論文の内容の要旨

すべて大文字

Title of Dissertation:

Enhancement of dye degradation and mitigation of membrane fouling in a membrane-coupled fungi reactor treating textile wastewater
(染色工場排水処理のための膜分離菌類リアクターにおける
染料分解促進と膜ファウリング制御)

Name of author: ハイ　ファイセル　イブネイ **(HAI Faisal Ibney)**

Abstract

The textile wastewater, which is rated as the most polluting among all industrial sectors considering both volume and composition of effluent, is a complex and highly variable mixture of many polluting substances ranging from inorganic and low molecular weight organic compounds to polymers. It induces persistent color coupled with organic load leading to disruption of the total ecological/symbiotic balance of the receiving water stream. Dyes with striking visibility in recipients may significantly affect photosynthetic activity in aquatic environment due to reduced light penetration and may also be toxic to some aquatic lives. It is difficult to remove dyes from effluents since dyes are stable to light, heat and oxidizing agents and are hardly biodegradable.

Several physico-chemical decolorization techniques have been reported (e.g. coagulation, adsorption, membrane separation, advanced oxidation processes), few, however, have been accepted by the textile industries due to high cost, low efficiency and inapplicability to a wide variety of dyes. Biodegradation is an environmentally friendly and cost competitive alternative but the conventional aerobic treatments have been proved ineffective while highly toxic aromatic amines can be formed by reductive fission under anaerobic conditions. However, wood rotting 'white-rot fungi' are able to degrade aerobically a wide variety of recalcitrant organic pollutants, including various types of dyes through extracellular secretion of non-specific oxidative enzymes.

This study proposed a hybrid membrane-coupled fungi reactor for treatment of textile dye wastewater. The application of white-rot fungi in large-scale waste treatment has so far been impeded by the lack of bioreactor systems that can sustain long-term steady production of high levels of extracellular enzymes under non-sterile environment together with a controlled

growth of fungi. On the other hand, although membrane bioreactor (MBR) has become a reliable alternative to conventional activated sludge processes and an option of choice for many domestic and industrial applications, membrane fouling and its consequences in terms of plant maintenance and operating costs limit the widespread application of this technology. Hence, the ultimate aim of this study was to enhance microbial degradation by adopting appropriate process designs and to mitigate membrane fouling by developing fouling-resistant membrane module.

A fouling-resistant compact hollow-fiber module was developed for utilization in the proposed membrane-coupled fungi reactor to treat high strength textile wastewater. Under similar conditions, while the usual hollow-fiber bundles exhibited fatal cake-layer fouling within a day or so, the modules with spacer sustained stable performance for a month. Among the explored modules, a hybrid module (fiber packing density =61.5 %, surface area=1.07 m^2) obtained by winding a rigid spacer (thickness=1 mm, opening=7 mm x 7 mm) on the surface of a module originally containing a thin spacer (opening=1 mm x 1 mm) exhibited the optimum compactness so as to minimize intrusion of sludge while simultaneously allowing wash-out of the small amount of sludge trapped within it. Periodic low-dose cleaning from the initiation of operation was found to be more effective than application of high-dose cleaning after occurrence of severe fouling. Periodic *in situ* chemical backwashing with a low dose (500 mg Cl /L, 100 ml/m^2, twice/week) and intermittent surface-cleaning with a specially designed aeration device (1 L air/ min, 1 min per 30 min) enabled stable operation for a prolonged period under the selected average flux ($1.27x10^{-7}$ m^3 /m^2. s) and MLSS concentrations (up to 25 g/ L). Under the similar conditions, four-fold reduction in total consumptions of both chemical and air was possible when the developed module was placed within a coarse-pore (50-200μm) pre-filtration cage. However, a three-fold reduction in compactness (membrane area per unit volume of composite module) was inevitable in this case.

On the other hand, an in-depth assessment of the enzymatic activity and efficiency of decoloration of wide varieties of dyes by pure fungi culture was conducted in preliminary batch tests. Almost complete color and reasonable TOC removal performances (66%) concurrent with detectable level of expression of extracellular enzyme were observed. A significant role of biosorption along with biodegradation in decoloration, especially at the initial stage, was noticed. Batch tests also confirmed significant dye decoloration (84.2%) in presence of polyvinyl alcohol—another hardly biodegradable common pollutant in textile wastewater.

The critical factors which influence the dye degradation performance of fungi, namely,

morphology, hydrodynamic conditions, bacterial contamination etc., were also thoroughly investigated in batch tests. Fungi sludge contaminated with bacteria exhibited moderate decoloration, no enzymatic activity and much faster rate of TOC consumption. Under sequential replenishment of the liquid media the sludge progressively agglomerated and demonstrated much improved decoloration; however, enzyme in the media was not within detection limit. Investigation under sterile environment with crude enzyme solution employing different modes (reciprocal/rotary) and intensities (shaking speed 80-150 rpm) of agitation revealed negligible mechanical inactivation of enzyme. Disintegrated pure culture inoculated aseptically under strong agitation (150 rpm) exhibited an enzymatic activity approximately four times higher than that in agglomerated culture under lower agitation (80 rpm). Conversely, disintegrated pellets of fungi were found to be more prone to bacterial contamination. Monitoring fate of crude enzyme solution contaminated with bacteria also confirmed bacterial disintegration of fungal enzyme.

A frequently reported problem associated with the long-term operation of reactor containing white-rot fungi is the intensive sludge-growth due to the high dose of carbon source as required for maintaining the viability of the fungi. On the other hand, it has been reported that, depending on the type of dye and level of enzymatic activity, sorption on fungal mass may play a significant role in total decoloration. In this study, the extent of removal of dyes possessing different biosorption properties was examined in an MBR bearing sludge bed to promote sorption of dyes onto settled biomass. The reactor design with sludge bed and a split-mode feeding strategy proved to be an efficient means to control the MLSS concentration ($MLSS_{aerobic}$) in direct contact with the membrane. The average stable $MLSS_{aerobic}$ concentrations in case of feeding from top, bottom or simultaneously from top (60%)-bottom (40%) were 25, 4 and 11 g/L, respectively. Feeding mode and MLSS concentration played a significant role in color and TOC removal. The respective average color and TOC removals in case of feeding from top, bottom or simultaneously from top (60%)-bottom (40%) were as follows: Color (93.2%, 57.5%, 91.3%), TOC (97%, 94%, 97%). In case of feeding from bottom, marked dependence of decoloration on pH and hindered TOC removal in presence of chemical cleaning of membrane were observed. Depending on the type of dye, the biomass at the settling zone offered considerable sorption while the wastewater passed through this zone, thereby aiding in overall decoloration. The MBR in this case achieved an excellent 99.7% decoloration. The removal by the MBR of a dye showing negligible sorption on biomass was, however, incomplete and necessitated GAC post treatment.

Prevention of continuous loss of extracellular enzyme along with treated effluent may be critical in maintenance of stable biological degradation of dye in an MBR. Such retention of enzyme may be achieved by application of simultaneous adsorption within MBR. The effect

of reactor-operation mode (continuous versus sequencing batch) and simultaneous adsorption on the performance of the membrane-coupled fungi reactor was investigated. Co-adsorption of dye and enzyme onto activated carbon and subsequent enzymatic dye degradation was observed to occur. The dye degradation potential on activated carbon per enzymatic activity was estimated as 1.33 mg dye/ (μM substrate/min). The performance of the MBR under sequencing batch mode without any GAC-coating on the membrane was much worse than that when GAC-coated mesh was wrapped on the membrane (color absorbance of 2 and 0.6, respectively, within 5 days). In the sequencing batch MBR, the dye concentration in the feed apparently had a little influence on the permeate quality under the same HRT and withdrawal rate. On the other hand, HRT (along with withdrawal rate) appeared to impose significant influence on permeate quality. The fact that the permeate quality deteriorated in case of the shorter HRT (color absorbance 0.6 under HRT of 1 day as compared to 0.01 under HRT of 3 days) even though the dye loading in the feed was kept the same suggested that the utilized amount of GAC was not enough to completely prevent the leakage of enzyme from the reactor under the applied withdrawal rate. The performance of the continuous flow MBR, in case of which a fixed lower withdrawal rate was applied, was comparatively less affected by HRT and amount of GAC on the membrane. Under similar conditions (except the withdrawal rate), the performance of the continuous-flow MBR was always better than that of the sequencing batch MBR (color absorbance varying from 0.01 to 0.225 and from 0.01 to 0.9 during different trials, respectively). The difference was particularly significant under shorter HRT and/or when a higher flow rate of withdrawal from the sequencing batch MBR was applied. The main reason of difference of performance between the two types of MBRs were more related to the inevitable differences in withdrawal rates that can be applied in association with those reactor types and the consequent differences in the required amount of GAC on the membrane to effectively prevent leakage of enzyme from the reactor.

The importance of agglomerated fungal morphology on the performance of the proposed reactor was assessed. Mild stirring resulted in granular morphology and concomitantly triggered high enzymatic activity of fungi (around 40 μM substrate/min) which allowed excellent decoloration. However, in the course of operation under non-sterile environment in sequencing batch mode, bacterial contamination eventually occurred. Following this, the fungi granules suffered irrecoverable damage which eventually led to disintegrated morphology with limited enzymatic activity. Promotion of agglomerated growth along with granular morphology was found to ensure resistance against bacterial disruption of fungal body as well as high enzymatic activity (around 30 μM substrate/min). In the course of operation, the granular pellets were observed to extend branches, gradually bond to each other and form networked masses which eventually settled on the reactor-floor. Despite this change, the excellent enzymatic activity and decoloration performance continued. During

continuous operation of an MBR containing attached growth under a shortened HRT (1 day as compared to 4.5 days as applied in case of SBR), the level of extracellular enzyme within the reactor plummeted significantly (79%).Nevertheless, the decoloration efficiency sustained. The agglomerated growth, however, was found to be very prone to mechanical shear imposed by accidental increase in stirring speed. Conversely, despite excellent decoloration, the TOC removal ranged from 31 to 70%.

Based on the trials with different reactor arrangements, a two-step removal process—decoloration in a fungi-dominated reactor followed by TOC removal in an MBR containing mixed microbial community—was proposed. By preventing over-flow of fungi from the first reactor to the subsequent MBR by placing a coarse-pore screen at the over-flow outlet, the expected fungal dominance in the stirred reactor and the congenial atmosphere for bacterial TOC removal in the MBR was achieved. The two-step process could attain excellent decoloration of wide varieties of dyes as well as impressive TOC removal (99%). Marked adsorption of dyes onto biomass, especially in the stirred reactor, was observed. Considerable number of white-patches amidst the colored biomass indicated local zones of high enzymatic activity. The fact that the permeate quality did not deteriorate during prolonged period of operation confirmed that the biosorbed dye was subsequently degraded.

The proposed system shows great potential in terms of devising an efficient membrane-based biological treatment system for textile wastewater.