ULTRASONIC ASSISTED PHOTODEGRADATION OF REACTIVE BLACK 5 BY ZINC OXIDE IMPREGNATED ACTIVATED RED MUD CATALYST

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ABSTRACT

This study focuses on the remediation of the anionic dye contaminated wastewater using the prepared ZnO/ARM sonophotocatalyst. In this AOP process, an anionic dye, Reactive black 5, is subjected to the sonophotocatalytic treatment process with the aim of establishing the effectiveness of the prepared ZnO doped activated red mud (ZnO/ARM) as sonophotocatalyst. ZnO/ARM was prepared by impregnation method at different weight ratios (0.25:1, 0.5:1, 0.75:1 and 1:1) and the ZnO/ARM at weight ratio of 0.75:1 was chosen as effective photocatalyst. The prepared sonophotocatalyst were characterized by XRD, BET, FTIR, SEM-EDX, DRS and PL. Parametric and kinetics studies for the removal of RB5 from the simulated wastewater were conducted to confirm the effectiveness of this sonophotocatalyst. A transducer sonicator (35 kHz) and a UV-C (254 nm) lamp were applied simultaneously to effectively degrade the selected recalcitrant dye-based pollutant. The influence of the solution pH, concentration and catalyst dosage were manipulated throughout this study to investigate the sonophotodegradation kinetics and synergistic effects on the RB5 degradation. Experimental results confirmed that the sonophotocatalysis rate of 20 ppm of RB5 was better under acidic medium (66.7%) in comparison to alkaline medium (46.1%) due to the surface charge of the catalyst. At acidic condition, a positive charge excess in the ZnO/ARM surface favours a strong electrostatic interaction with SO_3^- groups of the dye which is then consequently resulted in the higher degradation rate (0.0156 min^{-1}). Meanwhile at alkaline condition, catalytic activity of ZnO/ARM was diminished by the excess negative charge which promotes the repulsion of dye in ZnO/ARM surfaces which recorded degradation rate of 0.01 min^{-1}. The band gap energy E_g of the ARM was found to be 1.98 eV and the prepared ZnO/ARM (0.75:1)=2.04 eV. The introduction of ZnO does not strongly affect the optical absorption property of ARM. The accelerated photo induced electron–hole transfer and separation, decreased recombination rate and band energy matching lead to the enhancement of photocatalytic performance for Zn0/ARM composite. Synergistic effects were analyzed based on the first order kinetic rate model, and it was found that the synergistic effect was observed for all the experiments conducted.

ABSTRAK

FOTODEGRADASI BERBANTU ULTRASONIC BAGI REACTIVE BLACK 5 DENGAN PENGGUNAAN ZINK OXIDA IMPREGNAT DENGAN PEMANGKIN LUMPUR MERAH TERAKTIF

Kajian ini memberi tumpuan kepada pemulihan sisa air yang tercemar dengan pewarna anionik degan menggunakan ZnO/ARM sebagai sonofotopemangkin. Dalam proses AOP ini, pewarna anionik, Reactive black 5, telah digunakan dalam proses rawatan sonofotopemangkinan dengan tujuan untuk mewujudkan keberkesanan pemangkin yang disediakan (ZnO/ARM). ZnO/ARM telah disediakan melalui kaedah pengisitepuan pada nisbah berat yang berbeza (0.25:1, 0.5:1, 0.75:1 and 1:1) dan ZnO/ARM pada nisbah 0.75/1 telah dipilih sebagai sonofotopemangkin efektif. Pelbagai teknik sebagai XRD, BET, FTIR, SEM-EDX, DRS dan PL telah dianalisis untuk mengkaji sifat pemangkin yang telah disediakan. Kajian parametrik dan kinetik untuk penyingkiran RB5 dari larutannya telah dijalankan untuk mengesahkan keberkesanan sonofotopemangkin ini. Sebuah sonikator yang dilengkapi dengan pemindah arus (35 kHz) dan lampu UV-C (254 nm) telah digunakan pada masa yang sama untuk mendegradasi pewarna yang dipilih. Pengaruh pH dan kepekatan larutan RB5, dos pemangkin dan nisbah ZnO/ARM telah dimanipulasikan sepanjang kajian ini untuk mengkaji kinetik sonofotopemangkinan dan kesan sinergi pada degradasi RB5 itu. Dapatan kajian mengesahkan bahawa kadar sonofotopemangkinan bagi 20 ppm RB5 adalah lebih baik di bawah medium berasid (66.7%) berbanding dengan medium beralkali (46.1%) disebabkan oleh caj permukaan pemangkin. Pada keadaan berasid, caj positif yang berlebihan dalam permukaan ZnO/ARM berinteraksi dengan kumpulan SO_{3^-} yang terdapat pada pewarna RB5 yang menyebabkan kadar degradasi yang lebih tinggi (0.0156 min-1). Manakala pada keadaan beralkali, aktiviti pemangkin ZnO/ARM telah berkurang disebabkan oleh cas negatif yang berlebihan yang menggalakkan penolakan pewarna daripada permukaan ZnO/ARM yang mencatatkan kadar degradasi 0.01 min-1. Tenaga luang jalur E_g pada ARM didapati 1.98 eV dan bahan komposit ZnO/ARM (0.75:1) = 2.04 eV. Pengenalan ZnO tidak mempengaruhi penyerapan sifat optik ARM. Pemisahan dah pemindahan lubangelektron dipercepatkan, penurunan kadar penggabungan semula dan tenaga jalur yang hampir sama membawa kepada peningkatan prestasi fotopemangkinan untuk mangkin Zn/ARM. Pemisahan pembawa cas dalam semikonduktor yang berbeza secara berkesan menghalang penggabungan semula pasangan elektron-lubang dan menggalakkan kecekapan kuantum ARM. Kesan sinergi dianalisis berdasarkan model kadar kinetik tertib pertama, dan didapati bahawa kesan sinergi dapat diperhatikan untuk semua eksperimen yang dilakukan.

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LIST OF SYMBOLS, UNITS AND ABBREVIATIONS

°C	Degree Celsius
%	Percentage
>	More than
▪	Equals to or more than
&	And
tons	Tonnes
mol L^{-1}	Mol per liter
mmol L^{-1}	Millimol per liter
g L^{-1}	Grams per liter
mL	Milliliter
min	Minutes
Nm	Nanometers
ppm	Parts per million
g	Gram
M	Molar
▪	Theta
cm^{-1}	Per centimeter
–C=C–	Carbon to Carbon Double Bond
–N=N–	Nitrogen to Nitrogen Double Bond
$–SO_3$	Sulphonate group
AOP	Advanced Oxidation Process
BOD	Biochemical Oxygen Demand
=C=O	Carbonyl group
–COOH	Carboxyl group
C.I.	Colour Index
COD	Chemical Oxygen Demand
CO_2	Carbon Dioxide

Fe	Iron
HCl	Hydrochloric acid
H_2O	Water
H_2O_2	Hydrogen Peroxide
$^{\bullet}HO_2$	Hydroperoxide radical
$HO_2^{\cdot}$	Hydroperoxide ion
RB5	Reactive Black 5 (dye)
V	Volume
NaOH	Sodium hydroxide
O_2	Molecular Oxygen
$^{\bullet}O_2^-$	Superoxide ion
O_3	Ozone
–OH	Hydroxyl group
$^{\bullet}OH$	Hydroxyl radical
$^{\bullet}HO_4$	Tetraoxide radical
P	Phosphorus
S	Sulphur
SO_3^-	Sulphonate ion
TiO_2	Titanium Dioxide (IV)
TOC	Total Organic Carbon
UV	Ultraviolet
Vis	Visible
ZnO	Zinc Oxide
UV	Ultra Violet
ROS	Reactive Oxygen Species
Al_2O_3	Aluminium Oxide
SiO_2	Silicon Dioxide
SnO_2	Tin Oxide

CdS	Cadmium Silfide
CdTe	Cadmium Telluride
h	Planck constant
CB	Conduction Band
VB	Valence Band
$e^{\cdot}$	Negatively-charged electron
h^{+}	Positively-charged hole
*****	Electronically excited species
pH_{zpc}	Zero-point charge pH

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Water from the textile industry has been of concern to researchers because they are characterised by the prominent colour and COD content with varying pH from 2 to 12, resulting in polluted water bodies like lakes and rivers becoming toxic to aquatic life (Ramirez *et al.,* 2013). According to Rodríguez *et al.,* (2009) the colour and structural integrity of dyes in textiles effluents are hardy and degrade very little in the environment due to their design to persist under oxidising and reducing conditions or washing. Dyes are resistant to fading by exposure to sunlight and chemicals such as detergents due to their complex structure and synthetic origin. The structural varieties of dyes are acidic, basic, disperse, azo, diazo, anthraquinone based and metal complex dye. The municipal sewerage systems do not affect the decolourisation of textile dye when it is treated aerobically (Aouni *et al.,* 2012).

Existing conventional methods such as membrane technology, filtration, coagulation, and flocculation are used to treat the dyehouse effluent. Most of the traditional methods are ineffective to sufficiently address the treatment due to the complexity of the composition of dye house effluent (Ponraj *et al.,* 2017). The production of the huge amount of chemical sludge and the ineffectiveness in decolourising of some soluble dyes by these treatment methods are well documented (Mezohegyi *et al.,* 2012). The limitations of conventional chemical oxidation techniques can be overcome by treating this type of wastewater with advanced oxidation process (AOP) methods (Dewil *et al.,* 2017). AOPs, which include treatment with sonication, ozone, H_2O_2, Fenton's reagent or UV radiation are the potential alternatives for the traditional decolourisation methods for dye contaminated wastewater.

AOPs are a combination of non-biological technologies which are involved in the degradation of toxic pollutants such as biologically recalcitrant compounds in textile wastewater (Wang *et al.,* 2003; Garcia-Segura and Brillas, 2017). AOPs rely on the generation of reactive hydroxyl radical with a redox potential of 2.8 V. Hydroxyl radical rapidly reacts with the organic compound, either in addition to a double bond or by eliminating a hydrogen atom from an aliphatic organic molecule. The organic radicals formed will then react with oxygen to initiate a series of oxidation reactions ultimately leading to mineralised products of CO_2 and H_2O (Catalkaya *et al.,* 2009; Holkar *et al.,* 2016).

Sono-hybrid processes have been proposed and investigated, such as the sono-persulfate process, sono-Fenton process, sono-electrochemical process, sono-photoferrioxalate process and sonophotocatalytic process. Among these hybrid methods, the sonophotolytic process shows more promise for practical application due to its avoidance of chemical addition. Sonophotocatalysis comprises the use of a combination of ultrasound waves (20-1000 kHz) and light irradiation to enhance a catalysed chemical reaction by the formation of free radicals in aqueous systems. During this combination, the synergistic effect between the US waves and the light irradiation has resulted in improved degradation efficiencies with the aid of suitable sonophotocatalyst (Monteagudo *et al.,* 2014; Bahena *et al.,* 2008; Joseph *et al.,* 2015; Xu *et al.,* 2013). Ultrasonic sound waves are transmitted through the aqueous solution to generate "acoustic cavitation" (Durán *et al.,* 2013). Therefore, the selection of a suitable catalyst to utilise light energy with the aid ultrasound waves ultimately leading to efficient oxidation of target pollutant.

Recently, interest in photocatalysis has focused on the use of semiconductor materials for the removal organics and inorganics, purification of water and wastewater, industrial and health applications. Various other types of semiconductor photocatalysts, such as ZnO, TiO_2, ZrO_2, $SrTiO_3$ have been investigated for AOP applications. However, most oxides have an absorption edge only in the ultraviolet region (UV) which limits the use of most of the solar spectrum. The selection of iron oxide (Fe_2O_3) as a promising photocatalyst material is due to the narrow band gap of about 2.0-2.2 eV and can absorb light up to 600nm. However, researchers documented that the photoactivation of Fe_2O_3 is

limited by certain factors such as high recombination of an electron-hole pair, reduced conductivity, and poor diffusion length of holes (2-4 nm). To overcome this high recombination problem and to enhance its photocatalytic properties, countless attempts have been done such as improving charge transferability, doping with suitable metals and lowering the recombination by the formation of nanostructures. Doping Fe_2O_3 with suitable semiconductor increases the lifetime of charge carriers and consequently reduce the recombination of electron-hole. Zinc coupling with various semiconductors such as CeO_2 (Liu *et al.,* 2014), CdO (Samadi *et al.,* 2014), CuO (Liu *et al.,* 2008), Cu_2O (Xu *et al.,* 2010), GO (Dai *et al.,* 2014), and RGO (Zhou *et al.,* 2012) has been applied in photocatalytic studies. ZnO semiconductor has wide gap band energy (3.37 eV) and a large exciton binding energy of 60 meV at room temperature. The n-type ZnO has high breakdown voltages and higher electron mobility and is stable thermally, chemically and at high energy radiation. Thus, coupling Fe_2O_3 with ZnO increases the catalysed-photoreaction of organics. The use of red mud (bauxite residue) as the precursor for iron oxide and doped with ZnO was conducted in a batch sonophotoreactor and is based on a hybrid advanced oxidation process (AOP) type sonophotocatalysis system.

The alumina industry frequently generates a bauxite residue of commercial value namely red mud (RM). On average, between 1 and 1.5 tonnes of red mud is generated for every tonne of alumina produced. Since the demand for alumina is increasing worldwide, the generation of red mud is estimated to be 4 billion tonnes by 2015 based on its current production rate (Zhu *et al.,* 2015). Every tonne of alumina produced roughly generates between 1 and 2 tonnes of dry bauxite residues, which varies according to the bauxite source and alumina extraction efficiencies (Kobya *et al.,* 2014). The nature of red mud depends on the ore source and the technological process parameters used for the production of bauxite. It consists of iron oxides, primarily hematite (Fe_2O_3), boehmite (AlOOH), and goethite (FeOOH), titanium oxides, calcium oxides, aluminium hydroxides, and sodalite (Antunes *et al.,* 2012). Chemical analyses showed that it also contains radionuclides (e.g. ^{40}K, ^{226}Ra, and ^{230}Th), as well as heavy metals such as Cd, Co, Cr, Ni and V (Mišík *et al.,* 2014). Due to its alkaline nature (pH 10.0-12.5) and the presence of

the chemical and mineralogical species, this solid waste causes a significant impact on the environment.

Storing red mud in large quantities, however, could prove to be hazardous. Studies have revealed that disposing of red mud in the sea has a significant impact on the aquatic ecosystem. The issues regarding the massive generation and subsequent disposal of red mud leading to negative impacts continue to be of global concern for the alumina industry, as well as the regulatory authorities. Therefore, proper disposal or treatment of waste red mud is necessary where alumina refinery plants are located. (Samal *et al.,* 2013; Liu *et al.,* 2011).

1.2 Problem Statement

Various investigators around the world are currently researching on red mud treatment and its utilisation. Countless attempts have been made to determine an environmentally safe method to dispose or utilise the red mud waste. In an attempt to redefine the usage of red mud, potential applications are being investigated and developed. Iron oxide as the major compostion of red mud has potential as a suitable sonophotocatalyst. However, the narrow band gap of iron oxide favors faster recombination of electron-hole pair which needs to be modified.

1.3 Objectives of This Study

i. To produce a novel ZnO/ARM composite material and evaluate this material for the sonophotocatalysis of RB5
ii. To efficiently characterise the prepared novel sonophotocatalyst using using XRD, FTIR, SEM, EDX, BET, DRS, and PL.
iii. To evaluate the effect of sonocatalysis, photocatalysis and sonophotocatalysis in the degradation of Reactive Black 5 in aqueous solutions.
iv. To conduct a parametric and kinetic study of photocatalytic degradation in regards to different catalyst dosage, initial dye concentration and solution pH.
v. To evaluate the synergism between sonocataysis and photocatalysis in the sonophotocatalysis of the target pollutant

1.4 Scope of the Study

In order to accomplish the above-mentioned objectives, the scope of the investigation will be set as the following.

i. Raw red mud was activated with CO_2 gas followed by ZnO impregnation
ii. The synthesised ZnO/ARM is characterised using XRD, FTIR, SEM, EDX, BET, DRS, and PL.
iii. RB5 was used as the target pollutant to study the sonophotocatalytic activity of synthesised ZnO/ARM
iv. Sonophotoreactor was designed with a Sonorex-R35 sonicator and UV-C lamp as the light source.
v. First order kinetic rate and synergistic effect were evaluated using respective formulae.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater from Textile Industry

The textile industry is the most polluting sector among the different human activities with high effluent discharge volume due to the water demanding nature of its industrial process. These effluents are then released into the water system with little or no treatment at all. The effluents usually consist high concentrations of dyes, surfactants, suspended solids and organic matter (Rodríguez *et al.,* 2009). Textile wastewater also includes aqueous discharges from fibre and fabric preparations, de-sizing, scouring, bleaching, dyeing, finishing and other textile processing stages. Most mills operate their wastewater treatment or pre-treatment plants to remove contaminants from effluent prior to discharge to receiving waters or publicly owned treatment works (Alaton *et al.,* 2006).

Textile industrial wastewaters have been of highest concern because they are characterised by a high colour and COD content with varying pH from 2 to12, discharging high amounts of dyes to water bodies like lakes and rivers (Ramirez *et al.,* 2013). According to Rodríguez *et al.,* (2009) the colour and structural integrity of dyes in textiles effluents are retained due to their design to persist under oxidising and reducing conditions, washing and light exposure. The structural varieties of dyes are acidic, basic, disperse, azo, diazo, anthraquinone based and metal complex dye. The municipal sewerage systems do not affect the decolourisation of textile dye when it is treated aerobically (Aouni *et al.,* 2012).

2.2 Wastewater Treatment

2.2.1 Conventional Method

Conventional methods such as membrane technology, filtration, coagulation and flocculation are available to treat the dye house effluent. Most of the conventional method becomes inefficient due to the complexity of the composition of dye house effluent (Mohan & Balasubramanian, 2006; Hisaindee et al., 2013). Membrane technology such as ultrafiltration, nanofiltration and reverse osmosis are the filtration methods that have been used for water reuse and the chemical recovery (Yanan *et al.,* 2011; Zheng *et al.,* 2013). The type and porosity of filter are determined by the chemical composition and specific temperature of wastewater (Verma *et al.,* 2012; Lee *et al.,* 2014). The dye removal from textile wastewater is efficient with the utilisation of membrane technology. However, disadvantages of membrane technology such as high cost, frequent membrane fouling, and requirement of different pretreatments depending upon the type of influent wastewaters (Suopajärvi *et al.,* 2013) thereby limits the application of this expensive technology for wastewater treatment (Verma *et al.,* 2012).

In water and wastewater treatment, coagulation and flocculation are applied for the removal of high concentration organic pollutants, heavy metals and some anions (Hamoud *et al.,* 2017; Li *et al.,* 2017). Chemical coagulation and flocculation is essential in removing the waste materials in a colloidal form that do not settle out on standing or may settle by consuming a long time. Dye removal via this pretreatment needs loading of chemical coagulants and optimal operation conditions such as pH and coagulant dosage (Zahrim and Hilal, 2013; Liang *et al.,* 2014). Low capital cost is the reason for this pretreatment has been used for many years. However, the production of the massive amount of chemical sludge and ineffectiveness in decolourising of some soluble dyes are the disadvantages of this pretreatment (Mezohegyi *et al.,* 2012; Verma *et al.,* 2012).

Another most popular method is adsorption technology. It produces a high-quality product and is economically feasible. This technique incorporates the two principal mechanisms of adsorption and ion exchange in the process of colour removal. The affinity of various dyes for adsorbents is influenced by physical and