and Buckley (2003) reported that COD reduction was consistently more than 90% and color reduction averaged 86% by the anaerobic baffled reactor. The present study clearly indicated that the A_2-MAS reactor was found to be useful for simultaneous dye decolorization and organic compounds removal of the textile effluent. The following conclusions can be drawn: (1) The A_2-MAS reactor was found to be suitable for continuous treatment of textile effluent; (2) Operation of magnetic separation in the anaerobic treatment is new to anaerobic MAS reactor. (4) A_2-MAS reactor was found to keep zero emission of sludge in both anaerobic and aerobic conditions.

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