PHOTODEGRADATION OF DYES IN BINARY SYSTEM USING TITANIUM DIOXIDE THROUGH STATISTICAL APPROACH

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By

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ABSTRACT

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Phoon Bao Lee

The photodegradation of Basic Blue 3 (BB3) and Congo Red (CR) by using TiO_2 from company MERCK was investigated in this study. The experiment was carried out in batch study and immobilisation method was used. The removal of these dyes was pH dependent. First order kinetic model was fitted well in this study with rate constant 0.0050, 0.0040, 0.0032 min^{-1} for concentrations 5, 15, 25 mg/L of BB3, respectively. For CR, the rate constant was 0.0035, 0.0031 and 0.0028 min^{-1} in 5, 15, 25 mg/L, respectively. A decrease in rate constant was observed when initial dye concentration is high. Four parameters were studied in this project, which are initial dye concentration and irradiation time, photocatalyst loading, pH and reusability. Photodegradation efficiency was found to be lower after each repetitive usage of TiO_2 glass tank. SEM was used to study the surface morphology and characterisation of photocatalyst. Plackett-Burman design was used to determine the most significant parameters in removal of studied dyes using TiO_2 photocatalyst. Response Surface Methodology (RSM) was used to study the interaction between variables and the optimum condition for maximum percentage removal of BB3 and CR in binary system. The R^2 for both models near to unity and the models were significant. The observed response was agreed well with the predicted

response. The optimum condition for BB3 was found to be in pH 10 and 5 mg/L initial concentration of dye with 77.06% removal was predicted under this condition. For CR, the optimum condition was found to be pH 6 and 5 mg/L initial dye concentration. The percentage efficiency was predicted to be 64.51% after 300 minutes of sunlight irradiation.

ABSTRAK

TiO_2 dari syarikat MERCK telah digunakan sebagai fotomangkin untuk membuat kajian fotodegradasi pewarna Basik Biru 3 (BB3) dan Kongo Merah (CR). Penyingkiran pewarna ini adalah bergantung kepada pH. Model kinetik kadar pertama bersetuju dengan projek ini. Bagi pewarna BB3, kadar tetap adalah 0.0050, 0.0040, 0.0032 min^{-1} untuk kepekatan 5, 15, 25 mg/L masing-masing. Manakala bagi pewarna CR, kadar tetap adalah 0.0035, 0.0031 and 0.0028 min^{-1} untuk 5, 15, 25 mg/L masing-masing. Penurunan kadar tetap berlaku apabilla kepekatan awal pewarna adalah tinggi. Empat parameter telah dikaji dalam projek ini, iaitu kesan kepekatan awal pewarna dan masa penyinaran, kesan amaun fotomangkin, kesan pH dan kesan gunapakai semula fotomangkin TiO_2. Kecekapan fotodegradasi didapati lebih rendah selepas setiap kali mengulang guna TiO_2. SEM telah digunakan untuk mengkaji morfologi dan pencirian fotomangkin. Plackett-Burman telah digunakan untuk menentukan parameter yang paling penting dalam penyingkiran pewarna dikaji dengan menggunakan TiO_2 fotomangkin. RSM telah digunakan untuk mengkaji interaksi antara pembolehubah dan keadaan optimum untuk peratusan penyingkiran maksimum BB3 dan CR dalam larutan pewarna binari. R^2 untuk kedua-dua model berhampiran perpaduan dan model ketara. Peratusan diperhatikan telah dipersetujui dengan baik dengan peratusan yang diramalkan. Keadaan optimum untuk BB3 didapati bahawa dalam pH 10 dan 5mg/L kepekatan pewarna awal, 77.06 % penyingkiran telah diramalkan di bawah keadaan ini. Untuk CR, keadaan optima ditemui pada pH 6 dan 5 mg/L kepekatan pewarna awal, kecekapan peratusan berkenaan akan menjadi 64.51 % selepas 300 minit pancara matahari.

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DECLARATION

I hereby declare that the project report is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

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(PHOON BAO LEE)

Date: ___________________

APPROVAL SHEET

This project report entitled — **"PHOTODEGRADATION OF DYES IN BINARY SYSTEM USING TITANIUM DIOXIDE THROUGH STATISTICAL APPROACH"** was prepared by **PHOON BAO LEE** and submitted as partial fulfilment of the requirements for the degree of Bachelor of Science (Hons) Chemistry at Universiti Tunku Abdul Rahman.

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PERMISSION SHEET

It is hereby certified that PHOON BAO LEE (ID No: 11ADB02989) has completed this final year project entitled **— "PHOTODEGRADATION OF DYES IN BINARY SYSTEM USING TITANIUM DIOXIDE THROUGH STATISTICAL APPROACH"** supervised by **Asst. Prof. Dr. ONG SIEW TENG** from the Department of Chemical Science, Faculty of Science.

I hereby give permission to my supervisor to write and prepare manuscripts of these research findings for publishing in any form, if I do not prepare it within six (6) months from this data, provided that my name is included as one of the authors for this article. The arrangement of the name depends on my supervisor.

Yours truly,

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(PHOON BAO LEE)

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LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Process
AO7	Acid Orange 7
BB3	Basic Blue 3
BG	Brilliant Green
CR	Congo Red
CSB	Chicago Sky Blue 6B
IC	Indigo Carmine
MB	Methylene Blue
MG	Malachite Green
MO	Methyl Orange
QY	Quinoline Yellow
RB5	Reactive Black 5
RhB	Rhodamine B
RO16	Reactive Orange 16
RO84	Reactive Orange 84
RR2	Reactive Red 2
Ag	Silver
Cu	Copper
Mn	Manganese
Pt	Platinum
Zn	Zinc

$OH^{\bullet}$	Hydroxyl Radical
CdS	Cadmium Sulphide
CO_2	Carbon Dioxide
H_2O	Dihydrogen Monoxide
H_2O_2	Hydrogen Peroxide
K_2PtCl_6	Potassium Hexachloroplatinate
SnO_2	Tin Dioxide
TiO_2	Titanium Dioxide
ZnO	Zinc Oxide
ZnS	Zinc Sulphide
AFM	Atomic Force Microscope
ANOVA	Analysis of Variance
BET	Brunauer-Emmett-Teller
CCD	Central Composite Design
LH	Langmuir-Hinshelwood
PB	Plackett-Burman
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
UV	Ultraviolet
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
R^2	Correlation Coefficient
pH_{zpc}	pH at Zero Point Charge

CHAPTER 1

INTRODUCTION

1.1 Environmental issue

In many countries, the issue of environmental pollution has been a great concern. Wastewater is one of the major pollution. Wastewater is the spent water after homes, commercial establishments, industries and public institutions which used waters for various purposes. The main source of those polluted water is normally from domestic as well as industries. Moreover, the growing of population and industrial expansion making the environmental problem become serious, especially in the developing countries.

Department of Environment (DOE) used Water Quality Index (WQI) to evaluate the status of the river water quality which according to six parameters: dissolved oxygen (DO), ammonia nitrogen, biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solid (SS), and pH.

Contaminants such as heavy metal, cyanide, toxic organics, nitrogen, phosphorous, phenols, suspended solids, colour and turbidity from the untreated sewage sludge, industries and domestics are becoming a major concern to the public health and environment.

The presence of colour in effluent is an environment issue of continuing problem for dyestuff manufactures, dyers, finishers and water companies. This is because the increasing stringent colour consent standard is being enforced by regulatory bodies to reduce the quantity of colour in effluent and water sources. As a result, Department of Environment has established interim national water quality standards for Malaysia. For example, the maximum contaminant level for colour is 15 colour units. The unit of measurement of colour is the K_2PtCl_6.

Table 1.1: Physical Characteristic of Wastewater and Their Sources

Physical Characteristic	**Sources**
Colour	○ Domestic and industrial wastes ○ Natural decay of organic materials
Odour	• Decomposing wastewater • Industrial waste
Solids	○ Domestic water supply ○ Domestic and industrial wastes ○ Soil corrosion ○ Inflow-infiltration
Temperature	• Domestic and industrial wastes

Source: (Cheremisinoff, 1995)

1.2 Dye

Colorant is the substances which imparts colour such as pigment and dye. Dyes contain chromophore (-C=N-, -C=O-, -C=C-, -N=N-, -NO_2 and quinone), and auxochromes (-OH, -COOH, -SO_3H and –NH_3) which cause or intensify the colour of the chromophore by changing the overall energy of the electron system. Dyes have an aesthetic effect because they are visible pollutants. It is detectable even though in low concentration (few ppm). There are various industries disposing synthetic organic dyes to the aqueous environments such as textile, clothing, dyestuff, leather, plastic, paper, food processing and cosmetic.

In textile industry, it consumes huge amount of water during the dyeing process. By considering both volumes discharged and effluent composition, textile industry wastewater is one of the highest polluting among the entire industrial sector. Approximately 1 – 20 % of the total world production of dyes is lost during the dyeing process and it has been released as effluents (Houas, et al., 2001).

Presence of organic dyes in aqueous environments is one of the critical environmental problems because the toxicity of organic dyes to aquatic life and low biodegradability in such environments. Many dyes are made from known carcinogens such as benzidine and other aromatic compounds. Antroquinone-based dyes are most hardly to undergo degradation due to their fused aromatic ring structure. Furthermore, the intense colour is able to attenuate the sunlight transmission into water. Hence, it can affect aquatic plants, which ultimately disturb aquatic ecosystem.

Currently, there are about 3000 types of dyes that marketed worldwide. Dyes can be classified to anionic, cationic and non-ionic. The classification of dyes and usage has shown in Table 1.2.

1.2.1 Basic Blue 3 (BB3)

Basic blue 3 (IUPAC name: 3,7-Bis(diethylamino)phenoxazin-5-ium chloride) is a water soluble cationic dye with molecular formula $C_{20}H_{26}ClN_3O$.

Basic dye is widely used in acrylic nylon and wool dyeing. The structures of dye generally embody aromatic with several functional groups. Basic dye can also cause skin irritation, allergic dermatitis, mutations and cancer (Khataee, Fatinia and Aber, 2011). Therefore, it is utmost important to remove this dye. Table 1.3 shows the details of BB3 dye.

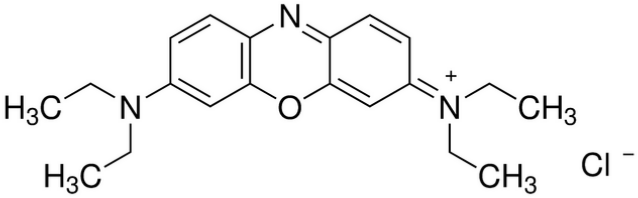
Cationic dye is high toxic than the anionic dye. It can react easily with the negatively charged cells membrane surfaces and get into the cells which will then gather in cytoplasm (Oseroff, 1986).

Table 1.2: Usage classifications of dyes

Class	Principal substrates	Method of application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather	Usually from neutral to acidic dyebaths	Azo, antraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine, henucyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxanine and anthraquinone
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, stilbene and oxanine
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, styryl, nitro and benzodifuranone
Reactive	Cotton, wool, silk and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxanine and basic
Solvent	Plastics, gasoline, varnishes lacquers, stains, inks, fats, oils and waxes	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone and phthalocyanine
Sulphur	Cotton and rayon	Aromatic substrate vatted with sodium sulphide and reoxidised to insoluble sulphur-containing products on fiber	Indeterminate structures
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilised by reducing with sodium hydrogensulphide, then exhausted on fiber and reoxidised	Anthraquinone (including polycyclic quinines) and indigoids

Source: (Hunger, 2003)

Table 1.2.1: Details of BB3

Dye	Basic Blue 3
Empirical formula	$C_{20}H_{26}ClN_3O$
C.I. number	51004
Dye content	25 %
Molecular weight	359.89 g/mol
Molecular structure	
λ_{max}	654 nm

1.2.2 Congo Red (CR)

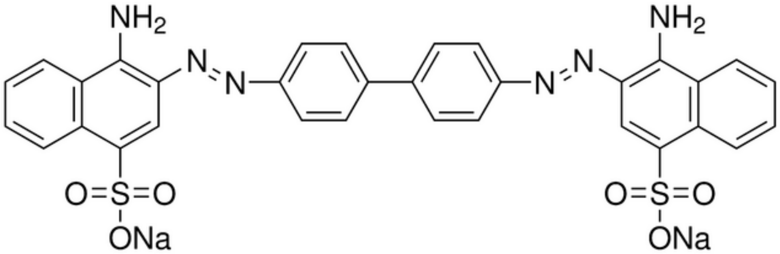
Congo Red, also named as “Direct Red 28”, (empirical formula $C_{32}H_{22}N_6O_6S_2Na_2$) is a water-soluble anionic dye which generally used as amyloid fibrils, and agricultural starch products. Some journal papers reported CR can be used to determine cooked and damaged starch grains in archaeological residues (Lamb and Loy, 2005).

CR is a diazo dye. It can also use in cellulose industries such as paper, wood pulp and cotton textile. Azo dye is an important class of synthetic, coloured and organic compound. Azo dyes are generally non-biodegradable because of their complex structures (Hashemian and Foroghimoqhadam, 2014).

CR was introduced by a young chemist Paul Böttiger in year 1884 from German. He was planning to synthesis a chemical which able to serve as pH indicator. Therefore, the first “direct” dye that did not require additional substances for fixation to the textile fibers was created. CR is in sulphonazo form in basic solution and chinone form in acidic solution, changing the colour from red to blue when decrease in pH.

CR is a benzidine based anionic dye. It is known to metabolise into benzidine, which suspected carcinogenic for human. Benzidine and CR were prohibited in many countries due to health concerns. However, it is still widely used in some countries. It was reported that brightly coloured dyes such as the shimmering CR commonly used in silk clothing manufacture are well known difficult for discharge to the environment (Sistla, et al., 2008). Hence, it is important to remove residual CR from water sources before discharge to receiving water bodies. Table 1.4 shows the details of CR dye.

Table 1.2.2: Details of CR

Dye	Congo Red
Empirical formula	$C_{32}H_{22}N_6Na_2O_6S_2$
C.I. number	22120
Dye content	91 %
Molecular weight	696.66 g/mol
Molecular structure	
λ_{max}	497 nm

1.3 Treatment of Wastewater Containing Dyes

In conventional methods of dye treatment, it has been classified to 3 categories, which are physical, chemical and biological.

i. Physical treatment methods normally include filtration, ion exchange, and membrane process. This physical treatment was the first method that applied in wastewater treatment due to it is derived from the human's first observations of nature. It uses physical force to remove pollutants.

ii. Chemical treatment methods involve the usage of chemicals, normally reducing agents, oxidizing agents, coagulants and other chemicals will be added, for example, chlorination by adding $Cl_{2,}$ precipitation-flocculation with $Fe(II)/Ca(OH)_2$, and O_3 is used for ozonation. The chemical techniques are often expensive. Although the dyes can be removed but it will build-up sludge and creates a disposal problem.

iii. For biological treatment process, it uses bacteria or microorganisms to remove the biodegradable substances. For example fungal decolourisation, bioremediation system, microbial degradation and adsorption by living or dead microbial biomass. These few methods are commonly applied to treat industrial effluents due to various kinds of microbes such as bacteria, yeasts, algae and fungi are able to gather and degrade different pollutants (Ong and Seou, 2013). Nonetheless, at certain condition, biological treatment is not favourable due to it need a large area and hardly to function well when in extreme pH.

However, some of the techniques mentioned above were non-destructive. It only transfers the non-biodegradable matter to become sludge, introducing of new type of pollution which requires undergoing post-treatment (Bansal and Sud, 2011). Therefore, attention has been focused on investigate an economic and alternative way to treat dye effluents.

1.4 Advanced Oxidation Process (AOP)

Advanced Oxidation Process (AOP) is currently being developed for remediation of contaminated organic effluent. This process is prefers because of no hazardous sludge is generated. It is to generate highly reactive species namely hydroxyl radicals ($OH^\bullet$) to oxidise the organic pollutants. So, it is able to remove industrial wastewaters and convert into non-toxic end product such as CO_2, H_2O and mineral acids (Barka, et al., 2010). APO has a few advantages over conventional methods such as complete mineralisation of pollutants, biologically and chemically inert, recyclable, and less energy consumptions.

1.4.1 Photodegradation

Photodegradation is a kind of AOP. This method used semiconductor as photocatalyst and the presence of light with suitable wavelength is required. In order to apply semiconductor photocatalysts for wastewater treatment, some of the criteria must be fulfilled (Akpan and Hameed, 2009):

i. Operation condition needs to be performed at room temperature/pressure
ii. Complete mineralisation without producing secondary pollution
iii. Able to use repetitively and low cost of operations

1.5 Types of photocatalyst

Under photocatalytic reaction, band gap of semiconductor energy with higher energy is used to emit light inside the semiconductor and induce a reaction with the pollutants onto its surface via redox reaction. All semiconductors can be used as photocatalyst due to the characteristic of filled valence band (VB), and an empty conduction band (CB).

1.5.1 Zinc Oxide (ZnO)

ZnO powder is white colour and insoluble in water. It is widely used as paints, lubricants, cement, ceramic, glass and so on. ZnO can absorb UV irradiation at below 385 nm. ZnO has the similar band gap energy with TiO_2; the photocatalytic capacity is expected to be about the same. However, for ZnO, photocorrosion often happens with the illumination of UV light, leading to a decrease of photocatalytic activity in aqueous solution (Barnes, et al., 2013).

1.5.2 Cadmium Sulphide (CdS)

CdS is a yellowish powder under room temperature. It occurs as two kinds of crystalline structures, hawleyite and greenockite. It has a small band gap of 2.42 eV, and its valence electron can easily excited to conduction band under irradiation of visible light at 495 nm. One of the disadvantages for CdS is high photocorrosion in aqueous media and low photogenerated electron-hole pair separation efficiency. As a result, CdS normally will combine with others semiconductor to minimize the drawbacks (Duan, et al., 2014).

1.5.3 Tin Dioxide (SnO_2)

SnO_2 is a white powder. Cassiterite is the main form of it. It widely use in glass coating, polishing, gas sensing and ceramic industry. SnO_2 has a large band gap (approximately 3.6 eV) and no light absorption above 330 nm. Therefore, under visible light, the photocatalytic activity is limited. In fact, SnO_2 is low in quantum efficiency. Besides that, the photocatalytic activity of SnO_2 is restricted by the rapid recombination of photogenerated electron and hole pairs (Vignesh, et al., 2013).

1.6 TiO_2 as photocatalyst

The efficiency of immobilised TiO_2 in removal organic synthetic dyes for pollution prevention will be report in this study. It is widely used in dye removal as well as other organic compounds.

TiO_2 is chosen as photocatalyst are based on two factors:

i. Industrially mass-produced material which easy to obtain and inexpensive.
ii. Chemically and photochemically stable, safe, non-toxic and non-photocorrosion.

TiO_2 has a strong oxidising power; it has a band gap 3.2 eV. An n-type semiconductor of TiO_2 is irradiated with light of wavelength below 390 nm and the electron-hole pair is produced. The generated electron-hole pairs are capable of initiating reduction and oxidation reaction on the surface of TiO_2 particles. In aqueous solution, the holes are scavenged by surface OH groups to generate the strongly oxidising hydroxyl radicals ($OH^{\bullet}$). Later, the reactive $OH^{\bullet}$ will react quickly with organic dyes leading to the mineralisation of the organic dye (Zainal, et al., 2005). The reaction between photocatalyst surface and dyes can expressed as below (Akpan and Hameed, 2009):

$TiO_2 + h\nu \rightarrow TiO_2(e_{CB}^- + h_{VB}^+)$ (1)

$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet$ (2)

$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet$ (3)

$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{-\bullet}$ (4)

$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet$ (5)

Dye + $OH^\bullet$ → degradation products (6)

Dye + h_{VB}^+ → oxidation products (7)

Dye + e_{CB}^- → reduction products (8)

where hν is the energy of photon needed to excite TiO_2 electron from the VB region to CB region.

Apart from environmental, TiO_2 photocatalyst also use in photocatalytic purification of food and medicine. In contrast, some other semiconductors cannot be used due to it may dissolve and produce toxic by-product during the photocatalysis process.

1.6.1 Immobilisation study

Immobilisation method is developed to save the extra cost for separation of photocatalyst as well as simplify the purification procedure (Chen, Wang and Lou, 2004). Besides that, it helps to fulfil one of the crucial criteria, which is attaching the dye on the surface of TiO_2 for an effective photosensitisation to occur. Since photocatalysis is mostly take place on the surface of photocatalyst, therefore, the surface area need to be increased to maximize the photodegradation rate.

1.7 Statistical Approach

To determine the optimum condition, conventional method is time consuming because it may need to conduct more experiments. On top of that, conventional method does not ensure the optimum condition will be found out (Rajendran, et al., 2007). In addition, investigating a process by maintain other parameters involved at non-specific fixed level by using conventional method does not describe the combined effect of all the parameters concerned (Ravikumar, et al., 2006) Therefore, Plackett-Burmann (PB) design and Response Surface Method (RSM) were introduced to improve the conventional method to determine optimum condition.

1.7.1 Plackett-Burman (PB) design

Plackett-Burmann design is to find out the significant parameters for further optimisation. It provides unbiased estimation for all parameters with high accuracy for a given number of observations (Rajendran, et al., 2007). Moreover, it brings several benefits of utilising factorial design to increase the efficiency; each variable is screened in the presence of all other variables, as different to conventional methods, and reducing the number of experiments as the number of experiments in conventional method is usually numerous (Motola and Agharkar, 1992).

1.7.2 Response Surface Methodology (RSM)

RSM is to optimise all the affecting variables collectively (Murat, 2002). The goal of RSM is to identify the best conditions of the experiment (Myers and Montgomery, 2002). On top of that, this method has a lot of benefits such as economical, reducing number of experiments, studying the relationship between parameters, predicting the result, and checking the adequate of method. Thus, investigation of dyes photodegradation using RSM is important.

1.8 Objectives

The aims of this project are:

- To identify the effect of various parameters on removal BB3 and CR by using TiO_2.
    - Effect of initial dye concentration and irradiation time
    - Effect of catalyst loading
    - Effect of pH
    - Effect of repetitive usage and recycle of coated TiO_2

- To identify the influential parameters in affecting the dyes removal by using the Plackett-Burman (PB) design and Response Surface Method (RSM).

- To study the surface morphology of TiO_2 before and after photodegradation process.

1.9 Scope of study

Dye contaminants are present in wastewater from many industries such as textile, paper, printing, food processing and cosmetic. Dye removal has become a serious environmental concern because of its toxicity. Titanium Dioxide is a large available photocatalyst which could be used for photodegradation of dye in wastewater. Therefore, this study focused on the photodegradation capabilities of immobilised Titanium Dioxide to remove dyes under various conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Immobilisation method

Immobilisation method was introduced in photodegradation study. This is because immobilise TiO_2 can save the extra cost to separate TiO_2 photocatalyst after irradiation. Under TiO_2 dispersion method, most of the time, the mixture of dye and TiO_2 is need to undergo centrifugation and filtration before measure the absorbance by using UV-Vis spectrophotometer. Gupta, et al. (2012) done the study of removal quinolone yellow (QY) by using TiO_2 photocatalyst. The photocatalyst was dispersed into photocatalytic reactor and mixed with dye solution. Although it has a good percentage removal within few hours, however, the mixture of TiO_2 and dye is needed to centrifuge for about 15-20 minutes after irradiation. Besides that, the solution sometimes still contains TiO_2 suspension after centrifuge, which may affect the reading of UV absorbance.

There are many kind of immobilisation method which introduce by different journal papers. Most of the time, to introduced immobilisation method, a few factor which need to consider, which are, cost, simple and reusability. Lee, et al. (2013) studied the removal of Malachite Green (MG) by photodegradation. In this study, TiO_2 was immobilised on glass plates $(2.5'' x\ 1.0'' x\ 0.1'')$. Six TiO_2 coated glass plates were used in each experiment set up. The TiO_2 photocatalyst was immobilised on glass plate and the maximum removal efficiency can reach up to 100 % under presence of sunlight.

Therefore, this indicates that the immobilisation method is suitable for photodegradation process.

Andronic and Duta (2008) conducted a photodegradation study of Methyl Orange (MO). Authors mentioned that TiO_2 films can prepare by many methods, for example, spray coating, spin coating, chemical vapour deposition, and magnetron sputtering. However, thin film of TiO_2 was prepared by doctor blade coating technique in this study due to it is a fast, easy and non-energy consuming even in mass production.

The study of photodegradation of azo pyridine dye using TiO_2 films was conducted by Dostanić, et al. (2012). Spray pyrolysis method was used to prepare the TiO_2 films due to it may save the production cost. Authors reported that thickness of films may affect the photodegradation rate due to increase in amount of photocatalyst.

2.2 Modification of TiO_2 photocatalyst

The unmodified Degussa P-25 TiO_2 powder is 80 % anatase form, 20 % rutile form with the particle size of 30 nm and 50 m^2/g BET surface area. Many researchers studied on removal dyes by using the unmodified TiO_2. In order to improve the photodegradation efficiency, modified TiO_2 has becoming a great concern to remove organic dyes. There are few ways to modify TiO_2 photocatalyst, such as thermal modification and chemical modification.

According to Dostanić, et al. (2012), the TiO_2 films was undergo thermal treatment and it was notice that by increase the temperature of calcination from 500 to 700°C, the photocatalytic activity will lost. This is because the anatase form of TiO_2 is converted to rutile form, consequent to reduce the specific surface area and porosity and increase in crystalline size. Apart from that, the interaction between anatase and rutile phase may leads to fast e^-/h^+ recombination, another reason for decrease in photocatalytic activity.

Chen, Wang and Lou (2004) conducted a study on photodegradation Acid Orange 7 (AO7) under visible light irradiation. In this study, the TiO_2 was supported by SiO_2. The (TiO_2/SiO_2) was prepared by acid-catalysed sol-gel method. The modified photocatalyst were characterised by BET analysis to determine surface area and pore volume, whereas XRD was used to identify the crystalline structure, and pH_{zpc} measurement was done by using mass titration method. By rising the calcination temperature, the BET surface area drop linearly. The study was fit to kinetic first order. One of the parameter in this study is to make comparison between TiO_2/SiO_2 and pure TiO_2 (Degussa P-25). Authors found that photocatalyst TiO_2/SiO_2 after calcinated at 300°C have larger surface area and great adsorption compared to the unmodified TiO_2, the photodegradation rate is fastening by 2.3 times.

Senthilkumaar, Porkodi and Vidyalakshmi (2005) used sol-gel derived TiO_2 as photocatalyst. It is a nanocrystalline TiO_2 and 100 % anatase titania which prepared by sol-gel method. Titanium (IV) butoxide was mixed with glacial acetic acid, it was dried, calcined under temperature 500°C, and the nanocrystalline TiO_2 was finally formed. Nanocrystalline TiO_2 was preferred in this study due to smaller size of particles and larger surface area over volume. The average crystalline size was found to be 12 nm and the surface area of nanocrystalline is 128.2 m^2/g.

Munusamy, Aparna and Prasad (2013) studied the effect of dopants of TiO_2 on photodegradation of Brilliant Green (BG). The TiO_2 was doped with Cu and Zn. Under SEM analysis, it showed that TiO_2/Cu has more porous structure than the unmodified TiO_2. Authors mentioned that highly porous structure may attribute to prevention of TiO_2 aggregation. TiO_2/Zn has similar structure with unmodified TiO_2. These three types of photocatalysts were then undergoing testing of photodegradation efficiency. Highly porous TiO_2/Cu does not have better efficiency. This may because presence of metal ions retards the photodegradation rate. Besides that, authors mentioned that not every dopants able to enhance the photodegradation rate due to different positions of the dopant in lost lattice.

Sharma, et al. (2008) also studied the doping effect of TiO_2. Authors used Mn doping by different amount, which are 0, 2, 5, 8 and 10 mol %. After that, it was tried on experiment by photodegrade Methylene Blue (MB). Authors commented that Mn doped TiO_2 are more photoactive than the undoped one, and it is based on three reasons:

i. Improve in life time of photogenerated charge carriers.
ii. More adsorption due to the charged crystalline surface.
iii. Small crystalline size and large surface area.

2.3 Previous study photodegradation of dye

Study on removal dyes using photodegradation method was conducted by many researchers. Most of it is focus on removal single dye. For example, Guo, et al. (2012) studied on removal Congo Red (CR) dye by using sulfailic acid-modified TiO_2, Lee, et al. (2013) studied on removal Malachite Green (MG) using unmodified TiO_2, Mahadwad, et al. (2011) studied on removal Reactive Black 5 (RB5) by using modified TiO_2. Table 2.3 shows the summary of the work done by various researchers in photodegradation of dye.

Nonetheless, removal of binary dyes is becoming a great concern nowadays. This is because in wastewater, it may contain more than one type of dyes in it. So, in terms to remove mixed dye from industrial effluent, removal of binary dyes is studied.

Juang, Lin and Hsueh (2010) studied removal of binary dyes under UV light photodegradation. The photodegradation efficiency of single dye was tried initially. For single dye, the photodegradation rate is faster than binary dye. For binary dye, different ratio concentrations of both dyes was tried, which are, 1:1, 2:1 and 1:2 ratio of Acid Orange 7 (AO7) and Reactive Red 2 (RR2).

Table 2.3: Summary of the work done by various researchers in removal different dyes using photodegradation method.

Photocatalyst	Light irradiation	Dye	Percentage removal (%)	Reference
CdS	Xenon	CR MB	84.0 51.0	(Li, Zhu and Li, 2012)
$(TiO_2/SiW_{12})_8$	Visible	MO	95.5	(Niu and Hao, 2014)
SnS_2	Xenon	CR RhB	90.0 10.0	(Li, Zhu and Li, 2012)
TiO_2 modified by acid catalyst sol-gel	Fluorescent	MB MO IC CSB	90.3 98.5 92.4 60.3	(Zainal, et al., 2005)
TiO_2 impregnated ZSM-5	UV	RB 5	89.4	(Madhadwad, et al., 2011)
Milennium PC-500 TiO_2	UV	BB3	N/A	(Khataee, Fathinia and Aber, 2011)
Degussa P-25 TiO_2	Visible	RO 84 RB 5 RO 16	47.0 66.0 59.0	(Chatterjee, et al., 2008)
Degussa P-25 TiO_2	Sunlight	MG	100.0	(Lee, et al., 2013)
Degussa P-25 TiO_2	UV	Procion Blue HERD	99.78	(Bansal and Sud, 2011)
Degussa P-25 TiO_2	UV	QY	92.6	(Gupta, et al., 2012)
TiO_2/SiO_2	Visible	AO7	99.0	(Chen, Wang and Lou, 2004)

Zainal, et al. (2005) studied the photodegradation efficiency in mixture of dyes. Mixture of dyes is usually difficult to undergo photodegradation. Therefore prolong of irradiation time may needed. Besides that, each of the dye have own characteristics in binary system. Thus, longer time for photodegradation is required. On top of that, authors mentioned when two dyes mixed together, the initial concentration is two times higher than the single dye. So, higher concentration may be another factor to make it difficult to undergo photodegradation.

2.4 Other semiconductor use as photocatalyst

A study of TiO_2, ZnO and nanobimetallic silica catalysed photodegradation of Methyl Green (MeG) was conducted by Senthivelan, et al. (2013). In this study, authors made comparison between the 3 photocatalyst. The nanobimetal silica is Ag and Pt doped silica sol-gel powder (SiO_2-Ag/Pt). The mechanisms of photocatalytic effect of those photocatalyst were discussed in this journal and ZnO and TiO_2 was found have the similar mechanism. However, silica sol-gel powder has better photodegradation efficiency.

Kansal, Singh and Sud (2007) studied the photodegradation efficiency by using different photocatalyst. TiO_2, ZnS, CdS, ZnO and SnO_2 were tested on the Rhodamine 6G (Rh6G) and Methyl Orange (MO). This study found ZnO has the better photodegradation efficiency due to it having bigger quantum efficiency than other photocatalyst and ZnS has the lowest efficiency. Table 2.5 shows the details of some semiconductors:

2.5 Photodegradation parameters

Under photodegradation study, there are few parameters is crucial, which are effect of initial dye concentration and irradiation time, effect of pH, and effect of photocatalyst loading. Most of the journal study will conduct these 3 parameters because it can tell the best conditions for photodegradation of dye. Apart from the 3 parameters, Lee, et al. (2013) studied the effect of light source parameter. Authors mentioned that light source is an indicator to assess the operating cost and photodegradation efficiency. Three types of light sources were used in the parameters, which are UV lamp, fluorescence lamp and sunlight.

Table 2.5: Band positions semiconductor photocatalysts in aqueous solution at pH 1.

Semiconductor	Valence Band	Conductance Band	Band Gap (eV)	Band Gap Wavelength (nm)
TiO_2	+ 3.1	- 0.1	3.2	387
SnO_2	+ 4.1	+ 0.3	3.9	318
ZnO	+ 3.0	- 0.2	3.2	387
ZnS	+ 1.4	- 2.3	3.7	335
CdS	+ 2.1	- 0.4	2.5	496

Source: (Kansal, Singh and Sud, 2007)

Senthikumaar, et al. (2005) studied the effect of H_2O_2 on photodegradation. The concentration of H_2O_2 will affect the photodegradation rate. This is because addition of H_2O_2 will increase the $OH^\bullet$ radical. Moreover, authors mentioned that H_2O_2 acts as two functions in the photodegradation system, which is forming $OH^\bullet$ radical as well as accepts photogenerated conduction band electron and therefore promotes the charge separations.

Niu and Hao (2014) studied the effect of surfactant and inorganic salts on the photodegradation of organic dyes. In textile industry, the major role of surfactant is to increase the solubility of dyes in water, to improve the dye-uptake and dye fastness, and to reduce the dyeing temperature. Therefore, the industrial dye waste may contain other auxiliaries like inorganic salts and surfactants, which might affect the efficiency of dye treatment. $(TiO_2/SiW_{12})_8$ was used as photocatalyst in this study. Besides that, three surfactants, SDS (Sodium Dodecylsulphate) and Polyoxyethylene Dodecyl Ether (PDE) and Dodecyltrimethylammonium Bromide (DTAB) were tried in different concentration. According to the outcome, PDE enhanced the photodegradation efficiency. This is because the extra lone pairs of electrons from surfactant can form weak complex with SiW_{12} and reduce the electrostatic repulsion between negatively charged catalysts and MO dye. However, high concentrations of SDS lower the photodegradation efficiency of MO due to the interaction between dye and anionic surfactant SDS, causing MO becomes inert to react with photocatalyst. Cationic surfactant DTAB will form white precipitate with MO dye at low pH. This may due to formation of complexation between cationic surfactant and dye.

Under the same journal paper, effect of inorganic salts was done by adding Sodium Chloride (NaCl) and Sodium Sulphate (Na_2SO_4) on the dye solution. Niu and Hao (2014) mentioned that presence of inorganic salts can cause the inhibition effect on degradation of MO dye. This often explained by the scavenging of $OH^\bullet$ radicals by anionic ions. Na_2SO_4 bring the higher inhibition effect for the photodegradation process. This might because the sulphonic group promotes dye aggregation or association in water.

2.6 Characterisation Study on Photocatalyst

The characterisation and surface morphology on photocatalyst can be done by several kinds of instrument. A SEM analysis was done by Mahadwad, et al. (2011). This SEM studies have shown the modified photocatalyst is different from the original photocatalyst in terms of shape and size. An AFM investigation was performed by Niu and Hao (2014). It is to obtain the detailed information regarding the surface morphology and homogeneity of multilayer films. The surface of photocatalyst can be present by AFM image in 2-dimensional and 3-dimensional way, so that can determine the roughness and size of particles.

X-ray crystallography method can be used to identify the arrangement of TiO_2 of a crystalline solid in 3-dimensional space. Munusamy, et al. (2013) used XRD to determine the XRD patterns of doped TiO_2 and undoped TiO_2. Based on the intensity of diffraction, it can be seen that all samples is in anatase form and the doped TiO_2 do not change the crystal form of TiO_2.

Besides that, Dostanić, et al. (2012) carried out the XPS measurements to determine the chemical state and composition of a material. XPS measurement is suitable for chemical modified photocatalyst such as metal doped TiO_2, as to identify the elemental composition and the empirical formula of modified photocatalyst.

2.7 Study the photodegradation intermediates

Erdemoglu, et al. (2008) studied the product of intermediates by using LC-MS technique. The intermediates identified by interpret mass spectra data presenting their molecule ion peaks with respect to *m/z*. CR dye is study in this journal paper. According to this journal, photodegradation of CR dye is based on four steps:

i. Cleavage of aromatic ring.
ii. Cleavage of C-S bond between benzene ring and sulphonate groups.
iii. Cleavage of various C-N and C-C bonds of the chromophore group.
iv. Cleavage of N=N double bond.

2.8 Optimisation study

Zuorro, Fidaleo and Lavecchia (2013) conducted a study of removal Reactive Green 19 (RG19) by UV/H_2O_2 process and RSM was used for analysis. Four parameters were considered. CCD matrix and RSM was applied to evaluate the interactive initial dye concentration effect, amount of H_2O_2, irradiation time and pH. The factor level is -2, -1, 0, +1 and +2. Total 31 sets of experiment were generated from this design, it was run and the percentage removal was recorded. In order to assess the validation of RSM, comparison between observe value and predicted value was done and it is in good agreement with the predicted values fell into 95 % prediction intervals.

Cho and Zoh (2007) studied on photodegradation of Reactive Red 120 (RR120) in TiO_2/UV system. It also undergo optimisation study, which used response surface methodology (RSM) based on the central composite design (CCD). The effect of TiO_2 concentration, initial concentration of dye and light intensity were studied using CCD method. After running the 20 experiments of CCD, it was found that initial concentration of dye was the most significant. The optimise condition was found to be 1.63 g/L TiO_2 photocatalyst loading, concentration 45.2 mg/L of dye, and 8.1 mW/cm^2 of UV intensity and it able to attain 100 % removal. Surface and contour plots are plotted to show the relationships between the variables. Besides that, main effect plot was plotted to analysing data with respect to important factors which have 2 or more levels.

2.9 Adsorption-Photodegradation study

Zainal, et al. (2009) incorporated photodegradation and adsorption method to remove monoazo dye. In photodegradation, TiO_2 was used. For adsorption, chitosan was used. A 1:1 ratio of TiO_2 and chitosan were mixed together and immobilised on a glass plates, and it was undergo 100°C of oven drying. Fluorescent light was used as light source in this study. Under XRD analysis, 3 dip-coated layers give the smallest crystalline size of TiO_2, which about 6 nm whereas 5 dip-coated layers give the largest crystallite size, 18 nm. Smaller crystallite size may have higher surface area. Under SEM analysis, the number of TiO_2 particles is increasing by increase the dip-coating. Also, it was suggested that the coating layer should not exceed 4 layers due to the penetration of light may be blocked. The kinetic study obeyed to Langmuir-Hinshelwood. The authors suggested that different ratios of TiO_2 and chitosan can try for further study.

2.10 Photodegradation study on other organic compounds

Apart from organic dye, photodegradation study can also apply for volatile organic compounds (VOCs). (Lee, Azelee and Ali, 2012) studied the photodegradation of benzene-toluene-xylene (BTX) mixture in aqueous phase by using ZnO photocatalyst. The experiment was tried in 3 different set up, which are

i. Presence of photocatalyst and light source.
ii. Presence of light source but absence of photocatalyst.
iii. Presence of photocatalyst but absence of light source.

The photodegradation efficiency was found approximately 30 % in after 210 minutes irradiation with presence of UV light and photocatalyst. This indicates that both photocatalyst and light source must present in order to undergo photodegradation process.

Photodegradation of bisphenol A (BPA) by using $H_3PW_{12}O_{40}/TiO_2$ was done by Lu, et al. (2013). The intermediates and the pathways of degradation were analysed by using mass spectrometer. First order of kinetic model was obey in this study. The percentage removal was up to 75 %. Besides that, reusability of photocatalyst is studied in the research and it was found the photocatalyst can reuse up to 10 times. Mineralisation and toxicity test was done in this study in order to test the oxidising ability of the photocatalyst which could to degrade the BPA into non-toxic CO_2 and H_2O.

CHAPTER 3

MATERIALS AND METHOD

3.1 Preparation of photocatalyst

Titanium dioxide, TiO_2 was selected as photocatalyst in this study. TiO_2 powder (mainly anatase form, mean the particle size of 30 nm, BET surface area of 50 m^2/g) was purchased from MERCK.

3.2 Preparation of dye

The dyes being studied were Basic Blue 3 (BB3) (C.I. = 51004) and Congo Red (CR) (C.I. = 22120). Both dyes were purchased from Sigma-Aldrich (M) Sdn. Bhd. and used as received without further purification. For each dye, 100 mg/L of standard dye solution was prepared as stock solution and afterwards diluted when needed. All prepared dye solutions were kept in dark to prevent light degradation.

3.3 Batch Studies

3.3.1 Immobilisation of TiO_2 on glass tank

TiO_2 suspension was prepared by dissolving 5 g of TiO_2 in 50 mL of 99.9 % methanol solution. The mixture was stirred continuously until all the TiO_2 powders were uniformly dispersed. The TiO_2 was coated at inner surface of glass tank (15 cm x 15 cm x 11.5 cm) by using brush. The initial weight and final weight of glass tank were weighed to calculate the amount of TiO_2 coated.

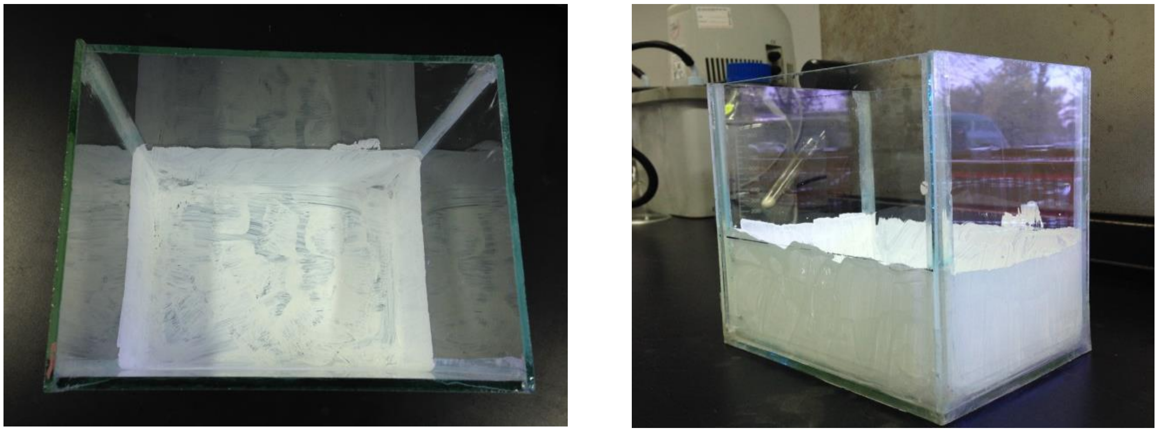


Figure 3.1: Glass tank coated with TiO_2 (Top view and Side view)

3.3.2 Batch experiments

Irradiation experiments were carried out by using 1000 mL of 15 mg/L of mixture dye solution (BB3 and CR) without changing its pH in a glass tank which coated with TiO_2. For each experimental run, the weight of immobilised TiO_2 used was maintained at approximately 1.0 g. Aeration was provided by bubbling air into the reaction solution by an air pump to ensure a constant supply of oxygen. All experiments were carried out under the similar conditions. All experiments were repeated and average results were presented with relative standard deviation (RSD) less than 5 %. At given intervals of irradiation, approximately 10 mL of the solution was withdrawn from the reservoir and the dye concentration in the solution was determined using Dynamica SB-10 UV/Vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum adsorption; for BB3, λ_{max} = 658 nm; for CR, λ_{max} = 510 nm.

The percentage removal of dyes is calculated using equation 3.1:

$$\text{Removal (\%)} = \frac{(C_o - C_t)}{C_o} \text{ x } 100\ \% \qquad [3.1]$$

where C_o = Initial concentration of dye (mg/L)

C_t = Concentration of dye at time t (mg/L)

3.3.3 Effect of initial dye concentration and irradiation time

The effect of initial concentrations of dye and irradiation time was investigated using 1000 mL of dye concentration of 5, 15, 25 mg/L. The samples were withdrawn and analysed for their dye concentrations at predetermined intervals 0.5, 1, 2, 5, 10, 15, 30, 60, 120, 180, 240 and 300 minutes.

3.3.4 Effect of photocatalyst loading

The study on the effect of photocatalyst loading on the photodegradation efficiency was carried out by varying the mass of TiO_2 coated. The mass of TiO_2 coating studied was 0.2, 0.5, 1.0 and 3.0 g. The volume of dye solution used was 1000 mL. The initial dye concentration was used as 15 mg/L and the final concentration was measured after 300 minutes.

3.3.5 Effect of pH

The effect of pH on the photodegradation of mixture of dye was tudied from pH ranging 6-10. The desired pH value was adjusted by dropwise addition of hydrochloric acid (HCl) and sodium hydroxide (NaOH), prior to the experiment. The initial dye concentration was used as 15 mg/L and the final concentration was measured after 300 minutes.

3.3.6 Effect of repetitive usage and recycle of coated TiO_2

The effect of repetitive usage was studied by repeating the experiment using the same glass tank. The TiO_2 glass tank was rinsed with distilled water and stored in dark area after each usage. After recycling, the TiO_2 glass tank was reused in order to study the efficiency of the recycled TiO_2 glass tanks in the subsequent photodegradation process.

3.4 Optimisation of dye photodegradation

3.4.1 Plackett-Burman (PB) design

Plackett-Burman design was used to assess the effect of several variables which affect the removal efficiency of dyes. In this study, 3 assigned variables (pH, initial dye concentration, and photocatalyst loading) were screened in 12 experimental designs.

3.4.2 Response Surface Methodology (RSM) analaysis

RSM was used for optimisation study. Those variables studied were obtained from the result of Plackett-Burman study and the percentage removal of dye was optimised using quadratic equation. All the experimental designs are tested by Design Expert Version 7.1.3 software. Statistical analysis of the data was carried out using the same software.

3.5 Instrumental analysis

3.5.1 Scanning Electron Microscope (SEM)

The surface morphology of TiO_2 before and after photodegradation was studied using SEM which equipped with energy dispersive X-ray Spectrometer (SEMEDX)-JOEL JSM-6400.

CHAPTER 4

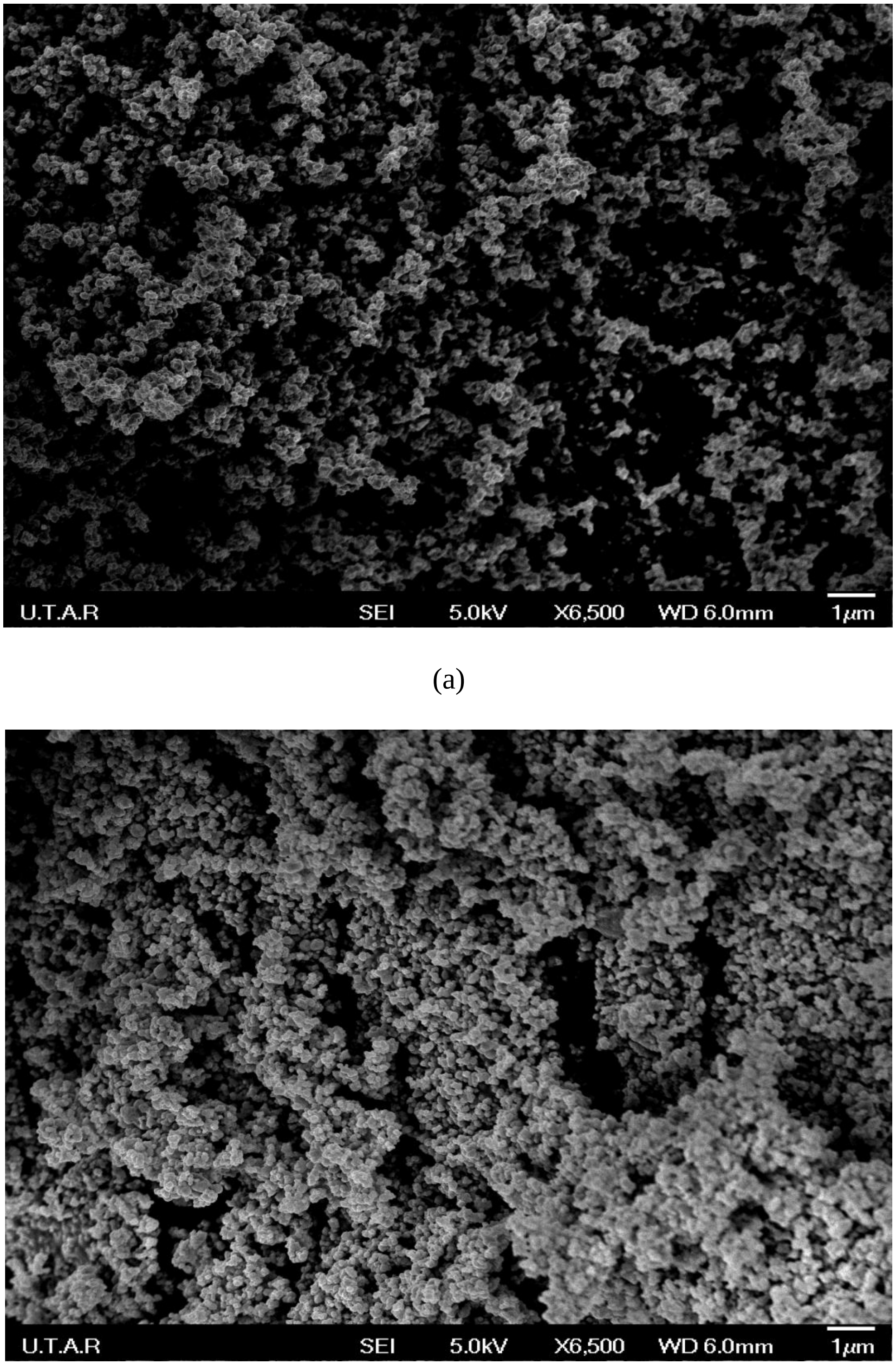
RESULT AND DISCUSSION

4.1 Characterisation of photocatalyst

4.1.1 Scanning Electron Microscope (SEM) Studies

Scanning electron microscope was used to study the surface morphology of TiO_2. Figure 4.1.1 (a) and (b) presented the SEM images of the TiO_2 before and after undergo photocatalysis with BB3 and CR dye.

Based on Figure 4.1.1 (a) and (b), both SEM micrographs are look similar in terms of shape and size. However, by comparing both SEM micrographs, Figure 4.1.1 (a) looks less compact but Figure 4.1.1 (b) shows high in compactness. This may due to after undergo photodegradation, some dye molecules (BB3 and CR) is adhere to the TiO_2 and this can be further verify using AFM.



(a)

(b)

Figure 4.1.1 SEM micrograph of TiO_2 (a) Original MERCK TiO_2, (b) TiO_2 after undergo photodegradation with BB3 and CR

4.2 Effect of initial concentration and irradiation time

The main goal to study the initial concentrations and irradiation time effect is to identify the equilibrium time for maximum photodegradation. Figure 4.2 (a) and (b) presented the photodegradation efficiency of BB3 and CR, respectively. Three different concentrations were studied, which are 5, 15 and 25 mg/L for both dyes. It was noticed the percentage removal increase by prolonging the irradiation time.

According to the Figure 4.2 (a) and (b), for both BB3 and CR, lower dye concentration has better efficiency compare to the higher concentration of dye. A 5 mg/L of BB3 was able to achieve 78.64 % of removal within 300 minutes whereas 25 mg/L have 63.35 % of removal under the same condition. Besides that, 5 mg/L of CR can reach 66.95 % of removal but 25 mg/L concentration of CR have only 60.61 % under irradiation of sunlight.

With increasing the initial dye concentration, more dye molecules was adsorbing on the surface of TiO_2. However, due to fixed amount of TiO_2 and low light penetration, dye molecules are not undergoing degradation immediately. Moreover, high concentration of dye solution leads to high intensity coloured, the path length of photons entering solution is lower and therefore insufficient photons reach the TiO_2 surface. This can explain why high concentration of dye will lower the photodegradation efficiency.

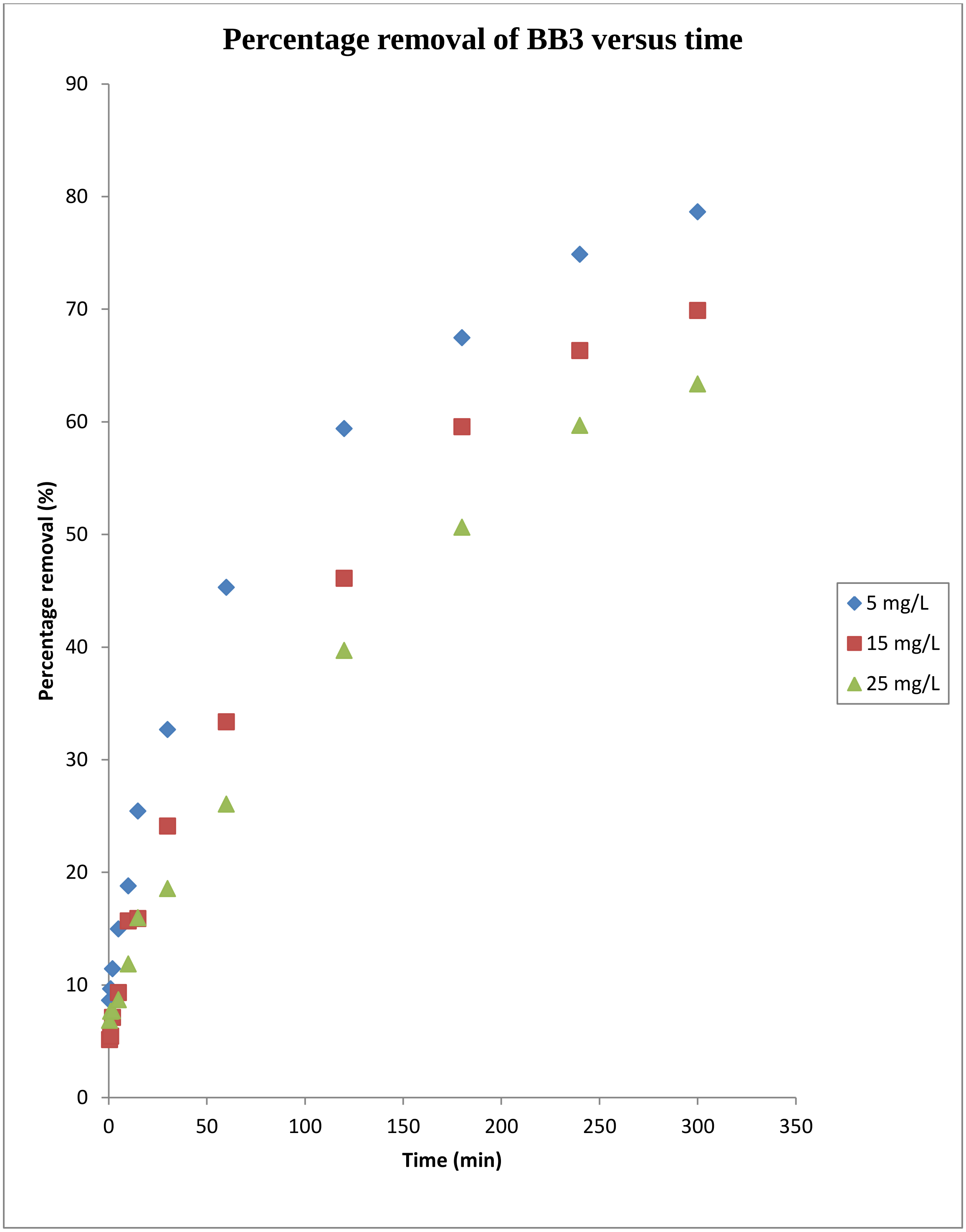


Figure 4.2 (a): Graph of percentage removal of BB3 versus time in binary system.

Condition: 1000 mL of 5, 15, and 25 mg/L of dye solution under sunlight for 300 minutes in approximately 1.0 g photocatalyst.

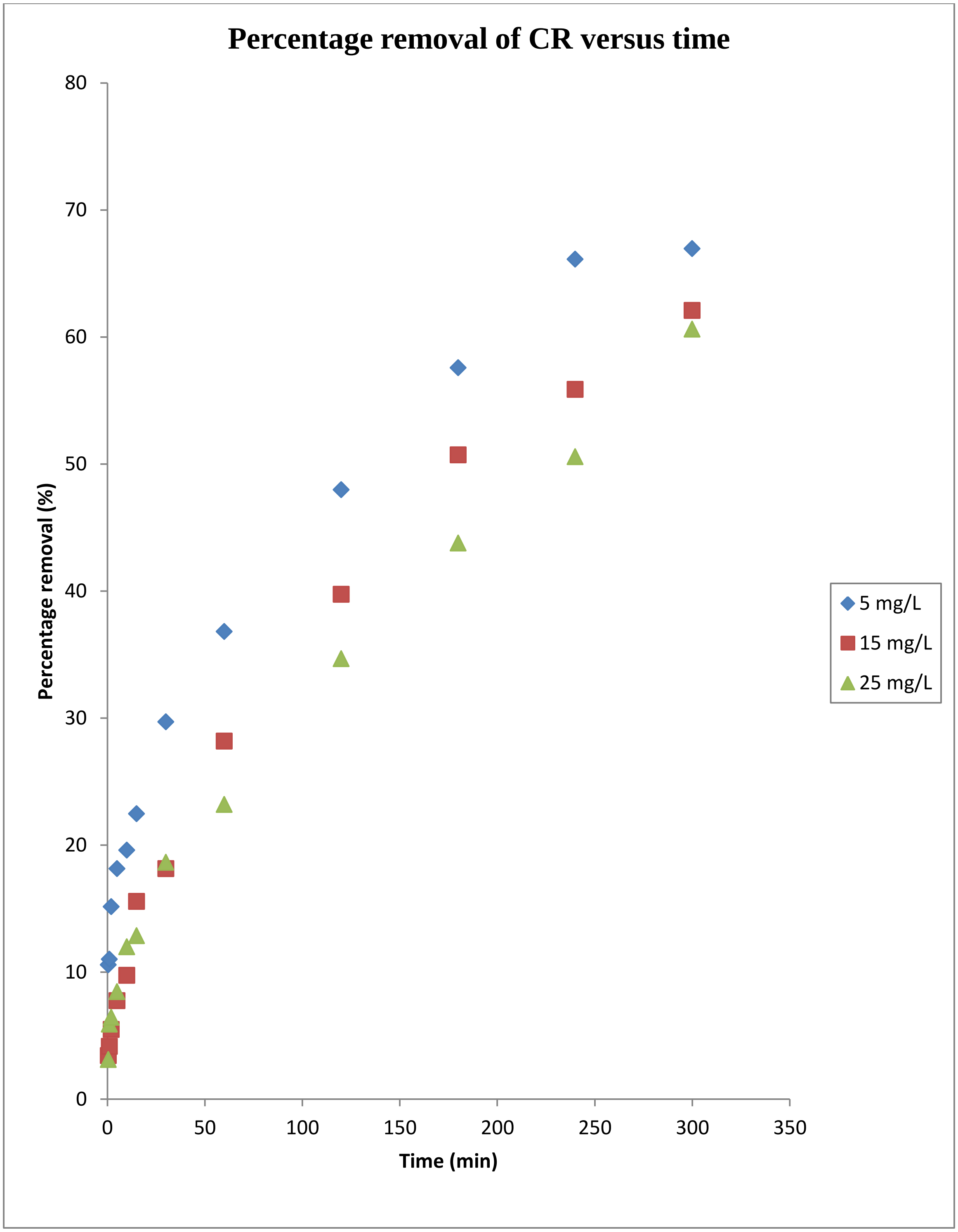


Figure 4.2 (b): Graph of percentage removal of CR versus time in binary system.

Condition: 1000 mL of 5, 15, and 25 mg/L of dye solution under sunlight for 300 minutes in approximately 1.0 g photocatalyst.

Furthermore, by comparing both BB3 and CR dye, BB3 have higher percentage removal than CR. Approximately 60 % of percentage removal indicates that CR is harder to undergo photodegradation. This may related to the size of dye molecules. By looking both molecular structure of BB3 and CR, BB3 structure has smaller size with molecular weight 359.89 g/mol whereas for CR, it is a diazo dye which bulkier than BB3. The molecular weight of CR is 696.66 g/mol, about double weight of BB3. Zainal, et al. (2005) reported the similar result by compared CSB with MB, MO, and IC. Authors mentioned that bulky molecular size may require a prolong irradiation time for it, so that it can be photodegrade completely. As a result, in order to increase percentage removal of CR, a longer irradiation time is required.

Figure 4.2 (a) and (b) do not show equilibrium at 300 minutes. At the same time, the percentage removal was at the range of 60-80 %. This indicates that the photodegradation process was yet to complete. Juang, Lin and Hsueh (2010) reported the photodegradation mixed dye is slow compare to single dye. This is the retarded effect. Thus, longer irradiation time may enhance the percentage removal of dye in binary system.

Besides that, the experiment was stop at 300 minutes even though it was yet to reach equilibrium. This is because the sunlight intensity starts to turn weak at the location which conducts the experiment. Sunlight is a free and natural source. In order to minimize the cost of dye treatment, sunlight is encouraged to use.

Since the photodegradation process is required both photocatalyst and light source, so, weak intensity of sunlight might slow down the process. However, the slow photodegradation rate problem may improve by modifying photocatalyst. Chen, Wang and Lou (2004) reported that modified TiO_2 has better photodegradation rate and Erdemoglu, et al. (2008) reported nanocrystalline TiO_2 was able to photodegrade CR up to 90 % within 30 minutes.

4.3 Effect of Photocatalyst Loading

The effect of TiO_2 photocatalyst dosage was studied. Result of both BB3 and CR percentage removal was shown in Figure 4.3. Four different amount of photocatalyst was tried, which are 0.2, 0.5, 1.0 and 3.0 g. According to the result of both BB3 and CR, rising of photocatalyst amount from 0.2 g to 1.0 g will lead to an increase in percentage removal from 60.66 % to 66.60 % for BB3, and 56.13 % to 60.12% for CR.

The increase of percentage removal by increasing photocatalyst loading is because the presence of more ready availability surface area, causing the number of active site increase and therefore enhance the photodegradation rate (Chen, et al., 2007).

Nevertheless, it was observed that the percentage removal of both BB3 and CR decreased when 3.0 g of photocatalyst was applied in the experiment. This may due to excessive of photocatalyst lead to agglomeration and sedimentation of TiO_2 particles. In other words, 3.0 g of photocatalyst may consider too much in this experiment set up.

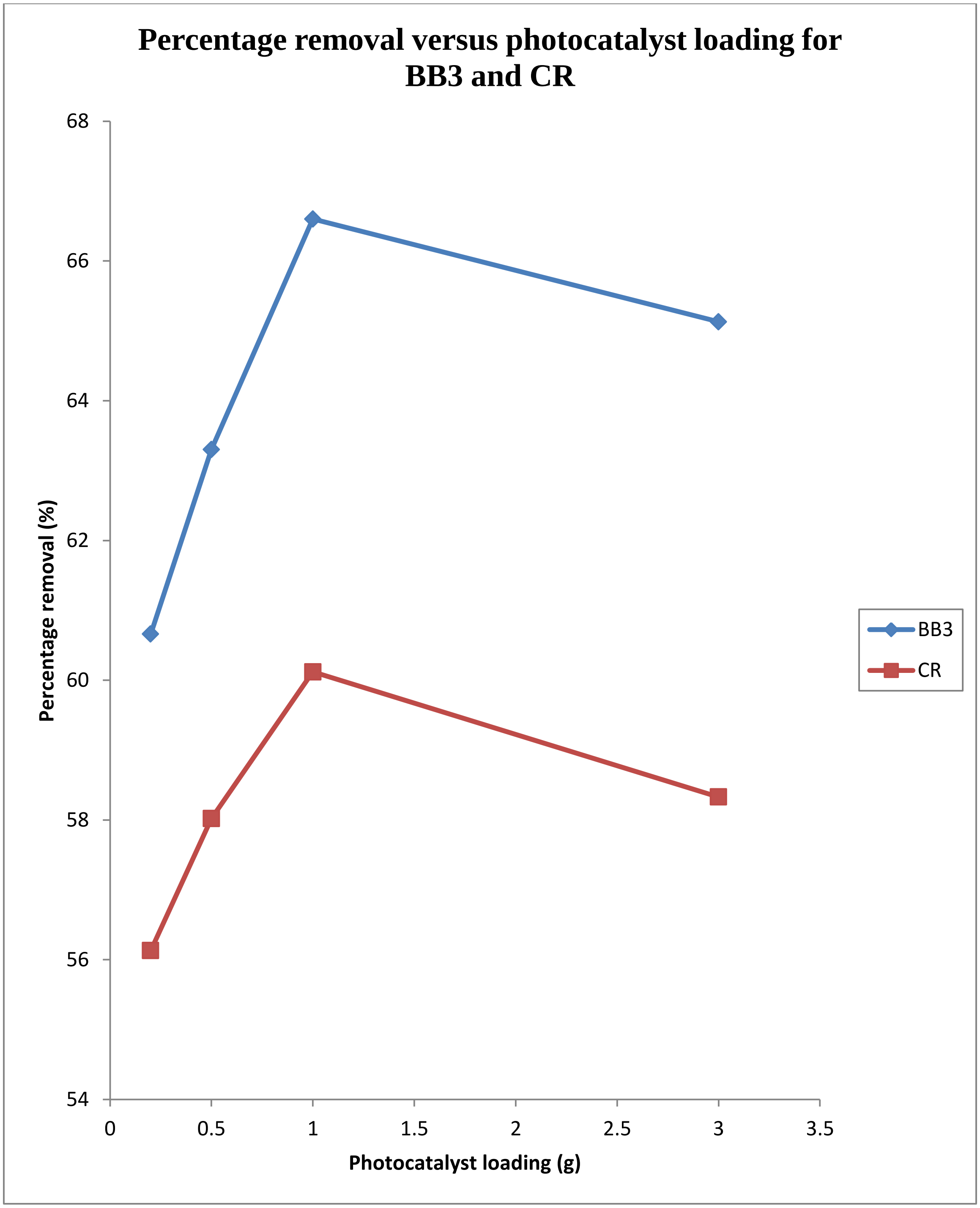


Figure 4.3 Effect of photocatalyst loading on percentage removal of BB3 and CR dyes by TiO_2 photocatalyst

Condition: 1000 mL of 15 mg/L dye solution under sunlight for 300 minutes without changing pH.

Therefore, it was predicted that further increase of photocatalyst loading will even lower the percentage of dyes removal. The photocatalyst may cluster together and lower the visible light penetration as well as enhance the light scattering effect.

Erdemoglu, et al. (2008) reported the same trend in this parameter. Authors mentioned that perhaps the decrease in photodegradation rate at high photocatalyst loading is because of the activated molecules was deactivate by collision with ground state molecules.

Guo, et al. (2012) suggested that 1.0 g of photocatalyst will give the best percentage removal in the photodegradation experiment to remove CR dye under visible light.

Consequently, increase of photocatalyst loading can increase the percentage removal. However, when photocatalyst is in excessive amount, the photodegradation efficiency may decrease.

4.4 Effect of pH

Effect of pH study was carried out in the range of pH 6-10 on the percentage removal of 15 mg/L of BB3 and CR. Figure 4.4 (a) shows the percentage removal of BB3 and CR versus pH. This result indicates that, there was a strong pH dependent of the solution on the heterogeneous photocatalytic process.

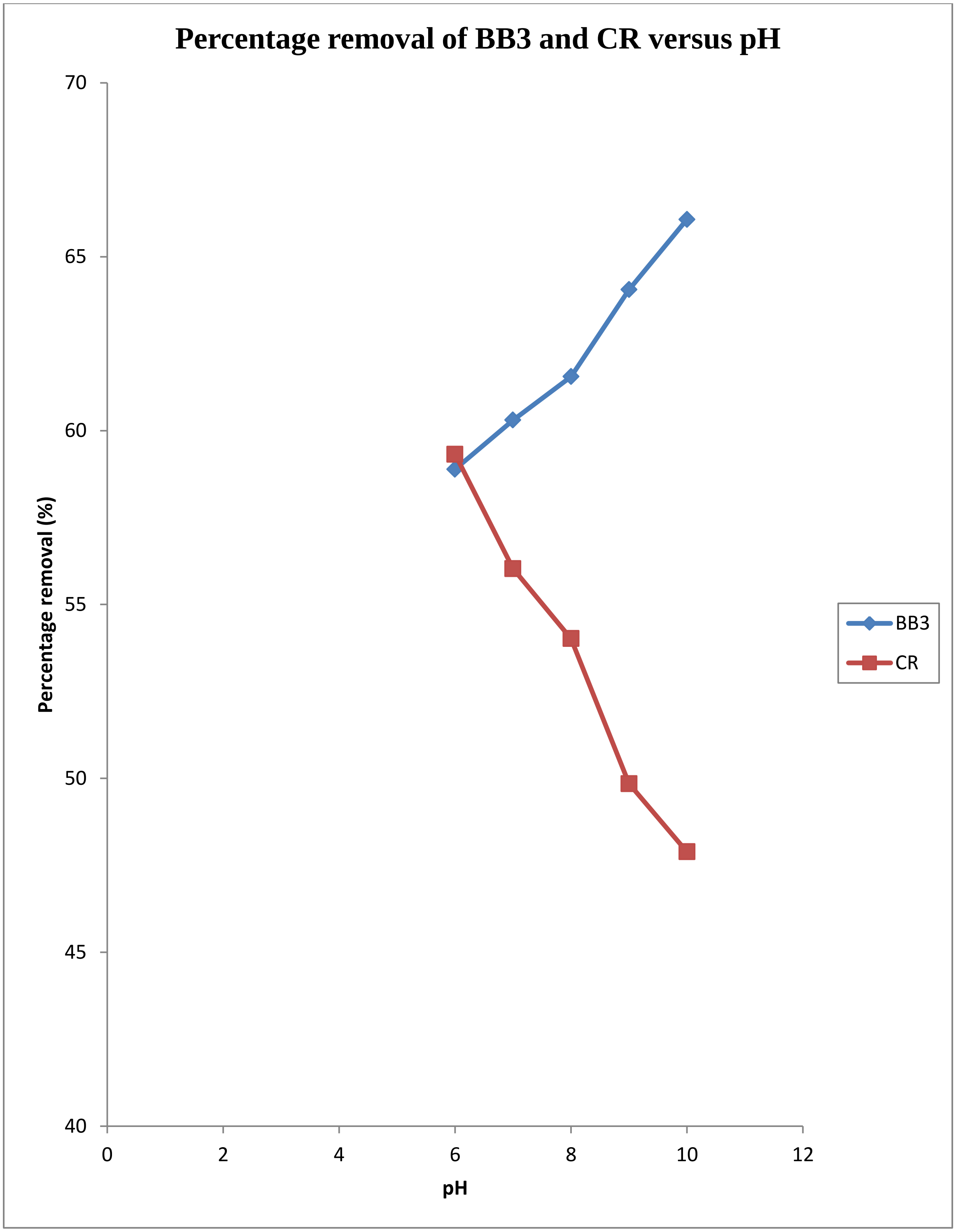


Figure 4.4 Effect of pH on removal of BB3 and CR by TiO_2 photocatalyst

Condition: 1.0 g of photocatalyst in 1000 mL of 15 mg/L dye solution under sunlight for 300 minutes.

For BB3 dye, the percentage removal was the lowest at pH 6, which only 58.89 % of removal. Between the pH 6-10, the percentage removal increased gradually and percentage removal was highest at pH 10, which is 66.07 %. For CR dye, a dropping trend was noticed between pH 6-10. CR dye has the highest percentage removal at pH 6, 59.32 % removal and it has lowest percentage removal at pH 10, which only 47.89 % removal.

Senthilkumaar, Porkodi and Vidyalakshimi (2005) mentioned that hydroxyl group of TiO_2 may undergo 2 acid-base equilibria as shown below:

$$TiOH_2^+ \leftrightarrow TiOH + H^+$$

$$TiOH \leftrightarrow TiO^- + H^+$$

As general, a significant dependency of the photocatalytic degradation efficiency on pH value had been observed for charged substrates. Since dye photooxidation was followed by releasing photons, its degradation rate can be affected due to the reversible protonation of TiO_2 surface.

The original pH of 15 mg/L BB3 in single dye system was 7.14 and the pH of 15 mg/L CR was single dye system is 5.60. When these 2 dyes mixed together, the binary dye solution was at pH 6.35. The pH_{zpc} or isoelectric point of unmodified TiO_2 was around pH 6.25, which means that below pH 6.25, the surface of TiO_2 is positive charge whereas above pH 6.25, the surface of TiO_2 is negative due to deprotonated (Andronic and Duta, 2008). Sometimes, the presence of impurities or specific adsorption of ions on the TiO_2 surface may change the pH_{zpc} value. In other literature, it was reported that the pH_{zpc} value of TiO_2 is pH 6.1 (Chen, Wang and Lou, 2004).

For BB3 dye, it is cationic form in aqueous solution and CR is anionic form in aqueous solution. When it is basic condition ($pH > 6.25$), that will have electrostatic interaction between surface of TiO_2 and cationic dye, which lead to strong attachment and therefore higher photodegradation rate. As the pH increase to higher, the TiO_2 surface will have more negatively charge and this explained why BB3 dye has highest percentage removal at pH 10.

On the other hand, under acidic condition ($pH < 6.25$), the surface of TiO_2 is positive, it will have electrostatic repulsion with the cationic dye, this explained why BB3 has lowest percentage removal at pH 6. However, the positive charged surface of TiO_2 will tend to attract negatively charged CR and this tells why CR has highest percentage removal at pH 6 but lowest percentage removal at pH 10. This behaviour was characteristics for majority photodegradation systems and comparable results have been reported in other journals (Konstantinou and Albanis, 2004).

The experiment was not carry out in acidic condition because CR dye will change the original red to blue colour at pH 5.3 and below. Therefore, a fair comparison may hard to be performed due to the differences in colour.

4.5 Effect of repetitive usage and recycle of coated TiO_2 glass tank

Reusability parameter was performed to determine the ability of repetitive usage. The technology of heterogeneous photocatalysis is applicable for practical usage due to the regeneration of TiO_2 photocatalyst. The higher reusability will bring benefits to the wastewater treatment industry. Figure 4.5 shows the effect of repetitive usage and recycle of coated TiO_2 glass tank on the percentage removal of BB3 and CR. In this parameter, a repetitive usage of 6 times was attempted.

The result showed that the photodegradation rates decreased with increasing number of usage for both dyes. The percentage removal of BB3 under sunlight for each cycles are 65.22, 64.92, 63.92, 62.32, 61.05, 59.81 % for 6 cycles of repetitive usage, respectively. In the first 2 times of recycle usage, the percentage removal of BB3 was able to be maintained at about 65 %. However, it decreased gradually thereafter.

For removal of CR, the percentage removals are 61.16, 60.29, 59.67, 58.73, 57.66, 56.36 % for 6 times of reuse, respectively. For each time of reuse, the percentage removal was decrease by approximately 1 %. As a result, both BB3 and CR dyes are not suitable to reuse too much of cycle as the removal efficiency might be affected.

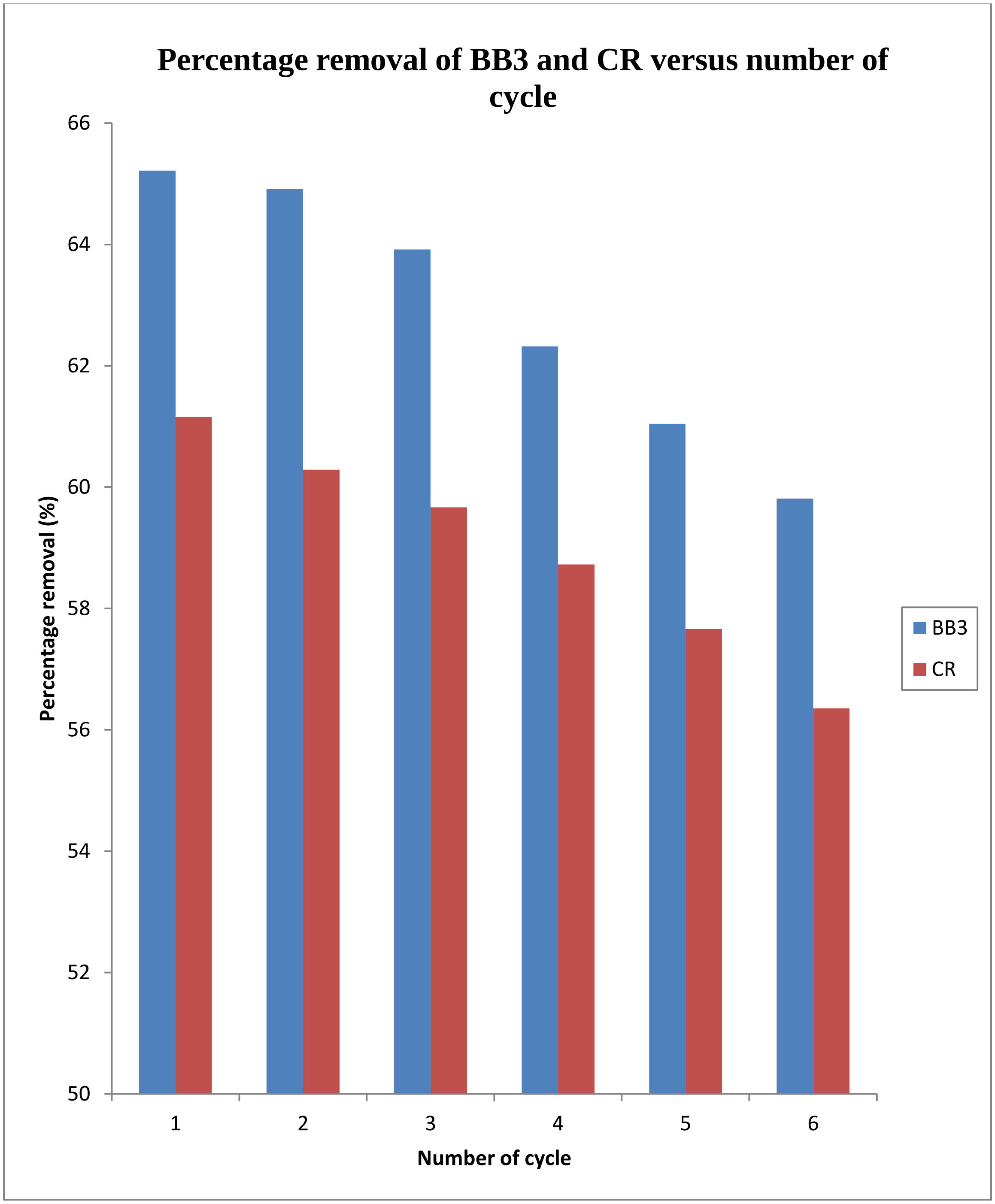


Figure 4.5 Effect of repetitive usage and recycle of coated TiO_2 glass tank on percentage removal of BB3 and CR

Condition: 1.0 g of photocatalyst in 1000 mL of 15 mg/L dye solution under sunlight for 300 minutes.

Each time of reuse cycle may cause the non-eligible dye molecules to be attached on the TiO_2 surface. These attached dyes molecules might block the TiO_2 photocatalyst from being illuminated by the light source and therefore hindered the formation of electron-hole pairs and slowing down the formation of beneficial radicals.

The similar observations reported by Jiang, et al. (2014) which can be reuse about 3-4 times to remove reactive brilliant red dye by using 250 W high-pressure mercury lamp at wavelength 365 nm.

Besides that, according to Lee, et al. (2013), the dye molecules which strongly attached on TiO_2 surfaces are unable to remove by recycling method and therefore lower photodegradation efficiency was anticipated.

4.6 Photodegradation kinetic study

Lee, et al. (2013) mentioned that kinetic study of photodegradation process can provide information regarding the mechanism of photodegradation and reaction pathways. This is crucial as it helps to maximize the photodegradation efficiencies in organic pollutants removal. In addition, it also describes the rate of removal, which in turn to control the irradiation time (Ho and Mckay, 1998). The kinetics data obtained from photodegradation of BB3 and CR dyes using TiO_2 photocatalyst was studied by using Langmuir-Hinshelwood (LH) kinetics model.

4.6.1 Langmuir-Hinshelwood (LH) Kinetic model

Under LH kinetic model, it has five assumptions:

i. Only one substrate able to bind at each surface site.
ii. The amount of surface adsorption sites is constant at equilibrium.
iii. No interaction between adjacent adsorbed substrates.
iv. Rate of surface adsorption is greater than the rate of any subsequent chemical reactions.
v. The heat of adsorption by the substrate is identical for each site and is independent of surface coverage.

Generally, the effect of initial organic pollutants concentration on the rate of photodegradation was expressed as equation 4.1:

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \qquad [4.1]$$

However, in low concentration of photocatalyst, the equation 4.1 able to be simplified to first-order equation (equation 4.2)

$$\ln\left(\frac{C_0}{C}\right) = kKt = k't \qquad [4.2]$$

Where

C_0 is the initial concentration of the reactant (mg/L)

C is the concentration of the reactant at time t (mg/L)

t is the irradiation time

k' is the reaction rate constant (min^{-1})

K is the adsorption coefficient of reactant onto the semiconductor particles (L/mg)

r is the oxidation rate of the reactant (mg/L min)

4.6.2 First-order Kinetic model

Figure 4.6.2 (a) and (b) presented the graphs of kinetic first order for both BB3 and CR dye. The plot of ln (C_o/C) versus time produce a straight line as indicated in equation 4.2. The rate constant, k' is determined from the gradient of the straight line.

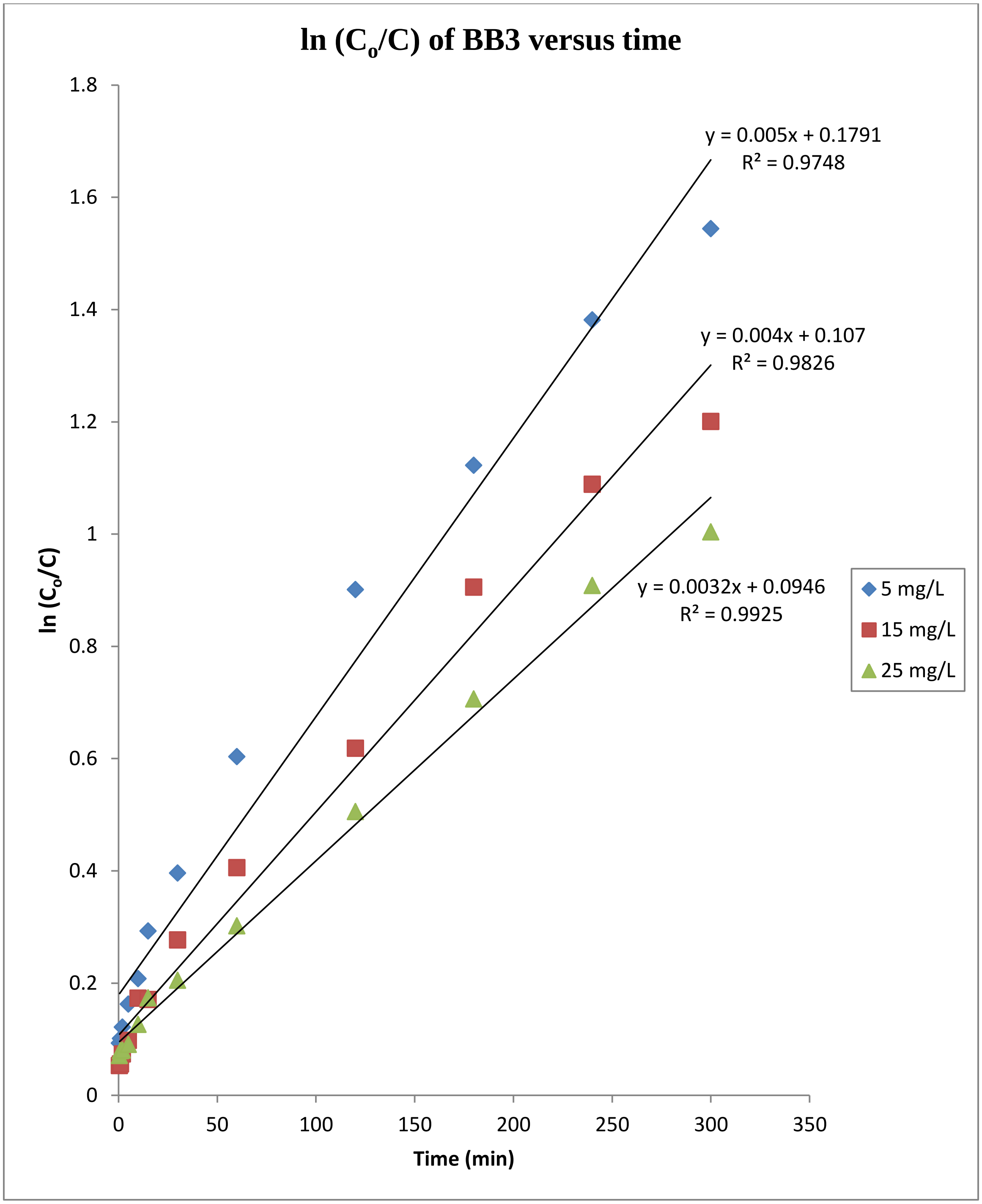


Figure 4.6.2 (a): First order kinetics for the photodegradation of BB3 in binary system.

Condition: 1.0 g of photocatalyst in 1000 mL of 5, 15, 25 mg/L of dye solution under sunlight for 300 minutes.

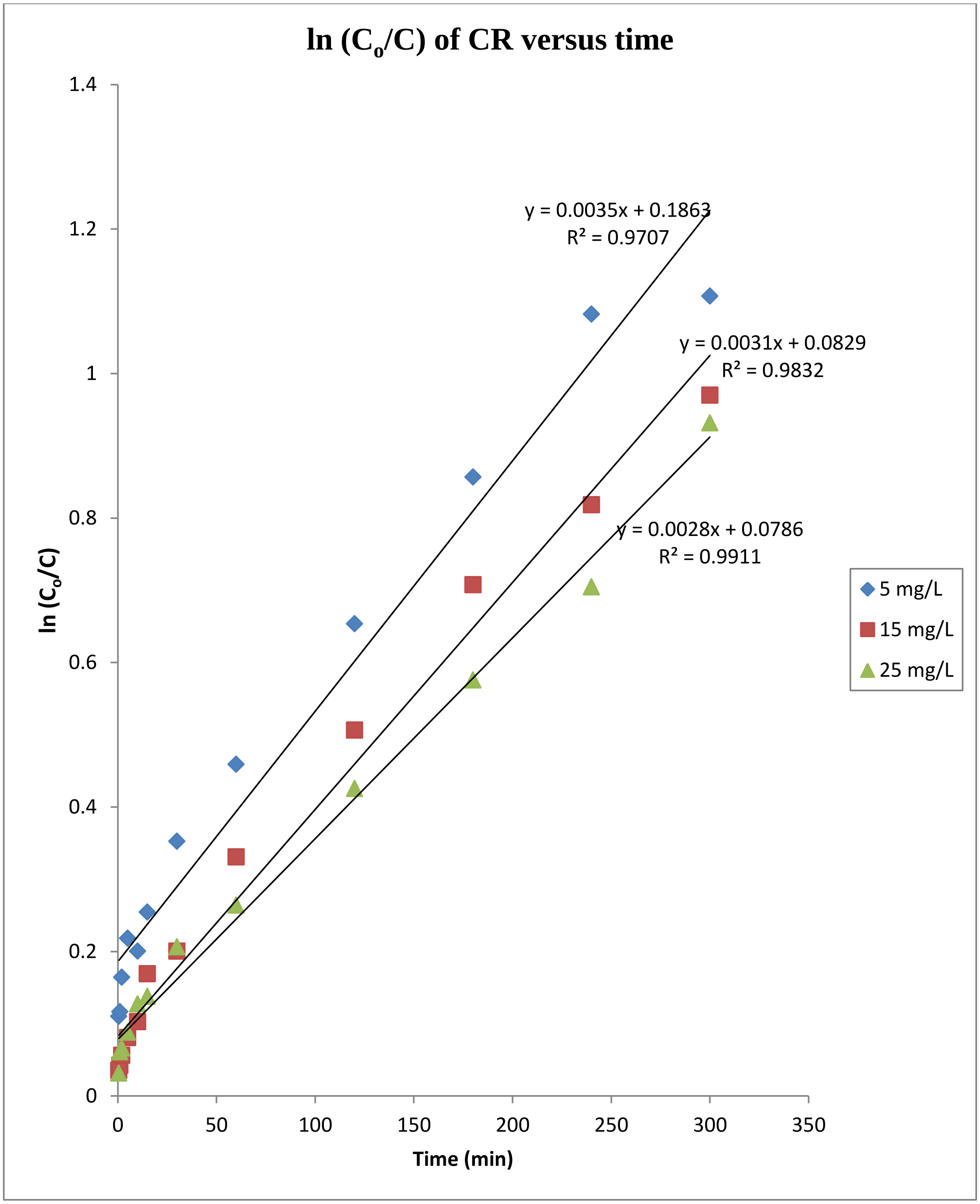


Figure 4.6.2 (b): First order kinetics for the photodegradation of CR in binary system.

Condition: 1.0 g of photocatalyst in 1000 mL of 5, 15, 25 mg/L of dye solution under sunlight for 300 minutes.

Table 4.6.2 (a) listed the observed rate constant and the R^2 for both BB3 and CR dye at several initial dye concentrations. With the R^2 above 0.9700, it means that the first order kinetic which derived from Langmuir-Hinshelwood kinetic model seems to be fit in this study. Senthilkumaar, et al. (2005) also reported the R^2 for first order kinetic with the range of 0.9719 to 0.9900, which photodegradation of MB in 3 different concentrations.

In addition, some journal study reported that first order kinetic is adequate to describe the photodegradation of organic dyes (Barka, et al., 2010).

By comparison, the rate constant value for BB3 was higher than CR. The rate constant was lower down from 0.0050 to 0.0032 min^{-1} when initial BB3 concentration was increased. Similar observation was found in CR, whereby the rate constant decreased from 0.0035 to 0.0028 min^{-1} with adjusting initial concentration of dyes from 5 mg/L to 25 mg/L. This might due to less light penetration at higher dye concentrations and the surface of TiO_2 was not fully irradiated. Juang, Lin and Hsueh (2010) reported the same trend regarding the study of removal AO7 and RR2 in binary system.

Table 4.6.2 (a): First order kinetic model for photodegradation of BB3 and CR

Initial dye concentration (mg/L)	**Basic Blue 3 (BB3)**		**Congo Red (CR)**	
	Rate, k_1 (min^{-1})	**R^2**	**Rate, k_1 (min^{-1})**	**R^2**
5	0.0050	0.9748	0.0035	0.9707
15	0.0040	0.9826	0.0031	0.9832
25	0.0032	0.9925	0.0028	0.9911

$$\frac{C_o}{C} = 0.5, \quad t_{1/2} = \frac{\ln 2}{k'} \qquad [4.3]$$

Furthermore, half-life ($t_{1/2}$), which showed in equation 4.3, is a useful indication for the chemical reaction which undergoes first order kinetic. It is able to describe time taken for dye to drop to half of its initial concentration. Table 4.6.2 (b) shows the half-life of BB3 and CR in different initial dye concentration.

Table 4.6.2 (b): Half-life of BB3 and CR in different initial dye concentration

Initial dye concentration (mg/L)	**Basic Blue 3 (BB3)**	**Congo Red (CR)**
	Half-life, $t_{1/2}$ (min)	**Half-life, $t_{1/2}$ (min)**
5	138.63	198.04
15	173.29	223.60
25	216.61	247.55

4.7 Optimisation Study of Dye Photodegradation

4.7.1 Plackett-Burman (PB) design

Plackett-Burman design is a software which able to assess the relative importance of miscellaneous variables which affect the photodegradation efficiency. It provides unbiased estimation for all parameters with high accuracy for a given number of observations (Rajendran, et al., 2007). Three parameters which most likely to influence the percentage removal are tested on their validity in this study by using Plackett-Burman design. The parameters studied are initial dye concentrations, photocatalyst loading and pH. Tables 4.7 (a) and (b) illustrates the validation result for the photodegradation of BB3 and CR.

The result of analysis of variance (ANOVA) of both BB3 and CR dye solutions is presented in Tables 4.7.1 (c) and (d). The model was known as significant when the *Prob*>F value is below 0.05. Both models of BB3 and CR are significant since the values are *Prob*>F value of 0.0038 and 0.0232, respectively.

However, the photocatalyst loading parameter in both dye of BB3 and CR shows insignificant with *Prob*>F 0.2057 and 0.1986, respectively. This indicates that amount of photocatalyst does not bring much effect on percentage removal in this study. Apart from that, initial dye concentration and photocatalyst loading was found to be factors that will affect the percentage removal for both BB3 and CR dye.

Table 4.7.1 (a): Plackett-Burman design and results of the removal BB3 from binary system

Experimental run	Variables			Observed response (%)	Predicted response (%)
	Initial dye concentration (mg/L)	Photocatalyst loading (g)	pH		
1	5.00	0.20	10.00	69.03	72.26
2	5.00	0.20	6.00	67.42	65.55
3	25.00	3.00	6.00	60.24	61.73
4	25.00	0.20	10.00	67.72	66.07
5	5.00	3.00	10.00	72.84	74.57
6	5.00	0.20	6.00	67.42	65.55
7	25.00	3.00	10.00	71.75	68.38
8	5.00	3.00	6.00	70.81	67.86
9	25.00	0.20	10.00	67.72	66.07
10	25.00	3.00	6.00	60.24	61.73
11	5.00	3.00	10.00	72.84	74.57
12	25.00	0.20	6.00	55.54	60.39

Table 4.7.1 (b): Plackett-Burman design and results of the removal CR from binary system

Experimental run	Variables			Observed response (%)	Predicted response (%)
	Initial dye concentration (mg/L)	Photocatalyst loading (g)	pH		
1	5.00	3.00	6.00	87.88	80.00
2	5.00	3.00	10.00	57.60	66.03
3	25.00	3.00	6.00	57.77	63.08
4	5.00	3.00	10.00	57.60	66.03
5	5.00	0.20	10.00	66.43	58.03
6	25.00	0.20	10.00	35.54	48.38
7	25.00	3.00	6.00	57.77	48.38
8	25.00	0.20	6.00	57.23	55.08
9	25.00	3.00	10.00	68.73	54.90
10	5.00	0.20	6.00	72.29	72.00
11	5.00	0.20	6.00	72.29	72.00
12	25.00	0.20	10.00	35.54	48.38

Table 4.7.1 (c): Regression analysis (ANOVA) of Plackett-Burman for the removal of BB3 from binary system

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**p-value (*Prob*>F)**
Model	265.91	3	88.64	10.49	0.0038
A- Initial dye concentration	115.01	1	115.01	13.61	0.0061
B- Catalyst Loading	16.03	1	16.03	1.90	0.2057
C- pH	134.87	1	134.87	15.96	0.0040
Residual	67.60	8	8.45		
Total	333.51	11			

Table 4.7.1 (d): Regression analysis (ANOVA) of Plackett-Burman for the removal of CR from binary system

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**p-value (*Prob*>F)**
Model	1635.99	3	545.33	5.57	0.0232
A- Initial dye concentration	858.69	1	858.69	8.77	0.0181
B- Catalyst Loading	192.24	1	192.24	1.96	0.1986
C- pH	585.06	1	585.06	5.98	0.0403
Residual	782.96	8	97.87		
Total	2481.95	11			

4.7.2 Response Surface Methodology (RSM) design

Two parameters (initial dye concentration and pH) are tested on their validity in this study by using RSM design. Total 13 sets of experimental run were generated for each dye. Table 4.7.2 (a) and (b) presented the validation result for photodegradation of BB3 and CR dye in binary system. The equations of percentage removal of both BB3 and CR dyes in binary system were generated by Design-Expert 7.1.3 as below:

BB3 dye solution:

$$\% \, removal = 64.43 - 5.66A + 1.14B + 0.17AB + 5.15A^2 + 0.85B^2$$

CR dye solution:

$$\% \, removal = 54.67 - 5.01A - 6.33B - 2.96AB + 2.14A^2 - 0.68B^2$$

where, A is initial dye concentration

B is pH

The result of analysis of variance (ANOVA) of both BB3 and CR dye solutions is presented in Tables 4.7.2 (c) and (d). According to the analysis, both models are significant with *Prob*>F less than 0.0001. The R^2 for both BB3 and CR model is 0.9963 and 0.9651 respectively, this relatively high value and indicates that it has a good agreement between observed and predicted response. There is less than 0.01%

opportunity that a “Model F-value” this high could occur due to noise. As a result, effect of initial dye concentration and pH effect are significant for both BB3 and CR model.

Adequate precision is to measure the signal to noise ratio. According to Design-Expert software, value larger than 4 is preferable. Since the adequate precision for both BB3 and CR was 50.148 and 22.190 respectively, so, it indicates an adequate signal. The predicted R^2 for BB3 was found to be 0.9678, which was in reasonable agreement with the adjusted R^2 value (0.9936). However, the predicted R^2 for CR was not close to the adjusted R^2. This may indicate some possible problem with this model.

Table 4.7.2 (a): RSM design and results of the removal BB3 from binary system

Experimental Run	Variables		Observed response (%)	Predicted response (%)
	Initial dye concentration	pH		
1	5.00	8.00	74.50	75.24
2	15.00	8.00	64.55	68.68
3	15.00	8.00	64.55	68.68
4	25.00	10.00	66.03	69.20
5	5.00	6.00	76.46	75.12
6	15.00	6.00	63.89	64.13
7	15.00	10.00	66.07	66.42
8	25.00	8.00	64.07	63.62
9	5.00	10.00	75.80	77.06
10	25.00	6.00	63.35	63.40
11	15.00	8.00	64.55	68.68
12	15.00	8.00	64.55	68.68
13	15.00	8.00	64.55	68.68

Table 4.7.2 (b): RSM design and results of the removal CR from binary system

Experimental Run	Variables		Observed response (%)	Predicted response (%)
	Initial dye concentration	pH		
1	15.00	8.00	55.02	54.67
2	25.00	8.00	55.84	51.80
3	15.00	8.00	54.02	54.67
4	5.00	10.00	58.43	57.75
5	15.00	10.00	47.89	48.46
6	25.00	6.00	60.61	60.41
7	5.00	6.00	66.29	64.50
8	25.00	10.00	40.9	51.05
9	15.00	8.00	54.02	54.67
10	15.00	6.00	58.32	60.32
11	15.00	8.00	54.02	54.67
12	15.00	8.00	54.02	54.67
13	5.00	8.00	59.34	61.81

Table 4.7.2 (c): Regression analysis (ANOVA) of RSM for the removal of BB3 in binary system

Source	Sum of Squares	df	Mean Square	F-value	p-value (*Prob*>F)
Model	299.00	5	59.80	374.71	< 0.0001
Initial dye concentration	192.33	1	192.33	1205.12	< 0.0001
pH	7.84	1	7.84	49.15	0.0002
Residual	1.12	7	0.16		
Total	300.12	12			

R^2: 0.9963, Adjusted R^2: 0.9936, Predicted R^2: 0.9678, Adequate precision: 50.148

Table 4.7.2 (d): Regression analysis (ANOVA) of RSM for the removal of CR in binary system

Source	Sum of Squares	df	Mean Square	F-value	p-value (*Prob*>F)
Model	438.92	5	87.78	38.77	< 0.0001
Initial dye concentration	150.46	1	150.46	66.45	< 0.0001
pH	240.74	1	240.74	106.33	< 0.0001
Residual	15.85	7	2.26		
Total	454.77	12			

R^2: 0.9651, Adjusted R^2: 0.9403, Predicted R^2: 0.6783, Adequate Precision: 22.190

Figure 4.7 (a) and (b) shows 3D surface plot about the correlation between initial dye concentration and pH for removal BB3 and CR dye. For BB3, the maximum removal was achieved when high pH and low initial dye concentration. For CR, the highest removal was attained in condition of low pH and low initial dye concentration. Based on the 3D plot, red colour region identified as maximum level in percentage removal whereas blue colour region shows less desirability. Consequently, both dyes also have better percentage removal when in low initial dye concentrations.

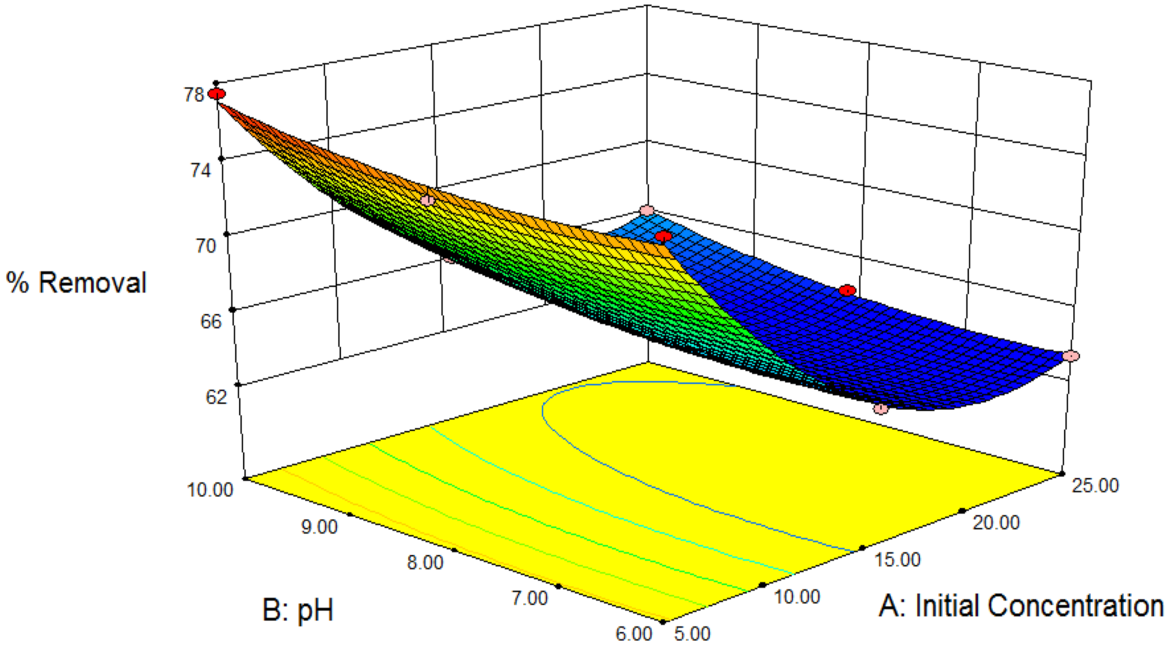


Figure 4.7 (a): 3D surface plot for removal of BB3 in binary system

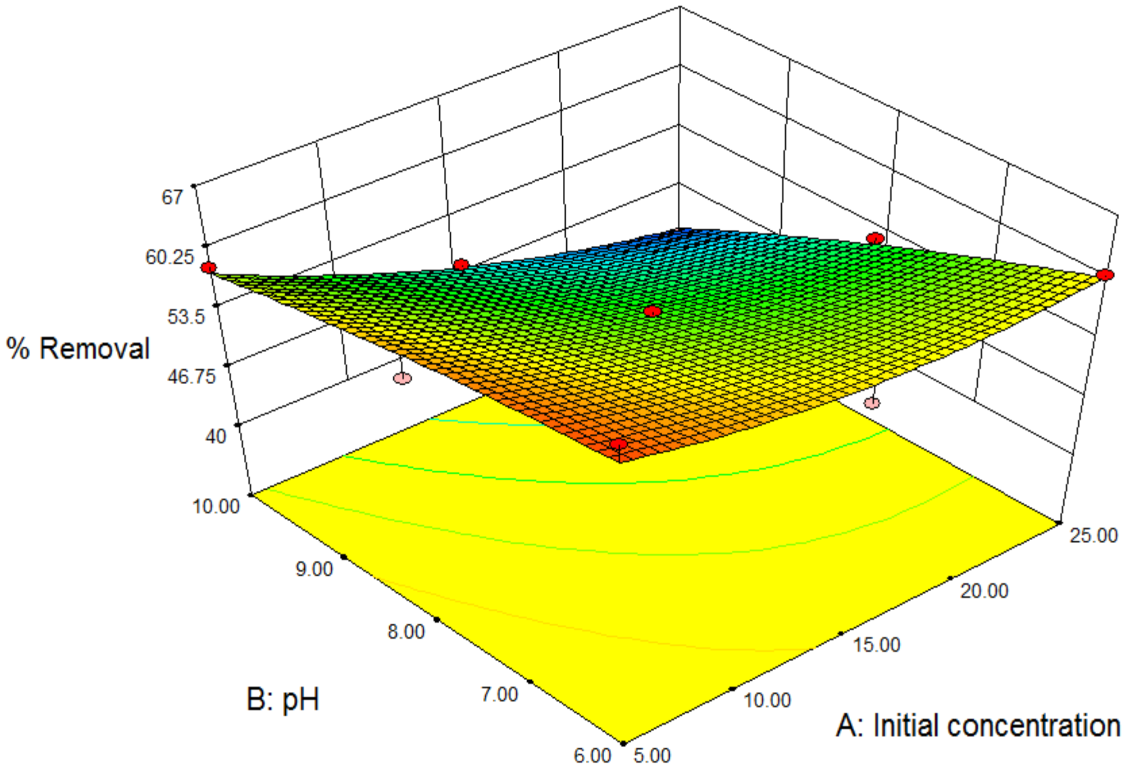


Figure 4.7 (b): 3D surface plot for removal of CR in binary system

CHAPTER 5

CONCLUSION

5.1 Conclusion

In this study, the effectiveness of TiO_2 as photocatalyst for the photodegradation of BB3 and CR in binary dye system was investigated. TiO_2 was found to be capable to remove BB3 and CR under batch studies. The surface morphology by study was carried out by using SEM and it was found that dye molecules adsorbed on the surface of TiO_2 and the surface more compact after undergo photodegradation.

The optimum initial concentration for the removal studied dyes was observed in low concentration, which was 5 mg/L under irradiation of 300 minutes. The optimum photocatalyst loading was determined at 1.0 g. The optimum pH for the photodegradation of BB3 was known as pH 10. For CR, it was at pH 6. The glass tank which coated with photocatalyst is able to reuse up to 2-3 times.

The kinetics of dye photodegradation obeys to first order kinetic which derived from Langmuir-Hinshelwood kinetic model. The rate constant was found to be 0.0050, 0.0040 and 0.0032 min^{-1} at 5, 15, and 25 mg/L, respectively for BB3. For CR, the rate constant was 0.0035, 0.0031 and 0.0028 min^{-1} at 5, 15, 25 mg/L, respectively.

For optimisation studies, Plackett-Burman design was used for determination the most significant variables for removal dyes by using TiO_2 photocatalyst. Initial concentration of dye and pH is found to be the significant parameters for removal of both BB3 and CR dye solutions. RSM was used to study the interaction between variables and the optimum levels for maximum percentage removal of BB3 and CR in binary dye system. Both models are significant with R^2 0.9963 and 0.9651 for BB3 and CR, respectively. The optimised condition for BB3 was at pH 10 and 5 mg/L initial concentration of dye, the percentage removal was estimated to be 77.06 % under this condition. For CR, the optimised condition is at pH 6 and 5 mg/L initial concentration of dye, the percentage removal was estimated to be 64.51 %.

5.2 Further Studies

Photodegradation by using TiO_2 method has shown its potential to remove binary mixture of BB3 and CR dyes in aqueous solution. For further studies, it could be carried out to the following areas:

- Modification on TiO_2 to enhance the photodegradation efficiency and characterisation of photocatalyst by using XRD, XPS, AFM and so on.

- Study on parameters such as presence of inorganic salts, effect of peroxides, effect of temperature, and determine the zero point charge of TiO_2.

- Study the mechanism of dye photodegradation process by using mass spectrometer, to identify the intermediates.

- Incorporate adsorption technique with photodegradation method to increase the efficiency of the process.

- To test the applicability of the current method with industrial wastewater.

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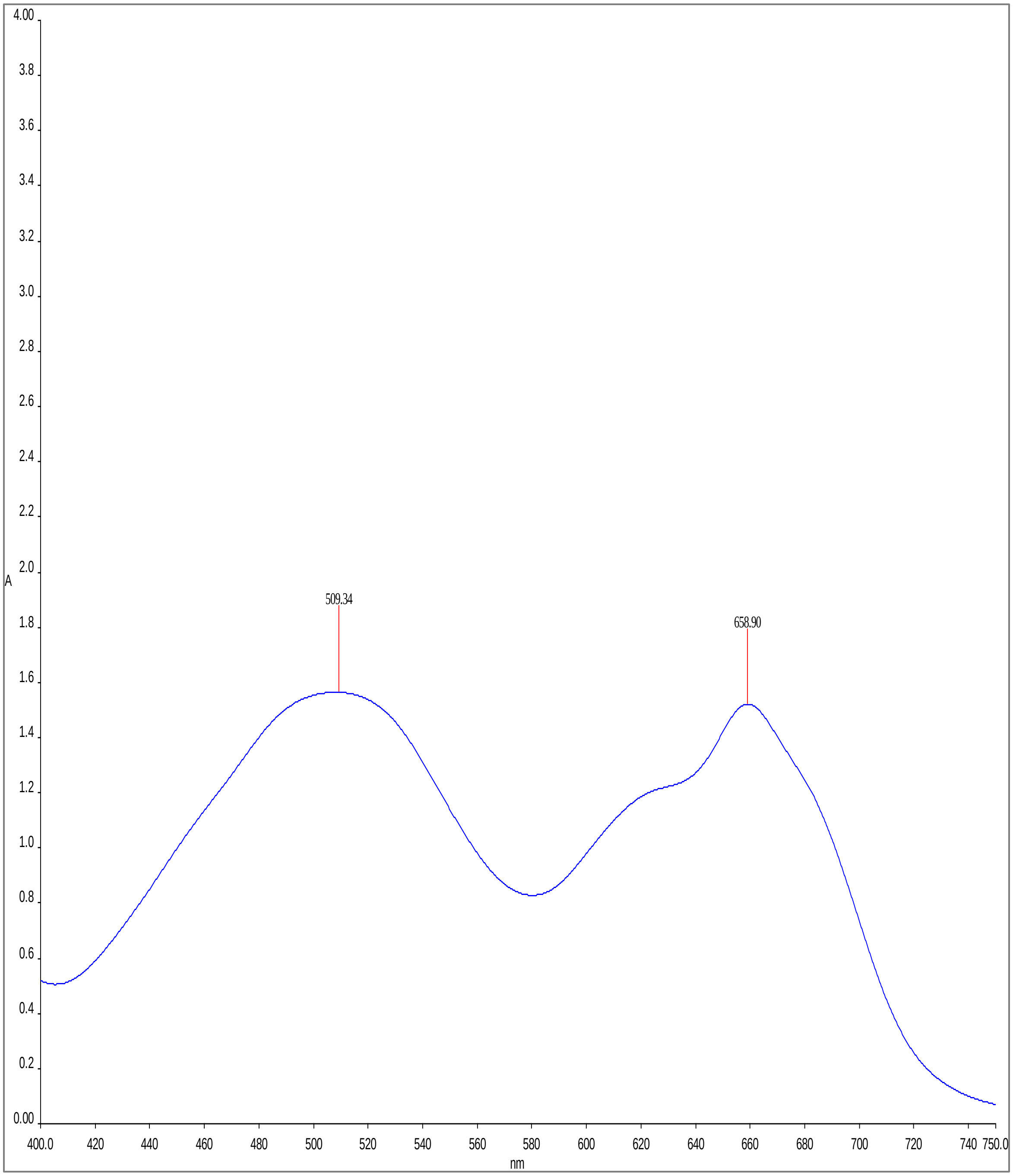
APPENDICES

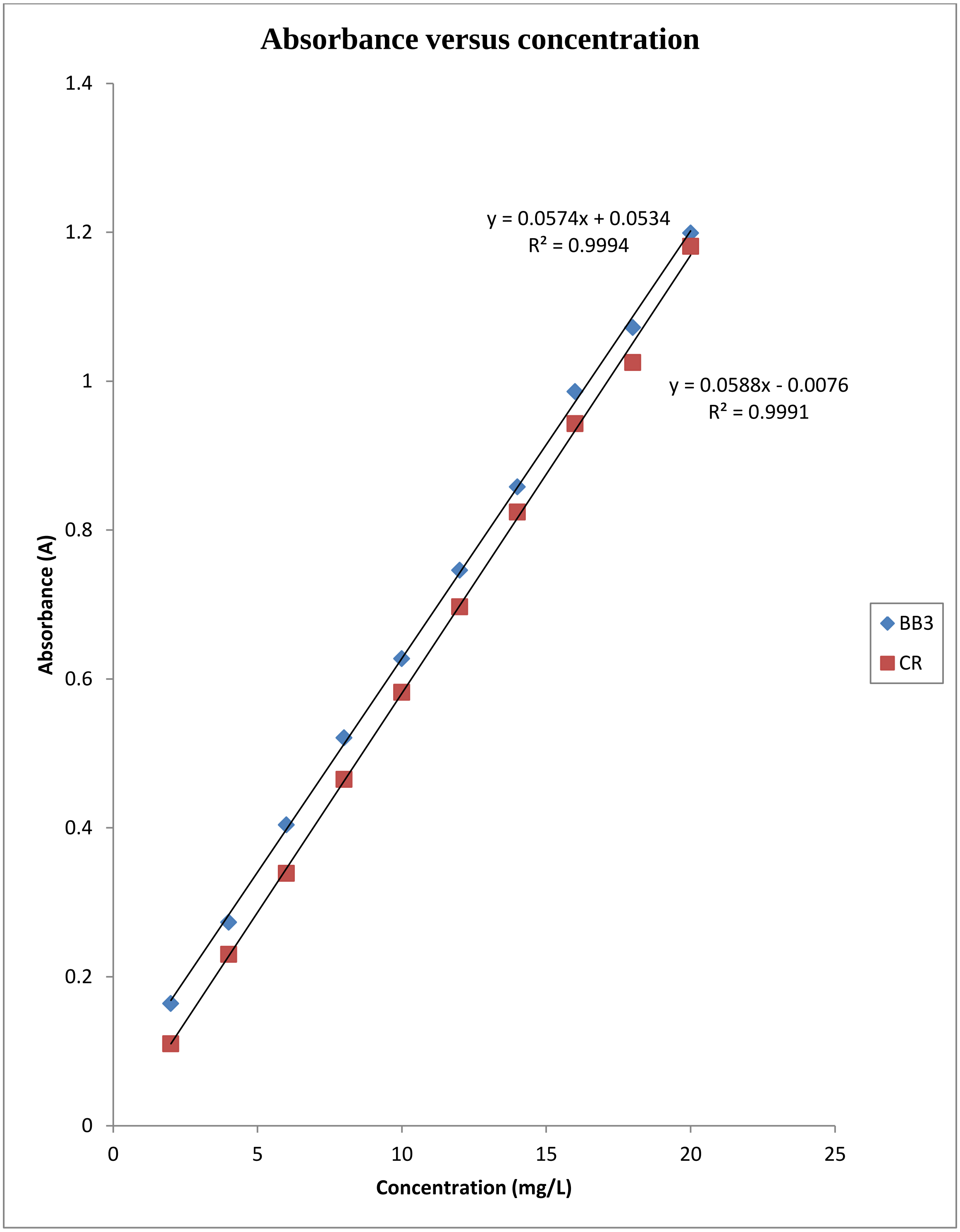
APPENDIX A

UV-Vis double beam spectrum of BB3 and CR in binary system



APPENDIX B

Calibration curve of BB3 and CR



APPENDIX C

Effect of initial dye concentration and irradiation time – BB3

Time (minutes)	**Percentage removal (%)**		
	5 mg/L	**15 mg/L**	**25 mg/L**
0.5	8.63	5.15	6.84
1	9.64	5.45	7.65
2	11.42	7.10	7.71
5	14.97	9.32	8.68
10	18.78	15.68	11.85
15	25.43	15.89	15.95
30	32.68	24.1	18.54
60	45.30	33.35	26.05
120	59.39	46.11	39.69
180	67.45	59.55	50.63
240	74.87	66.33	59.67
300	78.64	69.89	63.35

Effect of initial dye concentration and irradiation time – CR

Time (minutes)	**Percentage removal (%)**		
	5 mg/L	**15 mg/L**	**25 mg/L**
0.5	10.58	3.42	3.12
1	11.01	4.15	5.91
2	15.14	5.48	6.43
5	18.15	7.74	8.45
10	19.60	9.75	11.98
15	22.46	15.56	12.86
30	29.70	18.15	18.64
60	36.81	28.18	23.20
120	47.98	39.73	34.66
180	57.57	50.72	43.78
240	66.12	55.88	50.56
300	66.95	62.09	60.61

APPENDIX D

Effect of photocatalyst loading – BB3

Photocatalyst loading (g)	Percentage removal (%)
0.20	60.66
0.50	63.30
1.00	66.60
3.00	65.13

Effect of photocatalyst loading – CR

Photocatalyst loading (g)	Percentage removal (%)
0.20	56.13
0.50	58.02
1.00	60.12
3.00	58.33

APPENDIX E

Effect of pH – BB3

pH	**Percentage removal (%)**
6	58.89
7	60.30
8	61.55
9	64.05
10	66.07

Effect of pH – CR

pH	**Percentage removal (%)**
6	59.32
7	56.03
8	54.02
9	49.85
10	47.89

APPENDIX F

Effect of repetitive usage and recycle of coated TiO_2 glass tank – BB3

Number of cycle	**Percentage removal (%)**
1	65.22
2	64.92
3	63.92
4	62.32
5	61.05
6	59.81

Effect of repetitive usage and recycle of coated TiO_2 glass tank – CR

Number of cycle	**Percentage removal (%)**
1	61.16
2	60.29
3	59.67
4	58.73
5	57.66
6	56.36

APPENDIX G

Kinetic first order for photodegradation - BB3

Time (minutes)	**5 mg/L**			
	[C]	**[C$_o$]**	**[C$_o$] / [C]**	**ln [C$_o$] / [C]**
0.5	5.98365	6.56700	1.09749	0.09303
1	5.93364	6.56700	1.10674	0.10142
2	5.81696	6.56700	1.12894	0.12128
5	5.58361	6.56700	1.17612	0.16222
10	5.33360	6.56700	1.23125	0.20803
15	4.89698	6.56700	1.34013	0.29277
30	4.42091	6.56700	1.48544	0.39371
60	3.59199	6.56700	1.82823	0.60335
120	2.66685	6.56700	2.46246	0.90116
180	2.13756	6.56700	3.07219	1.12239
240	1.65009	6.56700	3.97979	1.38123
300	1.40255	6.56700	4.68219	1.54375

Kinetic first order for photodegradation - BB3

Time **(minutes)**	**15 mg/L**			
	[C]	**$[C_o]$**	**$[C_o] / [C]$**	**$\ln [C_o] / [C]$**
0.5	17.21603	18.15000	1.05425	0.05283
1	17.16085	18.15000	1.05764	0.05604
2	16.86129	18.15000	1.07643	0.07365
5	16.45855	18.15000	1.10277	0.09783
10	15.30315	18.15000	1.1889	0.17303
15	15.26621	18.15000	1.18603	0.17061
30	13.76209	18.15000	1.31884	0.27675
60	12.09718	18.15000	1.50035	0.40570
120	9.78062	18.15000	1.85571	0.61827
180	7.34169	18.15000	2.47218	0.90510
240	6.11119	18.15000	2.96996	1.08855
300	5.46433	18.15000	3.32154	1.20043

Kinetic first order for photodegradation - BB3

Time (minutes)	**25 mg/L**			
	[C]	**[C_o]**	**[C_o] / [C]**	**ln [C_o] / [C]**
0.5	26.08339	28.00000	1.07348	0.07091
1	25.85793	28.00000	1.08284	0.07959
2	25.84122	28.00000	1.08354	0.08023
5	25.57101	28.00000	1.09499	0.09075
10	24.68199	28.00000	1.13443	0.12613
15	23.53396	28.00000	1.18977	0.17376
30	22.80892	28.00000	1.22759	0.20505
60	20.70638	28.00000	1.35224	0.30176
120	16.88751	28.00000	1.65803	0.50563
180	13.82327	28.00000	2.02557	0.70585
240	11.29155	28.00000	2.47973	0.90815
300	10.26197	28.00000	2.72852	1.00376

Kinetic first order for photodegradation - CR

Time **(minutes)**	**5 mg/L**			
	[C]	**[C_o]**	**[C_o] / [C]**	**ln [C_o] / [C]**
0.5	4.44079	4.95770	1.11640	0.11011
1	4.41182	4.95770	1.12373	0.11665
2	4.20704	4.95770	1.17843	0.16418
5	4.05783	4.95770	1.22176	0.20029
10	3.98574	4.95770	1.24386	0.21822
15	3.84431	4.95770	1.28962	0.25435
30	3.48525	4.95770	1.42248	0.35240
60	3.13295	4.95770	1.58244	0.45897
120	2.57918	4.95770	1.92220	0.65347
180	2.10426	4.95770	2.35603	0.85698
240	1.67981	4.95770	2.95134	1.08226
300	1.63839	4.95770	3.02596	1.10723

Kinetic first order for photodegradation - CR

Time (minutes)	**15 mg/L**			
	[C]	**[C_o]**	**[C_o] / [C]**	**ln [C_o] / [C]**
0.5	15.76330	16.32826	1.03584	0.03521
1	15.65314	16.32826	1.04313	0.04223
2	15.43343	16.32826	1.05798	0.05636
5	15.06366	16.32826	1.08395	0.08061
10	14.73138	16.32826	1.10840	0.10292
15	13.78692	16.32826	1.18433	0.16918
30	13.36454	16.32826	1.22176	0.20029
60	11.72670	16.32826	1.39240	0.33103
120	9.84033	16.32826	1.65932	0.50641
180	8.04740	16.32826	2.02901	0.70755
240	7.20465	16.32826	2.26635	0.81817
300	6.19001	16.32826	2.63784	0.96996

Kinetic first order for photodegradation - CR

Time **(minutes)**	**25 mg/L**			
	[C]	**[C_o]**	**[C_o] / [C]**	**ln [C_o] / [C]**
0.5	27.68823	28.57868	1.03216	0.03165
1	26.89100	28.57868	1.06276	0.06087
2	26.74254	28.57868	1.06866	0.06641
5	26.16376	28.57868	1.09230	0.08829
10	25.15640	28.57868	1.13604	0.12755
15	24.90343	28.57868	1.14758	0.13766
30	23.25077	28.57868	1.22915	0.20632
60	21.94814	28.57868	1.30210	0.26398
120	18.67375	28.57868	1.53042	0.42554
180	16.06744	28.57868	1.77867	0.57587
240	14.12821	28.57868	2.02281	0.70449
300	11.25712	28.57868	2.53872	0.93166

APPENDIX H

Variation of rate constant with different initial dye concentration of BB3 and CR