

**HYBRID ADSORBENT FOR IN SITU WASTEWATER
TREATMENT**

TAVAYOGESHWARY THANGADURAI

UNIVERSITI SAINS MALAYSIA

2017

**HYBRID ADSORBENT FOR IN SITU WASTEWATER
TREATMENT**

by

TAVAYOGESHWARY THANGADURAI

**Thesis submitted in partial fulfilment of the requirement
for the degree of Bachelor of Chemical Engineering**

June 2017

ACKNOWLEDGEMENT

First and foremost, I would like to convey my sincere gratitude to my supervisor, Dr. Irvan Dahlan for his precious encouragement, guidance and generous support throughout this work.

I would extend my sincere gratitude towards all my colleagues as well for their kind cooperation and helping hands in guiding me carrying out the lab experiment. Besides sharing their valuable knowledge, they are willing to sacrifice their time in guiding and helping me throughout the experiment.

Moreover, I would also like to thank all SCE staffs for their kindness cooperation and helping hands. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated.

Lastly, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me directly or indirectly. Their contributions are very much appreciated. Thank you very much.

TAVAYOGESHWARY THANGADURAI

June 2017

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
LIST OF SYMBOL	viii
LIST OF ABBREVIATIONS	ix
ABSTRAK	x
ABSTRACT	xi
CHAPTER ONE : INTRODUCTION	1
1.1 Research background	1
1.2 Problem statement	3
1.3 Objectives	4
1.4 Scope of study	4
1.5 Organization of thesis	5
CHAPTER TWO : LITERATURE REVIEW	6
2.1 Dyes	6
2.2 Adsorption	9
2.3 BET (Brunauer, Emmett and Teller)	10
2.4 Fourier Transform Infrared Spectroscopy (FTIR)	11

2.5	Elemental analysis	12
2.6	Spectrophotometry	12
2.7	Colour strength	14
2.8	Decolourization rate	15
CHAPTER 3 : MATERIALS AND METHODS		16
3.1	Materials	16
3.2	Experimental procedures	21
3.3	Formation and characterization of dye conjugate-CaCO ₃	21
3.4	In situ treatment of organic wastewater	22
CHAPTER FOUR : RESULTS AND DISCUSSION		23
4.1	Experimental design	23
4.2	Result data	24
4.3	Characterization	28
CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATIONS		31
5.1	Conclusions	31
5.2	Recommendations	31
REFERENCES		32
APPENDICES		34

LIST OF TABLES

	Page
Table 2.1 Classification of dyes	7
Table 2.2 Methods of dye removal	8
Table 3.1 List of chemicals used	16
Table 3.2 Properties of Acid Violet 7	17
Table 3.3 Properties of Direct Blue 71	18
Table 3.4 Properties of Brilliant Green	19
Table 3.5 Properties of sodium carbonate	19
Table 3.6 Properties of calcium chloride	20
Table 3.7 List of equipment used	20
Table 4.1 Absorbance data of spectrophotometry for Brilliant Green	24
Table 4.2 Final absorbance and concentration percentage for Brilliant Green	24
Table 4.3 Absorbance data of spectrophotometry for industrial waste sample	25
Table 4.4 Final absorbance and concentration percentage for industrial waste sample	25
Table 4.5 Elemental analysis for Acid Violet-Brilliant Green-CaCO ₃	29

LIST OF FIGURES

		Page
Figure 2.1	Basic structures of spectrophotometer	24
Figure 2.2	Transmittance	25
Figure 3.1	Schematic flow diagrams of experiment activities	31
Figure 4.1	Fourier Transform Infrared spectroscopy graph for 1mM Acid Violet 7 and 1mM Brilliant Green	29
Figure A	Calibration curve for 1mM Acid Violet 7 with 0.25mM Brilliant Green	33
Figure B	Calibration curve for 1mM Acid Violet 7 with 0.5mM Brilliant Green	33
Figure C	Calibration curve for 1mM Acid Violet 7 with 0.75mM Brilliant Green	34
Figure D	Calibration curve for 1mM Acid Violet 7 with 1mM Brilliant Green	34
Figure E	Calibration curve for 1mM Direct Blue 71 with 0.25mM Brilliant Green	35
Figure F	Calibration curve for 1mM Direct Blue 71 with 0.5mM Brilliant Green	35
Figure G	Calibration curve for 1mM Direct Blue 71 with 0.75mM Brilliant Green	36
Figure H	Calibration curve for 1mM Direct Blue 71 with 1mM Brilliant Green	36
Figure I	Calibration curve for industrial waste sample with 0.25mM Acid Violet 7	37

Figure J	Calibration curve for industrial waste sample with 0.5mM Acid Violet 7	37
Figure K	Calibration curve for industrial waste sample with 0.75mM Acid Violet 7	38
Figure L	Calibration curve for industrial waste sample with 1mM Acid Violet 7	38
Figure M	Calibration curve for industrial waste sample with 0.25mM Direct Blue 71	39
Figure N	Calibration curve for industrial waste sample with 0.5mM Direct Blue 71	39
Figure O	Calibration curve for industrial waste sample with 0.75mM Direct Blue 71	40
Figure P	Calibration curve for industrial waste sample with 1mM Direct Blue 71	40

LIST OF SYMBOL

	Symbol	Unit
A	Absorbance	-
A_n	Absorbance at n nm	-
C_o	Liquid-phase concentration of dye at initial	mg/L
C_t	Liquid-phase concentration of dye at any time t	mg/L
C	Concentration	mg/L
ΔC	Change in concentration	mg/L
I_o	Light intensity before light beam passes through cuvette	-
I_t	Light intensity after light beam passes through cuvette	-
K	Absorbance	-
l	Light path	cm
S	Scattering	-
T	Transmittance	-
Δt	Time interval	hr
V	Volume of solution	L
W	Mass of dry adsorbent used	g
λ	Wavelength	nm
%	Percentage	-

LIST OF ABBREVIATIONS

AV	Acid Violet 7
BET	Brunauer-Emmett-Teller
BG	Brilliant Green
BOD	Biological Oxygen Demand
CaCO ₃	Calcium carbonate
DB	Direct Blue 71
FTIR	Fourier Transform Infrared
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
pH	Potential hydrogen
SO ₃ ⁻	Sulphur trioxide
3D	Three dimensional

PENJERAP HIBRID UNTUK RAWATAN AIR SISA DALAM SITU

ABSTRAK

Penghibridanan organik/organic biasanya digunakan untuk mensintesis bahan berfungsi. Walaubagaimanapun, ia jarang dipertimbangkan dalam rawatan air sisa industri. Melalui sekat gerak anionik (mis Acid Violet 7, Direct Blue 71) - kationik (mis Brilliant Green) pewarna kompleks dengan kalsium karbonat yang berkembang, pewarna konjugat penghibridan telah dibentangkan. Morfologi 3D dan struktur hybrid konjugat dicirikan dengan menggunakan Brunauer-Emmett-Teller (BET), jelmaan Fourier spektroskopi inframerah (FTIR) dan Analisis Elemental dan mekanisme pembentukan dijelaskan. Satu langkah penghibridan yang mudah digunakan dalam rawatan air sisa organic pekat. Teknik ini melibatkan penjerapan, pemberbukuan dan kompleksasi ion dan menyebabkan penyingkiran bahan-bahan organik pada tahap yang tinggi. Dengan "menggunakan sisa untuk merawat sisa", rawatan air sisa yang kos efektif dan mesra alam mudah dicapai. Teknik ini telah diuji dengan menggunakan air sisa industry dan air sungai. Penyingkiran pewarna paling baik telah diperolehi bagi penggunaan 1mM Acid Violet 7 untuk merawat 1mM Brilliant Green iaitu 97.53% manakala untuk merawat sampel sisa industri, penyingkiran pewarna yang paling tinggi 83% dengan 0.5 mM Direct Blue 71. Ini telah menjelaskan ion pasangan keseimbangan antara pewarna anionik dan pewarna kationik.

HYBRID ADSORBENT FOR IN SITU WASTEWATER TREATMENT

ABSTRACT

Inorganic/organic hybridization is usually used to synthesize functional materials. However, it is rarely considered in industrial wastewater treatment. By immobilizing the anionic (e.g. Acid Violet 7, Direct Blue 71)–cationic (e.g. Brilliant Green) dye complex with growing calcium carbonate, dye conjugate hybridization was presented. The structure of the conjugate hybrid were characterized by using Brunauer–Emmett–Teller (BET), Fourier transform infrared spectroscopy (FTIR), spectrophotometry and elemental analysis and the mechanism of formation was explained. The simple single-step hybridization applied in treatment of concentrated organic wastewaters. This technique involves adsorption, flocculation and ionic complexation and resulted a high level of removal of organic substances. By “using waste to treat waste”, a convenient, cost-effective and environment-friendly wastewater treatment was accomplished. This technique was tested by using industrial wastewater and river water. The best dye removal was obtained for the use of 1mM of Acid Violet 7 to treat 1mM of Brilliant Green which is 97.53% whereas for treating industrial waste sample, the highest dye removal of 83% with the 0.5mM of Direct Blue 71. This explained ion pair equilibrium between the anionic dye and cationic dye.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Colour removal techniques includes coagulation/adsorption of dyes by physical methods or completely destruct of dye molecules by chemical methods such as electrolysis and ozonation. Conventional municipal wastewater treatment system in textile wastewater treatment has drawback of generating sludge or forming hazardous by-product which causes secondary pollution. This combination of physical and biological treatment achieve satisfactory organic contaminant removal, but has complicated procedure and long period which leads to high running cost and secondary pollution (Motlagh et al., 2014).

Among various treatment for pollutant removal from wastewater such as chemical coagulation, photodegradation, biodegradation and active sludge, adsorption is efficient in separating wide range. Selectivity to remove specific toxic chemical can be endowed for adsorbent. Universality of adsorbent application is limited by complex conventional method and use of poisonous chemicals. Porous silicates that is widely used as adsorbing material with well-defined pore structure, anchor binding groups for removing pollutants. Functionalization porous silica via attaching a series of functional group onto surface through surface modification that require organic solvent refluxing condition, by organic silanes which is expensive, to increase adsorbing capacity. Good adsorbent prepared using eco-friendly and cheap material with high efficiency, low cost and remove various pollutants from wastewater is the targeted innovation (Wang et al., 2016).

Conventional abiotic in azo dye wastewater treatment like adsorption, flocculation, ion exchange and membrane filtration and destructive treatment such as electrolysis, oxidation and reduction. Activated carbon as most efficient and effective adsorbent popular in treating various wastewater. Apart from producing additional effluent and causing adsorbent loss, it require chemical and thermal regeneration of used carbon which is expensive and impractical on large scale. Adsorption by conventional sorbent depend on specific surface area and thus low adsorption capacity, poor selectivity, slow adsorption rate and difficult reproduction restrict extensive use. Moreover, membrane filtration is slow and high cost of use whereas colour reversion of treated water and disposal of sludge with high water content in flocculation. Destructive treatment causes secondary pollution and high cost. “Using waste to treat waste” paradigm is adopted as optimal solution in wastewater treatment by reusing waste. Fly ash, de-oiled soya, wheat husk are wastes reused and applied in dye wastewater treatment to control pollution and partly reuse resource (Hu et al., 2010).

Inorganic/organic hybridization synthesise functional material but rarely considered in industrial wastewater treatment. Immobilizing the anionic-cationic dye complex with growing calcium carbonate for dye conjugate hybridization. 3D-morphology and structure of conjugate hybrid were characterized and mechanism of formation explained. The shell-core structural hybrid is formed and stacked into cubes. When the simple single-step hybridization applied to treatment of concentrated organic wastewater, it performed adsorption, flocculation and ionic complexation and high level organic substances removal, providing convenient, cost-effective and environment-friendly wastewater treatment (Zhao et al., 2009).

1.2 Problem statement

Coloured effluent discharged from textile processing and dye-manufacturing industries consist of 15% of unreacted dyestuff which doesn't bind to fibers during dyeing process and released as pollutants. Azo dyes is highly substituted aromatic rings joined by azo group (-N=N-) which affect flora and fauna, and their metabolites are mutagenic and carcinogenic. These dyes which are adherent, long lasting, resistant to sunlight and chemical process, are also stable in acidic and alkaline media and resistant to temperature, heat, light and microbes, providing stable persistence and long-term accumulation in environment. Physical and chemical treatment methods investigated are flocculation-coagulation, photodegradation, biological degradation, active sludge, ion exchange, membrane separation/filtration and destructive treatment such as oxidation, electrolysis and reduction. Conventional municipal wastewater treatment system which treats textile wastewater, generates sludge or form hazardous by-product that causes secondary pollution. These methods has complicated procedure and time-consuming which results in high operating cost. Adsorption as simple, operational convenience, effective and economical method in low-concentration pollution treatment, by conventional sorbents depends on specific surface area and surface ion exchange sites, leading to low adsorption capacity, poor selectivity, slow adsorption rate and difficult reproduction restrict extensive use. Hence, dye conjugate hybridization by immobilizing waste anionic-cationic dye complex onto inorganic skeleton CaCO_3 is proposed as "using waste to treat waste". Plus, feasibility of dye-immobilized CaCO_3 sludge reuse investigated based on dye wastewater characteristic.

1.3 Objectives

The purpose of this research proposed,

- i. To establish in situ dye wastewater treatment method by hybrid adsorbent.
- ii. To produce dye conjugate hybridization by immobilizing anionic-cationic dye complex with growing calcium carbonate.
- iii. To characterize dye conjugated-CaCO₃ using BET, FTIR and element analysis

1.4 Scope of study

In this work, hybrid adsorbent was prepared to produce dye conjugate hybridization by immobilizing anionic-cationic dye complex with growing calcium carbonate for in situ dye wastewater treatment. The anionic dye used was Acid Violet 7 and Direct Blue 71 whereas the cationic dye was Brilliant Green. The optimal molar ratio of Ca²⁺ to CO₃²⁻ of 2:1 to form calcium carbonate by adding sodium carbonate and calcium chloride for rapid sedimentation. To investigate ion pair equilibrium of the anionic dye and cationic dye, the optimal concentration ratio of both the dyes was identified.

The dye conjugate hybrid was characterized in terms of surface area, surface morphology, proximate content, elemental content and surface chemistry by means of BET, FTIR, spectrophotometry and elemental analysis. The industrial wastewater sample and river water were also included for comparison purposes. The initial concentration of dyes used were within the range of 0 to 1mM to study on the interaction between the anionic and cationic dyes as a result of ion pair complexation.

1.5 Organization of thesis

The following are the contents for each chapter in this study:

Chapter 1 introduces the usage of dyes in textile industries, problem statement, research objectives and organization of thesis.

Chapter 2 discusses the literature review of this study which includes the dyes, adsorption, BET, FTIR, elemental analysis, spectrophotometry, colour strength and decolourisation rate.

Chapter 3 covers the materials and details of methodology which discusses on the description of equipment and materials used, adsorption experiment, experimental procedure and description of factors affecting the adsorption process.

Chapter 4 refers to the experimental results, discussions of the data obtained, further elaboration on the effect of factors on adsorption and the results collected.

Chapter 5 concludes all the findings obtained in this study as well as the recommendations are included.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dye is a coloured substance that has affinity to the substrate being applied to. The dye is applied in an aqueous solution, and to enhance the fastness of the dye on the fibre, it may require a mordant. The dyes adhere to compatible surfaces by solution, by physical adsorption or by mechanical retention, by forming covalent bond or complexes with salts or metals. A group of atoms which is responsible for the dye colour, known as chromophores and chromophore-containing centers are based on diverse functional groups, such as azo, anthraquinone, methine, nitro, arilmethane, carbonyl and others. Auxochromes like amine, carboxyl, sulfonate and hydroxyl, are electrons withdrawing or donating substituents to generate or intensify the colour of the chromophores (Chequer et al., 2013).

Consumer products such as textiles, paints, cosmetics, pharmaceuticals, food, paper, photographic industry, printing inks, and plastics requires the usage of dye in production where colour and texture are added to the material (Kumar, 2014). Since 3500 BC, extraction from vegetables, fruit and flowers are used as natural dyes. Alternatively, chemical dyes provide and retain richer colour throughout washing and exposure by bonding with the fabric. Annually, over 700 000 tons synthetic dyes are being produced worldwide and around 10 000 different dyes and pigments are used industrially. Depending on the type of textile or product, various types of dyes with assorted chemical compounds are used in production. There are few types of dyes being natural, synthetic, food and other dyes like leather, laser and also based on chemical classification as shown in Table 2.1. (Adegoke et al., 2015)

Table 2.1: Classification of dyes

Type	Product Material
Acid dye	Animal fiber
Basic dye	Paper
Direct dye	Cotton wool or Cotton silk
Pigment dye	Paints and Inks

Out of several chemicals as heavy metals, sulphuric acid and other metallic elements, these dyes are manufactured by mixing, synthesizing in a reactor, filtering for impurities, drying out and then blending. To induce reactions, additives, solvents and chemical compounds are used and high demand for variable patterns and unique colours for clothing and other textiles involves chemical use.

Textile dyeing and treatment estimated to contribute around 17 to 20 percent of total industrial water pollution. In dye application processes, the presence of residual colour, high levels of electrolytes, toxic substances such as metals and unreacted raw materials produce wastewaters that cause unacceptable environmental risks. Dye content in wastewater diminishes light penetration and photosynthesis as it absorbs and reflects sunlight entering the water. Highly toxic dye results in oxygen deficiency and the reactive ones may cause respiratory sensitisation when exposed to. Whereas, dye and its breakdown products are carcinogenic or mutagenic. Dyes increases Biological Oxygen Demand (BOD) and turbidity of effluent thereby affecting aquatic life (Civil Digital, 2017). Water treatment systems is important as the textile industry is a water consuming. Due to its high thermal and photo stability to resist bio degradation, dyes remain in the environment for an extended period of time.

2.2 Adsorption

Emerging concepts of sustainability and eco-friendly alternatives has drawn the attention towards treating dye industry effluent. Various methods for dye removal from the industrial effluent have been reported as shown in the Table 2.2.

Table 2.2: Methods for dye removal (Kharub, 2012)

Process	Technology	Advantage	Disadvantage
Conventional Treatment Processes	Coagulation Flocculation Biodegradation	Simple, economically feasible	High sludge production, handling and disposal problems
		Economically attractive publicly acceptable treatment	Slow process, necessary to create optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce high quality treated effluent	Ineffective against disperse and vat dyes, expensive regeneration and results in loss of adsorbent, nondestructive process
Established recovery processes	Membrane separations	Removes all dye types, produce high quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required

Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bio-adsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, nondestructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms	Slow process, performance depends on some external factors (pH and salts)

The adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface in contact is known as adsorption (Kandisa et al, 2016). Solids used to adsorb gases or dissolved substances are referred as adsorbents whereas the adsorbed molecules called as the adsorbate (Chemistry Learning, 2009). Adsorption is generally classified into physisorption (weak van der Waals forces) and chemisorption (covalent bonding) (Diffen, 2017). Physisorption is reversible which involves electrostatic attraction between polar molecules that possess negative and positive charges whereas non-polar substances without distinct surface charge attracted to non-polar adsorbents. However, chemisorption is an irreversible process where substances are held by chemical bonds and it is influenced by factors such as interactions between adsorbate and adsorbent, nature of adsorbate, surface area and pores structure of adsorbent, operating temperature and contact time.

2.3 BET (Brunauer, Emmett and Teller)

Using a fully automated analyser, BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure. In studying the effects of surface porosity and particle size, the technique encloses external area and pore area evaluations to determine the total specific surface area in m^2/g . The specific surface area of a sample including pore size distribution is measured by BET. Using this information, the dissolution rate which is proportional to the specific surface area. As all porous structures adsorb the small gas molecules, the specific surface determined relates to the total surface area (reactive surface) and thus larger than the surface area determined by air permeability.

By physical adsorption of a gas on the surface of the solid and calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface, the specific surface area of a powder is determined. Relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder results in physical adsorption (Particle Analytical, 2017). BET surface area characterization of disperse, nonporous or macroporous materials pore diameter $>50\text{nm}$ (type II isotherms), mesoporous materials with pore diameter between 2 nm and 50 nm (type IV isotherms) and microporous materials (<2 nm, type I isotherms) (Lucideon, 2017)

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by detecting functional groups and characterizing covalent bonding information. It produces an infrared absorption spectrum which produces a profile of the sample that is used to screen and scan samples for many different components. (Intertek, n.d.).

The sample absorb some radiation and some are transmitted when Infrared radiation is passed through a sample. The spectrum representing a distinctive molecular ‘fingerprint’ of the sample is the resulting signal at the detector. It converts the detector output to an interpretable spectrum and generates spectra with patterns that provide structural insights. To record information about a material placed in the IR beam, the FTIR uses interferometry to modulate the wavelength from a broadband infrared source and results in spectra that used to identify or quantify the material. The detector measures the intensity of transmitted or reflected light as a function of its wavelength. FTIR spectrum arises from interferograms decoded into recognizable spectra and since molecules exhibit specific IR fingerprints, the sample is identified by the pattern in spectra (Thermo Fisher Scientific, 2017)

The FTIR spectra are presented as plots of intensity versus wavenumber (in cm^{-1}) which is reciprocal of the wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wavenumber. This analytical technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures. Absorbed IR radiation excites molecules into a higher vibrational state when a material is irradiated with infrared radiation. Function of the energy

difference between the at-rest and excited vibrational states is the wavelength of light absorbed by a particular sample which is the characteristic of its molecular structure (Materials Evaluation and engineering Inc, 2014).

2.5 Elemental Analysis

Elemental analysis and testing involve determination and quantification of elements in a sample, identification of the elemental and isotopic composition and trace level elements. Quantitative analysis is the determination of the atom% or weight% of each element present whereas qualitative analysis is to determine elements exist in a sample (Nanolab Technologies, 2017). The sample heated in either oxygen or an inert gas atmosphere and the relative amounts of Carbon, Hydrogen, Nitrogen and Sulphur produced by the flash combustion is measured (University of Birmingham, 2016)

2.6 Spectrophotometry

Spectrophotometry is a method to measure the amount of light absorbed by a chemical substance where the intensity of light is measured as a beam of light passes through sample solution. As a compound absorbs, transmits or reflects light (electromagnetic radiation) over a certain range of wavelength, the amount of a known chemical substance is measured (Vo et al, 2017)

According to Beer's Law, the amount of light of a particular wavelength absorbed by a substance across a constant distance (light path) is proportional to the concentration of that substance:

$$A_n = l \times c \quad \dots (2.1)$$

where A_n is the absorbance at n nm

l is the light path (cm)

c is the concentration (The University of Queensland, 2017)

An instrument that measures the amount of photons (the intensity of light) absorbed after it passes through sample solution is known as spectrophotometer.

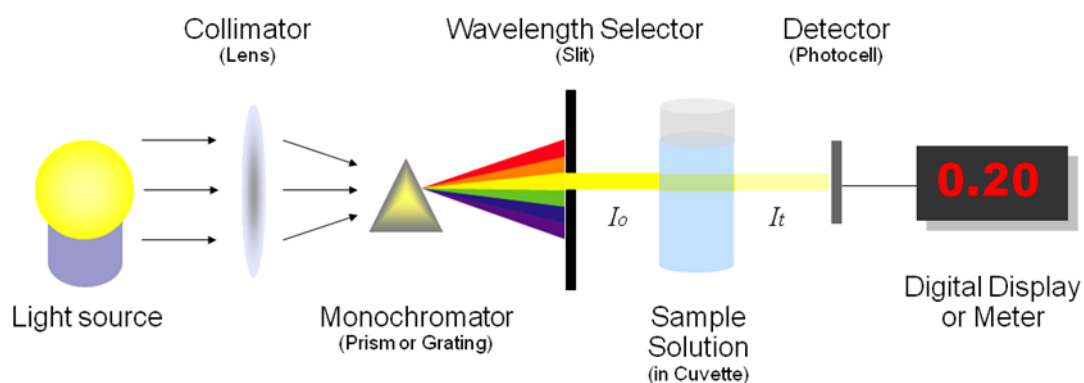


Figure 2.1: Basic structures of spectrophotometer

A spectrophotometer comprised of two devices such as a spectrometer and a photometer. A spectrometer produces, disperses and measures light whereas a photometer is photoelectric detector that measures the intensity of light. Transmittance is the fraction of light that passes through the sample:

$$\text{Transmittance } (T) = \frac{I_t}{I_o} \quad \dots (2.2)$$

where I_t is the light intensity after the beam of light passes through the cuvette

I_o is the light intensity before the beam of light passes through the cuvette

And thus, absorbance is the amount of photons absorbed:

$$\text{Absorbance } (A) = -\log(T) = -\log\left(\frac{I_t}{I_o}\right) \quad \dots (2.3)$$

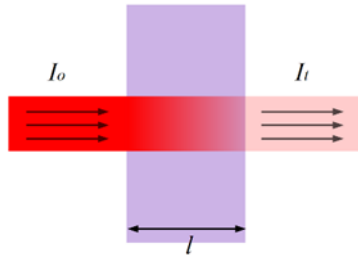


Figure 2.2: Transmittance

2.7 Colour Strength

Colour strength of a dye or pigments is its ability to impart colour to other materials which is determined by comparing to standard with known amount of colorant (Hunter Lab, 2008). The colour strength of coloured pigments is greater as the concentration of a coloured pigment required to achieve a defined impression of colour that is a given depth of a shade is lower. Strength of colorant (dyestuff / pigment) is related to absorption property and however, reflectance is measured. The strength of colorants is higher as the absorption coefficient is higher. Higher scattering coefficient (S) cause better reducing power of TiO₂ white (Tinting Strength of white). Black scatters the least and absorbs the most whereas white acts vice versa. The relation between reflectance and absorbance is stated by Kubelka – Munk theory:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad \dots (2.4)$$

where R is reflectance

K is absorbance

S is scattering

K/S versus Wavelength curve is characteristics of colorant and colour strength is defined as (Chromatic Notes, 2013):

$$\text{Colour Strength} = \frac{\left(\frac{K}{S}\right)_{\text{Batch}}}{\left(\frac{K}{S}\right)_{\text{Standard}}} \times 100 \quad \dots (2.5)$$

2.8 Decolourization rate

Volumetric rate of dye decolorization (r_{vol} ; $\text{mg L}^{-1} \text{h}^{-1}$) is calculated by using the following equation:

$$r_{\text{vol}} = \frac{\Delta C(t)}{\Delta t} \quad \dots (2.6)$$

where $\Delta C(t)$ (mg L^{-1}) is the change in dye concentration over the time interval Δt (h). Decolorization percentage is defined by the following formula (Gulnur Arabaci, 2014)

$$\text{Decolorization percentage (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad \dots (2.7)$$

The amount of adsorption at time t , q_t (mg/g) is calculated by (M. Hassan, 2007):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad \dots (2.8)$$

where C_0 is liquid-phase concentration of dye at initial (mg/L)

C_t is liquid-phase concentration of dye at any time t (mg/L)

V is the volume of the solution (L)

W is the mass of dry adsorbent used (g)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

In this experiment, dyes such as Acid Violet 7 and Direct Blue 71 as anionic dye while Brilliant Green as cationic dye and chemicals like sodium carbonate and calcium chloride are used. The table below shows their characteristics:

Table 3.1: List of chemicals used

Chemical	Purity	Supplier	Usage
Acid Violet 7	40%	Sigma-Aldrich	Studied (Sigma-Aldrich Corporation, 2017) to determine the degradation of the dye by various microorganisms such as <i>Pseudomonas</i> sp. (Santa Cruz Biotechnology, 2010)
Direct Blue 71	50%	Sigma-Aldrich	used for colouring of rayon, paper, leather and to a less extent nylon (Santa Cruz Biotechnology, 2010)
Brilliant Green	90%	Sigma-Aldrich	used for staining of nodule initials in <i>Lupinus angustifolius</i> and <i>Arachis hypogaea</i>
Sodium Carbonate	99.99%	Sigma-Aldrich	as water softener, food processing aid, pH modifier, swimming pool chemical and electrolyte and used in manufacture of glass, paper, soaps and detergents, and many other useful chemicals. (Softschools.com, 2017)
Calcium Chloride	99.99%	Sigma-Aldrich	Dust control on roadways, food processing, as an accelerator for ready mix concrete curing and as an anti-freeze for coal storage and transportation. (Tetra Technologies, Inc., 2017)

The properties of these chemicals used are as in table below:

Table 3.2: Properties of Acid Violet 7 (Aldrich, 2002)

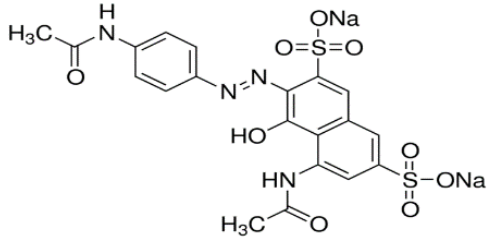
Properties	
Common name	Acid Violet 7
IUPAC name	Disodium;(3E)-5-acetamido-3-[(4-acetamidophenyl)hydrazinylidene]-4-oxonaphthalene-2,7-disulfonate
Other name	Acid Naphthol Red 6B
Molecular formula	C ₂₀ H ₁₆ N ₄ Na ₂ O ₉ S ₂
Molecular weight	566.467 g/mol
CAS number	4321-69-1
Maximum wavelength, λ_{\max}	520nm
Chemical structure	 The chemical structure of Acid Violet 7 is a complex naphthalene derivative. It features a central naphthalene ring system. At the 1-position, there is a hydroxyl group (-OH). At the 2-position, there is a sulfonate group (-SO ₃ Na). At the 3-position, there is a hydrazinylidene group (=N-N-), which is connected to a 4-acetamidophenyl ring. At the 4-position, there is an acetamido group (-NH-C(=O)-CH ₃). At the 5-position, there is another acetamido group (-NH-C(=O)-CH ₃). At the 6-position, there is a sulfonate group (-SO ₃ Na). The overall structure is a disodium salt of a naphthol derivative.

Table 3.3: Properties of Direct Blue 71 (Aldrich, 2002)

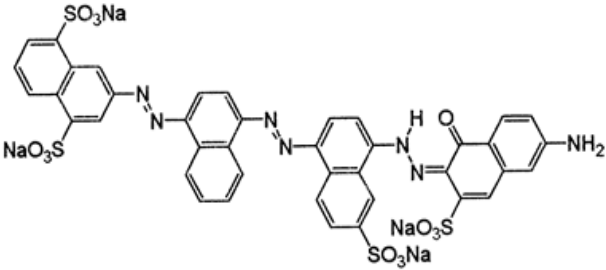
Properties	
Common name	Direct Blue 71
IUPAC name	Tetrasodium;3-[[4-[[4-[2-(6-amino-1-oxo-3-sulfonatophthalen-2-ylidene)hydrazinyl]-6-sulfonatophthalen-1-yl]diazanyl]naphthalen-1-yl]diazanyl]naphthalene-1,5-disulfonate
Other name	DurazolBlue2R
Molecular formula	C ₄₀ H ₂₃ N ₇ Na ₄ O ₁₃ S ₄
Molecular weight	1029.87g/mol
CAS number	4399-55-7
Maximum wavelength, λ _{max}	594nm
Chemical structure	

Table 3.4: Properties of Brilliant Green (Aldrich, 2002)

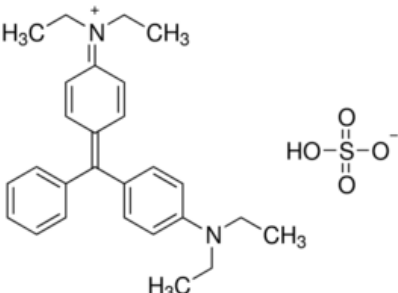
Properties	
Common name	Brilliant Green
IUPAC name	4-[[4-(diethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-diethylazanium;hydrogen sulphate
Other name	Malachite Green G
Molecular formula	C ₂₇ H ₃₄ N ₂ O ₄ S
Molecular weight	482.639g/mol
CAS number	633-03-4
Maximum wavelength, λ _{max}	625 nm
Chemical structure	

Table 3.5: Properties of Sodium Carbonate (Aldrich, 2002)

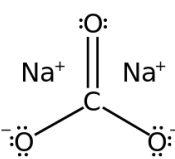
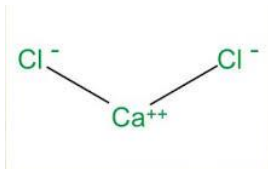
Properties	
Common name	Sodium carbonate
IUPAC name	Disodium carbonate
Other name	Carbonic acid disodium salt
Molecular formula	Na ₂ CO ₃
Molecular weight	105.988 g/mol
CAS number	497-19-8
Chemical structure	

Table 3.6: Properties of Calcium Chloride (Aldrich, 2002)

Properties	
Common name	Calcium chloride
IUPAC name	Calcium dichloride
Other name	Calcium chloride anhydrous
Molecular formula	CaCl ₂
Molecular weight	110.978 g/mol
CAS number	10043-52-4
Chemical structure	

Moreover, the river water is obtained from the Nibong Tebal river in Penang, Malaysia whereas the wastewater sample is taken from a textile industry company which contains azo-dye as the cationic dye.

The table below shows the equipment used for conducting this experiment.

Table 3.7: List of equipment used

Equipment	Brand	Purpose
Beaker	Pyrex	To hold the chemicals and used for mixing
Volumetric flask	Pyrex	To prepare a chemical solution of known volume
UV/Vis Spectrophotometer		To identify and measure organic and inorganic compounds in a wide range of products and processes
Stirrer	Pyrex	To agitate liquids for speeding up reactions or improving mixtures
Cuvette		To examine coloured or colourless solutions that are free of turbidity and light scattering of turbid suspensions

3.2 Experimental procedures

The overall experimental activities carried out in this study are presented in the following schematic flow diagram:

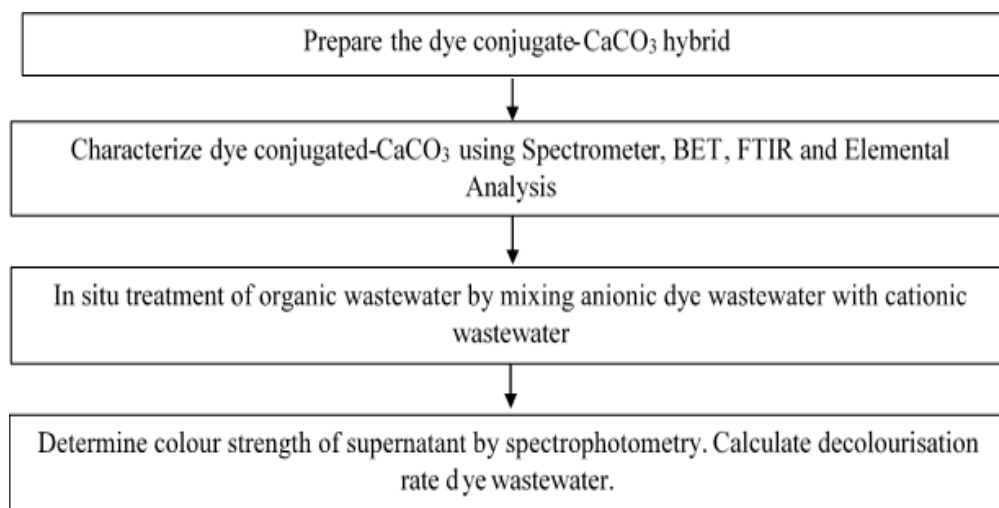


Figure 3.1: Schematic flow diagrams of experimental activities

3.3 Formation and characterization of the dye conjugate-CaCO₃

About 1.0mM of Acid Violet solution was prepared with 0.1416g powder in 250mL distilled water. By adding 0.1207g powder to 250mL of distilled water, 1mM of Brilliant Green solution was prepared. Then, 0.02M of sodium carbonate solution was prepared with 0.53g of powder and 250mL of distilled water. To prepare 0.04M of solution, 1.11g of calcium chloride powder was added to 250mL of distilled water. The Acid Violet solution, Brilliant Green solution and sodium carbonate solution were poured into a 1000mL beaker and mixed thoroughly. Calcium chloride solution was added slowly to the mixture in the beaker under stirring. The solution in the beaker was allowed to suspend for 24 hours and the suspended product substance was precipitated by filtration method. The precipitate was washed with deionized water. Around 10% product liquid was prepared with deionized water and aged for

48 hours. Particle characteristics were determined using spectrophotometer, BET, FTIR and elemental analysis. This experiment was repeated for Direct Blue as the anionic solution with 0.2575g powder in 250mL distilled water. The procedures were repeated for Brilliant Green at different concentrations such 0.75mM, 0.5mM and 0.25mM.

3.4 In situ treatment of organic wastewater

Acid Violet solution of 1.0mM was prepared with the river water and 0.1416g of powder as anionic dye wastewater. The solution was mixed with cationic dye wastewater sampled from textile industry. Next, 0.53g of sodium carbonate is dissolved in distilled water to prepare 250mL of 0.02M solution. These solutions prepared were mixed for 5 minutes and then 250mL of 0.04M calcium chloride solution by dissolving 1.11g of powder in distilled water. This solution was then added to the mixture and stirred thoroughly. The mixture was allowed to precipitate and the solution is filtered. Colour strength and concentration of supernatant was determined by spectrophotometry and decolourisation rate of the dye wastewater was calculated. These steps were repeated by replacing Acid Violet with Direct Blue as anionic dye by dissolving 0.2575g powder in 250mL distilled water. The procedures were repeated at different concentrations like 0.75mM, 0.5mM and 0.25mM.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter consisting of two sections where the experimental results and discussion are presented. The experimental design applied for preparing the dye-conjugate hybrid adsorbent and optimization of the parameters used illustrated in the first section. Whereas, in the second section, the characterization of the samples is discussed.

4.1 Experimental design

Two variables concentration (*mM*) and type of dye used with absorbance as the response was considered in this study. Table 4.1 shows the data obtained for initial absorbance of the mixture of 1mM Acid Violet 7 and 1mM Direct Blue 71 with different concentrations of Brilliant Green (BG) and 0.02M sodium carbonate as well as 0.04M calcium chloride at different molarity percentage to construct a calibration curve for spectrophotometry. This experiment was tested for its application of dye removal with river water and industrial waste sample. Table 4.3 shows the data obtained for initial absorbance of the mixture of industrial waste sample and different concentrations of Acid Violet 7 and Direct Blue 71 in river water with 0.02M sodium carbonate as well as 0.04M calcium chloride at different molarity percentage to construct a calibration curve for spectrophotometry.

4.2 Result Data

Table 4.1: Absorbance data of spectrophotometry for Brilliant Green

Percentage	Absorbance							
	Acid Violet 7				Direct Blue 71			
	0.25mM BG	0.5mM BG	0.75mM BG	1mM BG	0.25mM BG	0.5mM BG	0.75mM BG	1mM BG
0	0	0	0	0	0	0	0	0
20	0.837	0.911	0.887	0.856	1.127	1.218	1.61	1.575
40	1.583	1.593	1.56	1.687	1.933	2.002	2.564	2.682
60	2.183	2.232	2.357	2.361	2.788	2.561	3.365	3.321
80	2.771	2.678	3.073	2.845	3.431	3.053	3.963	3.549
100	3.391	3.395	3.422	3.481	4	3.633	3.985	3.996

Table 4.2: Final absorbance and concentration percentage for Brilliant Green

Brilliant Green	1mM Acid Violet 7				1mM Direct Blue 71			
	Absorbance	Percentage	r _{vol}	%	Absorbance	Percentage	r _{vol}	%
1mM	0.222	2.4685	4.0638	97.5315	1.402	23.372	3.1928	76.628
0.75mM	0.316	5.6823	3.9299	94.3177	1.48	24.7153	3.1369	75.2847
0.5mM	0.232	2.5194	4.0617	97.4806	1.159	24.3093	3.1538	75.6907
0.25mM	0.233	3.4604	4.0225	96.5396	0.804	14.9473	3.5439	85.0527