Development of Integrated Anaerobic-Aerobic Bioreactors for the Complete Degradation of Synthetic Wastewater Containing Mono and Diazo Dye

by

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LIST OF ABBREVIATIONS

AA	Aromatic Amine
Abs	Absorbance
C.I	Color Index
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
GC-MS	Gas Chromatography and Mass spectrometry
IAACF	Integrated Anaerobic-Aerobic Coconut Fiber
IAAGAC	Integrated Anaerobic-Aerobic Granular Activated Carbon
IAAGCF	Integrated Anaerobic-Aerobic Gravel and Coconut Fiber
mg/L	Milligram per liter
MO	Methyl Orange
mV	Millivolt
NH_3-N	Ammonia Nitrogen
nm	Nanometer
ORP	Oxidation Reduction Potential
RR120	Reactive Red 120
SD	Standard Deviation
SS	Suspended Solids
TDS	Total Dissolved Solids
UASB	Upflow Anaerobic Sludge Blanket
UV-region	Ultra Violet region
UV-Vis	Ultra Violet – Visible light
VSS	Volatile Suspended Solids

Pembangunan Bersepadu Bioreaktor anaerobik-aerobik untuk Degradasi yang Lengkap air sisa sintetik yang mengandungi Mono dan Diazo Dye

ABSTRAK

Pewarna adalah bersifat karsinogenik dan mutagenik. Mesra alam, ekonomi dan tidak menghasilkan pencemaran sekunder adalah merit rawatan biologi untuk pewarna azo daripada kaedah lain. Rawatan semata-mata anaerobik atau aerobik dan rawatan digabungkan tidak berjaya untuk mencapai penyingkiran serentak warna dan perantaraan dalam kebanyakan kes. Rupa-rupanya, masih terdapat keperluan untuk membangunkan bioreaktor untuk melaksanakan pembasmian sepenuhnya azo pewarna termasuk warna dan perantaraan. Kajian ini bertujuan untuk membangunkan bioreaktor yang mampu melakukan dalam warna dan perantaraan yang berkesan penyingkiran pewarna azo. Kajian ini dijalankan satu anaerobik dan tiga anaerobik-aerobik bioreaktor bersepadu yang berbeza iaitu, Upflow anaerobik Enapcemar Blanket (UASB) reaktor, Integrated anaerobik-aerobik Kelapa Fiber (IAACF) reaktor, Gravel Bersepadu anaerobik-aerobik dan Kelapa Fiber (IAAGCF) reaktor dan anaerobik Bersepadu -Aerobic berbutiran Karbon Diaktifkan (IAAGAC) reaktor. Prestasi di atas semua reaktor terhadap degradasi air sisa sintetik yang mengandungi mono azo pewarna Methyl Orange (MO) dan diazo pewarna reaktif Merah (120 RR120) dinilai dalam kepekatan influen warna yang berbeza. . The penyingkiran warna MO dalam UASB reaktor 94%, 90% dan 96% masing-masing dalam fasa 1A, 2A dan 3A. The penyingkiran warna MO dalam IAACF reaktor adalah 97%, 96%, 97%, 97% dan 96% dalam fasa 1B untuk 5B, masing-masing. Perantaraan daripada MO tidak dikeluarkan dalam UASB reaktor dan sebahagiannya dikeluarkan di reaktor lain. Belahan simetri ini bon azo dalam MO cenderung kepada pembentukan N, N-dimetil p-phenylenediamine dan asid sulfonic 4-amino sebagai perantaraan. Analisis GC-MS menyebabkan kehadiran N, N-dimetil p-phenylenediamine dalam efluen. Penyingkiran warna MO dalam IAAGAC dan IAAGAC reaktor hampir 98% dan 100% masing-masing dalam semua peringkat. Perantaraan daripada MO telah dibuang sepenuhnya dalam reaktor IAAGAC dengan masa operasi yang meningkat. The penyingkiran warna RR120 dalam reaktor UASB dengan peningkatan influen bersama substrat adalah 67%, 76% dan 80% dalam fasa IA, IIA dan IIIA, masing-masing. Dalam IAACF reaktor, yang penyingkiran warna RR120 adalah 87%, 88% dan 86% dalam fasa IB, IIB dan IIIB, masing-masing. Penyingkiran warna RR120 dalam IAAGCF dan IAAGAC reaktor lebih daripada 90% dalam semua fasa. Belahan bon azo dalam RR120 membawa kepada pembentukan sebatian aromatik Sulfonated sebagai perantaraan. Penyingkiran lengkap perantaraan RR120 diperhatikan dalam reaktor IAAGAC dengan masa operasi yang meningkat. Hasil kajian ini menunjukkan bahawa persekitaran anaerobik yang sangat penurunan yang sesuai untuk penyingkiran warna berkesan MO dan RR120 bukannya penyingkiran perantaraan. Mineral separa MO dan RR120 perantaraan diperhatikan dalam sistem anaerobik-aerobik bersepadu. Pembasmian sepenuhnya MO dan RR120 perantaraan adalah mustahil dalam sistem anaerobik-aerobik bersepadu dengan bahan bio yang sesuai seperti karbon diaktifkan berbutir. Perubahan pemalar kinetik dalam kajian kinetik mendedahkan bahawa prestasi warna dan penyingkiran COD adalah dalam trend penurunan berkenaan dengan peningkatan pengaruh warna dalam kedua-dua MO dan RR120. Walau bagaimanapun prestasi telah berkurangan, penyingkiran warna berkesan diperhatikan dalam warna yang munasabah antara influents (100 hingga 1000 mg / L).

Development of Integrated Anaerobic-Aerobic Bioreactors for the Complete Degradation of Synthetic wastewater containing Mono and Diazo Dye

ABSTRACT

Dyes are carcinogenic and mutagenic nature. Eco-friendly, economical and not producing secondary pollutants are the merits of the biological treatment for azo dye than other methods. Purely anaerobic or aerobic treatment and combined treatments were not successful to attain the simultaneous removal of color and intermediates in most of the cases. Apparently, still there is a need to develop the bioreactors to perform complete removal of azo dye including color and intermediates. The present study aimed to develop the bioreactor which able to perform in effective color and intermediates removal of azo dye. The study conducted one anaerobic and three different integrated anaerobic-aerobic bioreactors namely, Upflow Anaerobic Sludge Blanket (UASB) reactor, Integrated Anaerobic-Aerobic Coconut Fiber (IAACF) reactor, Integrated Anaerobic-Aerobic Gravel and Coconut Fiber (IAAGCF) reactor and Integrated Anaerobic-Aerobic Granular Activated Carbon (IAAGAC) reactor. Performance of the above all reactors against the degradation of synthetic wastewater containing mono azo dye Methyl Orange (MO) and diazo dye Reactive Red 120 (RR120) were assessed in different influent color concentrations. . The color removals of MO in UASB reactor were 94%, 90% and 96% in phase 1A, 2A and 3A respectively. The color removals of MO in IAACF reactor were 97%, 96%, 97%, 97% and 96% in phase 1B to 5B, respectively. The intermediates of MO was not removed in UASB reactor and partially removed in other reactors. Symmetric cleavage of this azo bond in MO tends to the formation of the N,N-dimethyl p-phenylenediamine and 4-amino sulfonic acid as intermediates. GC-MS analysis resulted the presence of N,N-dimethyl p-phenylenediamine in the effluent. The color removal of MO in IAAGAC and IAAGAC reactors were nearly 98% and 100%, respectively in all phases. The intermediates of MO were completely removed in IAAGAC reactor with increased operation time. The color removals of RR120 in UASB reactor with increased influent co-substrate were 67%, 76% and 80% in phase IA, IIA and IIIA, respectively. In IAACF reactor, the color removals of RR120 were 87%, 88% and 86% in phase IB, IIB and IIIB, respectively. The color removal of RR120 in IAAGCF and IAAGAC reactors were more than 90% in all the phases. The cleavage of azo bonds in RR120 leads to the formation of sulfonated aromatic compounds as intermediates. The complete removal of RR120 intermediates were noted in IAAGAC reactor with increased operation time. The results of present study revealed that the highly reductive anaerobic environment suited for effective color removal of MO and RR120 rather than intermediates removal. Partial mineralization of MO and RR120 intermediates was observed in integrated anaerobic-aerobic system. Complete removal of MO and RR120 intermediates was possible in integrated anaerobic-aerobic system with suitable biomaterials like granular activated carbon. The variation of kinetic constants in kinetic study revealed that the performance of color and COD removal was in decreasing trend with respect to increased color influent in both MO and RR120. However the performance was decreasing, effective color removal was observed in the reasonable color influents range (100 to 1000mg/L).

CHAPTER 1

INTRODUCTION

1.1 Environmental issues

Textile dying industries consumes large quantity of water and proportionally produces the higher amount of wastewater. Due to the incomplete use and washing operation, considerable amount of dye have been noticed in textile dyeing wastewater. With respect to both the quantity and composition, the textile processing wastewater is reported as the most polluted source among all industrial sectors (Chang, et. al., 2009). Ecological risk was noticed in recent years due to the textile dyeing wastewater discharge in the environment. The following are the some of the recent case studies reporting the contamination of soil, agricultural fields and water sources by the textile dying effluent.

1.1.1 Soil contamination due to textile effluent

Mehta & Yadav (2013) conducted a study at Bagru, located in the south-west of Jaipur region (India). The town is famous for textile printing and dyeing. Nearly 250 printing and dyeing units are available around the town. The printing and dyeing are mainly carried out by the natural dyes but some units make use of synthetic dyes. The untreated effluents from the printing and dyeing units were disposed in open drains and directly used for crop cultivation. To assess the contamination of soil due to this discharge, physicochemical properties of soil were examined.

The soil samples were collected in three different seasons namely August, December and March. Reason for selecting the samples in different seasons was the period of production which varies in its activities, resulting in variation in amount of effluent discharged. The soil samples were analyzed for physicochemical parameters like alkalinity, organic carbon, nitrogen, calcium, magnesium, potassium, moisture content and metals like iron, lead, copper, cadmium and chromium. Based on the parameters assessed, the study reported that Bagru Textile Printing units discharge effluent with high degree of acidity, chlorides, cations and anions which are not comparable with standards. The result indicated that the application of textile effluent affected the physicochemical property of the soil. The study suggested that the continuous application of effluent leads to deteriorate the quality and fertility of the soil.

Similar assessment of physicochemical parameters of agricultural area affected by the textile effluent discharge was carried out by Priya & Chauhan (2014). The study conducted in Sanganer town which is about 16 km of south of Jaipur (India). Various physicochemical parameters including heavy metals were analyzed from the wastewater, which was used for irrigation in agriculture areas of Sanganer area of Jaipur District. Average concentration of copper, Lead, Cadmium and Chromium is 4.74mg/l, 1.097mg/l, 1.93mg/l, 3.74 mg/l in 2011-12 respectively and 4.95mg/l, 1.385mg/l, 1.97mg/l, 4.02mg/l in 2012-13 respectively, found in the textile wastewater samples which are more than the permissible limits set by the WHO. Similar to the heavy metals, the pH, chloride, total dissolved solids, calcium hardness, magnesium hardness and total hardness were also higher than permissible limits. The study concluded that the increasing physicochemical parameters have significantly toxic and hazardous effects on soil environment.

1.1.2 Impacts of textile effluent discharge on water source

Khalid Hasan & Miah (2014) assessed the textile dyeing effluents on surface water quality. The study area is situated in Araihazar Thana of Narayanganj District, beside Padma Textile Mills, which is located about 40 km South of Dhaka (Bangladesh). Water samples were collected from ten different locations to a depth of 10cm to 15cm below from the surface water level. Various physicochemical parameters including heavy metal analysis were examined. The average electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO) and BOD were 783.8µs/cm, 2330.3mg/L, 3.03mg/L and 8.38mg/L, respectively. These were not comparable with desirable limit of EC, TDS, DO and BOD. The study also reveals that the average value of NH_4-N was 81.28mg/L as against permissible level of 0.2 to 10mg/L, sulphate was found ranging from 204.90mg/L to 370.28 mg/L as against the permissible level of 100mg/L and phosphate ranging from 19.10–28.56 mg/L as against the permissible range of 0.1–0.6mg/L. Further analysis ensured the availability of heavy metals in the water source. The study concluded that the quality of water turned as unfit to use as drinking and other applications due to the discharge of textile dyeing effluent.

Nearly 729 bleaching and dyeing units are in operation in Tiruppur area, is located on the bank of Noyyal river, Tamil Nadu, India. Initially, they discharged untreated effluent into the river. In year 1997, after the Tamil Nadu Pollution Control Board (TNPCB) directions they installed Common Effluent Treatment Plants (CETP). Even then, the treated effluent from the CETPs causes impacts on the Noyyal River and it was studied by Samuel Rajkumar & Nagan (2011). The Noyyal river water quality reveals that the TDS level in the upstream of Tiruppur was in the range of 900 - 5336mg/L, downstream was in the range of 372 - 6636mg/L as against the permissible level of 1500mg/L. Chlorides in the upstream was in the range of 233 - 2547mg/L and in the downstream was in the range of 808-2721 mg/L as against the permissible level of 600mg/L. BOD in the upstream was in the range of 1- 48 mg/L and in the downstream 1-36mg/L as against the permissible level of 3mg/L. COD in the upstream was 2- 324mg/L and in the down 17 - 292mg/L. The study reported that the discharge CEPTs effluent into Noyyal River had significantly affected the river water quality, groundwater quality as well as the Orathupalayam dam which is constructed across Noyyal River at 32km downstream of Tiruppur.

1.1.3. Toxicity of treated textile effluent

In many developed countries, toxicity tests on industrial effluents are required to ensure that such discharges will not have adverse effects on the environment. A textile industry in Lagos, Nigeria was undergone to the toxicity assessment of the treated effluent by Odjegba & Bamgbose (2012). The effluent samples were collected and immediately evaluated in its physicochemical variables. Seeds of C. argentea were allowed to grow on the nursery for 3 weeks after germination to enable them attain an appreciable height. The grown plants were treated with 1 L effluent water sample every 3 days up to 3 weeks while the control plants received equal amount of water devoid of effluent. At the end of the treatment period, plants were harvested and various parameters were evaluated. Root growth, dry weight, total chlorophyll, lipid peroxidation and metal content in leaves were determined from the harvested plants. The study demonstrates that treated textile effluent water sample affected growth, biomass, photosynthetic pigment, and membrane integrity of C. argentea. The results implied that treated textile effluent cause bio-toxicity on organisms.

1.2 Dyes discharge and impacts

More than 100000 commercial dyes are available with a production of over 700000 metric tons per year (Vijayaraghavan, et. al., 2013). Worldwide textile industries consume the total dye more than 10,000 tonnes per year (Gupta, et. al., 2013). The textile dyeing process consumes large quantities of water which are up to 150 liters of water to per kilogram of fiber. This leads to generates huge amounts of wastewaters (Jadhav, et. al., 2010). In typical dyeing process, 0 to 50% dyes are discharges in wastewater as unfixed dyes (Jiraratananon, et. al., 2000). Among the various dyes in textile industries, azo dyes are accounted more than 60% which results the higher accountability of azo dye in wastewater (Fu & Viraraghavan, 2001).

Most of the dyes are visible in water even the concentration less than 1mg/L. The textile wastewater is characterized as the dye concentration generally below $1g/dm^3$ which is equal to 1g/L (Srinivasan & Viraraghavan, 2010). Thus, usually highly colored discharge in open waters presents an aesthetic problem. In addition to that, the dyes are highly persistent in natural environment due to their stability against degradation. The untreated dye causes several impacts on men and environment. Plenty of research was carried out by various researchers about the impacts of dyes on human being and environment. Few of recent researches were listed in Table 1.1.

The common impacts of dyes on human beings were reported by the various researchers were the ability of cancer causing, damage to DNA, damage to specific cell growth in human body, attack on specific microorganisms which favor to human body and acted as endocrine disturbing agent etc. Apart from the human being, exposure of dyes also causes impacts on aquatic environment and soil environment by affecting their habitations. Effluent treatments become the option to overcome the impacts of the dyes on human being and environment. Even the treated effluent also causes certain impacts which insist to focus further research to arrive complete removal of dye from the effluent.

1.3 Dye removal techniques

One of the options to overcome the impacts of dye is treatment. The most common classification of textile wastewater treatment is physical, chemical and biological treatment. The physical force involved in the contaminant removal is categorized as physical treatment. Chemical reaction and biological activity to the removal of dye are under the class of chemical and biological treatment respectively.

In the various physical treatments, adsorption and membrane filtration were employed for the removal of dye. Modified-alumina, activated-clay, activated-carbon, kaolin, activated-rice husk, bentonite, fly ash, pine leaves, Fe_2O_3, pine cone, tobacco stem ash, modified sawdust, red mud, sawdust, sugarcane bagasse, rice husk, raw mango seed, modified mango seed and Apricot seed were the adsorbents used to remove various dyes in recent research (Yagub, et. al., 2014). Initial dye concentration, pH and temperature are the major governing factor against the adsorption of dye. Membrane filtration was evolved as microfiltration, ultrafiltration and nanofiltration membranes for the removal of dye (Saffaj, et. al., 2006; Zheng, et. al., 2013).

Table 1.1: Impacts of dyes on human and environment

Category of Dye	Dye	Impact	Reference
Mono azo dye	Sudan I,II and Para Red	Potential reduction metabolites on eleven prevalent human intestinal bacterial strains	Pan et al., 2012
Diazo dye	Sudan III and IV		
Mono azo dye	CI Disperse Blue 373, CI Disperse Violet 93, and CI Disperse Orange 37	The intermediates nitro-aminoazobenzenes and benzidine are mutagenic and carcinogenic	Alves de Lima et al., 2007
Mono azo dye	CI Disperse Blue 291	Dye contains the aminoazobenzene 2-[(2-bromo-4,6-dinitrophenyl)azo]-5(diethylamino)-4-methoxyacetanilide caused genotoxicity and cytotoxicity in the human hepatoma cell line HepG2 which is respond to stimulation with human growth hormone	Tsuboy et al., 2007
Mono azo dye	Disperse Red 1	The bio-transformed dye was genotoxic and mutagenic potential	Chequer et al.,2011
Mono azo dye	Disperse Orange 1	The azo dye induces DNA damage and cytotoxic effects	Ferraz et al., 2011