SYNTHESIS AND CHARACTERISATION OF CARBON, NITROGEN CO-DOPED-TITANIUM DIOXIDE/SODIUM ALGINATE BUOYANT PHOTOCATALYST FOR DEGRADATION OF DIAZINON

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by

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Zhexun. Last but not least, I am thankful to the most precious people in my life, my late mother, Mrs. Hayani, my parents, Mr. Mohamad Idris and Mrs. Khairiah and my siblings, Mr. Ikhfar, Ms. Husna, Mr. Irfan, Mrs. Aisyah, Ms. Nisa, Ms. Seha, Mrs. Aisyah and Mr. Naim, as well as to my cute nieces, Nuha and Nufa for their love, sacrifices and unconditional support throughout my PhD's journey.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SCHEMES

LIST OF SYMBOLS

%	Percentage
^{o}C	Degree celcius
e^-	Electrons
h^+	Hole
$\cdot O_2^-$	Superoxide radical
$\cdot OH$	Hydroxyl radical
$^1O_2$	Singlet oxygen
eV	Electrovolt
g	Gram
L	Litre
mL	Millilitre
cm	Centrimetre
pm	picometre
mW	Milliwatts
mins	minutes
h	hour
t	time
C	Concentration
J	Joule
χ	Electronegativity of semiconductor
λ	Wavelength

LIST OF ABBREVIATIONS

TTIP	Titanium (iv) tetraisopropoxide
CMC	Carboxymethylcellulose
C	Carbon
N	Nitrogen
XRD	X-ray diffraction
HRTEM	High-resolution transmission electron microscopy
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
FTIR	Fourier-transform infrared
XPS	X-ray photoelectron spectroscopy
UV-Vis	Ultraviolet-visible
GC-MS	Gas chromatography-mass spectroscopy
PL	Photoluminescence
TOC	Total organic carbon
IC	Ion chromatography
TiO_2 NPs	Titanium dioxide nanoparticles
C, N-TiO_2 NPs	Carbon, nitrogen co-doped titanium dioxide nanoparticles
MoS_2	Molybdenum disulfide
NaOB	Organobentonite
RGO	reduced graphene oxide
RhB	Rhodium B
MO	Methyl orange
MB	Methylene blue
DIZ	Diazinon
UNESCO	United Nations Educational, Scientific and Cultural Organization
CO_2	Carbon dioxide
H_2O	Water
O_2	Oxygen
IMP	2-isopropyl-6- methylpyrimidin-4-ol
CB	Conduction band
VB	Valence band

COD	Crystallographic Open Database
IEP	Isoelectric point
pH_{PZC}	Point of zero charges
N/A	Not applicable

LIST OF APPENDICES

SINTESIS DAN PENCIRIAN KARBON, NITROGEN DWIDOP-TITANIUM DIOKSIDA/SODIUM ALGINAT FOTOPEMANGKIN TERAPUNG BAGI PENGURAIAN DIAZINON

ABSTRAK

Penggunaan fotopemangkin titanium dioksida (TiO_2) telah mendapat perhatian penting dalam kalangan penyelidik kerana potensinya yang berkesan untuk menyingkirkan bahan pencemar daripada air sisa. Fotopemangkin terapung diterokai sebagai calon yang berdaya saing untuk aplikasi rawatan air sisa, bertujuan untuk menangani cabaran penapisan semasa proses rawatan tersebut. Dalam kajian ini, reka bentuk TiO_2 yang diubah suai dengan pembawa terapung yang sangat tahan lama adalah penting untuk meningkatkan prestasi fotopemangkinnya dalam menyingkirkan bahan pencemar daripada air sisa. Oleh itu, karbon (C) dan nitrogen (N)-dwidop TiO_2 NP dengan peratusan C:N yang berbeza berjaya dibangunkan menggunakan kaedah sol-gel. C, N-TiO_2 NP yang optimum mempamerkan sifat yang menggalakkan, termasuk aktiviti di kawasan cahaya nampak dengan luang jalur yang lebih rendah sebanyak 2.94 eV berbanding dengan 3.0 eV bagi TiO_2 NP yang disintesis, serta gabungan semula pasangan lubang elektron yang lebih perlahan daripada TiO_2 NP yang disintesis. Analisis Spektroskopi Fotoelektron Sinar-X (XPS)

selanjutnya mengesahkan dop bersama C dan N ke dalam TiO_2, dibuktikan oleh peralihan tenaga ikatan Ti2p. Dalam kajian ini, bahan pencemar model yang dipilih ialah diazinon (DIZ) kerana ikatan P-O yang kuat yang sukar diputuskan semasa fotokatalisis. C, N-TiO_2 NP yang optimum menunjukkan kecekapan fotopenguraian DIZ yang unggul, mencapai penyingkiran 88.52% berbanding TiO_2 NP yang disintesis (46.82% penyingkiran DIZ) dalam tempoh 4 jam di bawah sinaran cahaya suria. C, N-TiO_2 NP yang dioptimumkan ini kemudiannya dipegunkan ke atas manik alginat menggunakan kaedah pengegelan ionotropik. Analisis SEM mendedahkan bahawa serbuk C, N-TiO_2 NP yang disintesis terkumpul dengan taburan sekata pada permukaan manik alginat, disebabkan oleh pertautan silang yang kuat antara polimer alginat, ion kalsium (Ca^{2+}) dan pemangkin. Oleh itu, penyingkiran DIZ yang mengagumkan dijangka mencapai 80.61% penyingkiran selama 8 jam di bawah sinaran suria dengan kebolehgunaan semula yang konsisten (78.23% penyingkiran DIZ) walaupun selepas lima kitaran. Pencapaian ini menggariskan potensi tinggi novel reka bentuk fotopemangkin terapung berasaskan TiO_2 untuk aplikasi dalam rawatan air sisa.

SYNTHESIS AND CHARACTERISATION OF CARBON, NITROGEN CO-DOPED-TITANIUM DIOXIDE/SODIUM ALGINATE BUOYANT PHOTOCATALYST FOR DEGRADATION OF DIAZINON

ABSTRACT

The utilisation of titanium dioxide (TiO_2)- based photocatalysts has garnered significant attention among researchers due to their promising potential for removing pollutants from wastewater. Buoyant photocatalysts are being explored as viable candidates for wastewater treatment applications, aiming to address filtration challenges during the treatment process. In this study, the design of modified TiO_2 with a highly durable buoyant carrier is essential to enhance its photocatalytic performance in degrading pollutants from wastewater. Subsequently, carbon (C) and nitrogen (N)-codoped TiO_2 NPs with varying C:N percentages were successfully developed using the sol-gel method. These optimised C, N-TiO_2 NPs exhibit favorable attributes, including activity in the visible light region with a lower bandgap energy of 2.94 eV compared to the 3.0 eV of the synthesised TiO_2 NPs, as well as slower recombination of electron-hole pairs than the synthesised TiO_2 NPs. X-ray Photoelectron Spectroscopy (XPS) analysis further verified the co-doping of C and N into TiO_2, evidenced by the shift in Ti2p binding energy. In this study, the

model pollutant chosen was diazinon (DIZ) due to its strong P-O bond that was difficult to break down during photocatalysis. The optimised C, N-TiO_2 NPs demonstrated superior photodegradation efficiency of DIZ, achieving an 88.52% removal compared to the synthesised TiO_2 NPs (46.82% DIZ removal) over a 4 h period under solar light irradiation. These optimised C, N-TiO_2 NPs were subsequently immobilised onto alginate beads using the ionotropic gelation method. SEM analysis revealed that the accumulated powders of the synthesised C, N-TiO_2 NPs were evenly distributed on the alginate bead surface, owing to the strong crosslinking between the alginate polymer, calcium (Ca^{2+}) ions, and the catalyst. As such, the impressive DIZ elimination was expected to achieve 80.61% removal for 8 h under solar light irradiation with consistent reusability (78.23% DIZ removal) even after five cycles. These achievements underscore the high potential of the designed novel TiO_2-based buoyant photocatalysts for application in wastewater treatment.

CHAPTER 1

INTRODUCTION

1.1 Overview

Water pollution is one of the crucial issues faced in the universe, whereby more than 70% of the earth's surface is covered by water. According to UNESCO in the 2021 World Water Development Report, the use of freshwater has seen a six-fold increase in the past 100 years, and has been growing about 1% per year since the year of 1980 (Lin et al., 2022). However, the rapid growth of industrialisation and urbanisation has resulted in the pollution of the environment, affecting the aqueous system that is necessary for life (Xu et al., 2022). There are various toxic chemicals, organic and inorganic substances, toxic solvents and organic chemicals that appear in industrial production. For instance, toxic chemicals such as dyes were discovered in textile industries (Azami et al., 2022). Agricultural activities can also contaminate the water with the introduction of pesticides such as diazinon and chlorpyrifos due to their usage to control weeds, insect infestation and diseases (Syafrudin et al., 2021). Although only low concentrations of harmful substances are found in the water, this can be the reason for water being contaminated. These wastes may be discharged into aquatic ecosystems without proper treatment, leading to water pollution (Chowdhary et al., 2020).

The presence of these pollutants in the water gives a high risk to water quality and has severe implications for human health. At very low concentrations, they can instigate multiple organ damage affecting the stomach, lungs and kidneys and; can also lead to neurodegenerative disorders and diseases, including Alzheimer's and Parkinson's diseases (Cabral Pinto et al., 2019). Moreover, it was reported that diarrhea is the most common disease originates from water pollution (Lin et al., 2022). The previous study reported that skin diseases such as scabies and skin cancer are also caused by water pollution (Arif et al., 2020; Hanif et al., 2020). Therefore, the development of effective treatment is required to eliminate the pollutants from water, improving it towards better water quality.

Instead of various techniques in wastewater decontamination such as membrane filtration, precipitation and adsorption, it is vital to perceive milder reaction conditions which are at ambient temperature and pressure; and effective photocatalysts to treat wastewater (Yagub et al., 2014; Azimi et al., 2017). As such, photocatalysis has been chosen as an effective method to remove harmful pollutants from wastewater. This is caused by its benefits such as being environmentally friendly, cost-effective, high efficiency and advanced process that helps treat wastewater (Ren et al., 2021). This unique approach requires the catalyst with the presence of light to degrade pollutants from wastewater (Hanafi & Sapawe, 2020). Among the semiconductors, titanium dioxide (TiO_2) is more widely applied than zinc oxide (ZnO) and tin oxide (SnO_2) as a catalyst in photocatalysis (Mohamad Idris et al., 2021; Rodrigues et al., 2021; González et al., 2022). The unique traits of TiO_2 such as high chemical stability, non-toxicity, low cost, and excellent optical and electronic properties, making it a promising catalyst for wastewater remediation (Dharma et al., 2022). Even though TiO_2 has a high potential for degrading pollutants in wastewater, it encounters large bandgap energy (bandgap energy of anatase: 3.20 eV) with low absorption region (ultraviolet light only) and rapid recombination of electron-hole pairs (Hosseini-Sarvari & Valikhani, 2021).

To circumvent the drawbacks, several modifications of TiO_2 are vital to enhancing its performance by narrowing the bandgap energy, shifting the light absorption into the visible region, creating nanostructured particles and reducing the recombination of electron-hole pairs of the modified catalysts (Dharma et al., 2022). Most researchers focused on designing catalysts with nanostructured particles, aiming to enhance the photocatalytic efficiency of the catalyst (Reghunath et al., 2021). This strategy promotes better molecular diffusion kinetics, increased surface area and good charge carrier separation of the modified catalysts (Reghunath et al., 2021). Other than that, the doping of TiO_2 is one of the strategies, whereby it is conducted by inducing impurity ions, metal and non-metal elements into the lattice plane to substitute the host cations and/or anions (Lin et al., 2022). Subsequently, this efficient strategy can enhance the conductivity of TiO_2 and the mobility of photoexcited charge carriers that improve the charge carrier separation of the modified TiO_2 (Hosseini-Sarvari & Valikhani, 2021). In addition, it can reduce the bandgap energy, enlarge the light absorption region and enhance the optical properties of the designed catalysts (Wang et al., 2022). Thus, these systematic strategies can improve TiO_2-based photocatalyst which is expected to gain much higher performance in photodegradation of pollutants from wastewater.

Employing TiO_2 suspended system in degrading pollutants from wastewater might not be effective for a prolonged duration due to the recovery issue after the next treatment. Therefore, the immobilisation of TiO_2 particles is addressed as an innovative solution to overcoming the challenging issue (Mohamad Idris et al., 2022). Cork, perlite and polymer are some examples of buoyant substrates that possess the unique feature of low density, whereby they can float on the surface of the water (Mehmood et al., 2020; Khen et al., 2021; Mohamad Idris et al., 2021). This impressive feature will make the photocatalyst will be more accessible to light radiation and exposure to a large surface area during the photocatalytic reaction. Furthermore, this promotes an easier post-treatment, leading to lower costs than the powder TiO_2 system. Moreover, the ideal fabricated buoyant photocatalyst is expected to procure good reusability during wastewater treatment. This special character plays a key role in achieving an effective buoyant photocatalyst.

Herein, the main goal of this study is to develop innovative carbon (C), nitrogen (N)-TiO_2/sodium alginate buoyant photocatalyst with high photocatalytic performance as an excellent candidate for wastewater treatment applications using diazinon as the model pollutant.

1.2 Problem statement

Titanium dioxide (TiO_2) suffers from a few drawbacks that limit its practical applications in photocatalysis. The anatase TiO_2 has a large bandgap energy of 3.2 eV that is active under ultraviolet (UV) light only, resulting in low efficiency in using solar light. As such, visible light cannot excite electrons from the valence band to the conduction band of TiO_2. The best photocatalyst can work well in both ultraviolet and visible light due to sunlight/solar light being composed of 46% visible light and followed by 47% infrared and 4-5% ultraviolet light (Mohammadhosseini et al., 2022). Furthermore, it also obtains rapid recombination of electron-hole pairs after photoexcitation. The recombination of electron-hole pairs will vanish the energy. Subsequently, it will reduce the photocatalytic activity. To circumvent the limitations, the modification of TiO_2 is crucial. Therefore, this is made possible by creating nanostructured particles with large surface areas to promote good photocatalytic activity of pollutants. Furthermore, the introduction of non-metals such as carbon and nitrogen as the dopants into TiO_2 is expected to tune the electronic structure of TiO_2 and create new states into TiO_2 bandgap for the visible light response. Moreover, the lattice defects induced by the dopants will generate new charge-carrier trapping and recombination centers, suggesting a degrading effect on the photocatalytic activity occurs. Consequently, the modified TiO_2 catalyst exhibits small bandgap energy with shifted longer light absorption and efficient photoinduced charge separation. However, the powder form of the existing photocatalyst causes a filtration issue during wastewater treatment. Additionally, the suspended TiO_2 system also will reduce its performance due to lowering active surface area, decreasing light utilisation and restraining contact area with the pollutants. Hence, the buoyant photocatalyst with excellent reusability properties is designed as an innovative solution to provide a potential platform for wastewater treatment applications.

1.3 Research objectives

The objectives of this research are as follows:

i. To investigate the structural and morphological characteristics of the synthesised titanium dioxide nanoparticles (TiO_2 NPs) and carbon, nitrogen co-doped-titanium dioxide (C, N-TiO_2 NPs) *via* the sol-gel method.

ii. To design C, N-TiO_2/sodium alginate buoyant photocatalyst by ionotropic gelation method.

iii. To discuss the characteristics of C, N-TiO_2/sodium alginate buoyant photocatalyst acquired through spectroscopy and microscopy techniques.

iv. To evaluate the photocatalytic performance of the fabricated C, N-TiO_2/sodium alginate buoyant photocatalyst in the degradation of diazinon.

1.4 Scope of the study

This research involved characterisation of TiO_2 and C, N-TiO_2 NPs using FTIR, XRD, PL, UV-Vis DRS, HRTEM and zeta potential analyses. XPS analysis was conducted for only optimised C, N-TiO_2 NPs (2%C, 3%N). Meanwhile, C, N-TiO_2 /sodium alginate buoyant photocatalyst with optimised catalyst dosage of 3 g was characterised using FTIR, SEM-EDX and digital microscopy. The adsorption isotherm models including Langmuir and Freundlich were used to determine the equilibrium data. Photocatalytic activity of pesticide where diazinon was utilised as the model pollutant was carried out and zero-order, first-order and second-order kinetics were applied to determine its kinetic study using the C, N-TiO_2/sodium alginate buoyant photocatalyst with different catalyst dosage loading on the sodium alginate beads (1, 2, 3 and 3.5 g). The mineralisation and scavenging studies that used the optimised C, N-TiO_2/sodium alginate buoyant photocatalyst were carried out. Based on the scavenging study, the possible mechanism of diazinon degradation was elucidated. GC-MS analysis was employed to identify the intermediate product present during the photodegradation of diazinon.

1.5 Outline of the thesis

The thesis consists of five chapters:

Chapter 1 delivers an overview of the study. It highlights the problem statements, research objectives, scope of the study and outlines of the content.

Chapter 2 is a detailed literature review on some basic knowledge of water contamination, methods for wastewater treatment, application of TiO_2 as a photocatalyst in wastewater treatment, methods of enhancing TiO_2 efficiency, immobilisation of photocatalyst and photocatalytic kinetic studies and Green Chemistry principles.

Chapter 3 displays the general methodology used for this study. The methods for preparing TiO_2 NPs and C, N-TiO_2 NPs were explained. Additionally, the fabrication of C, N-TiO_2/sodium alginate buoyant photocatalyst as well as its adsorption and photocatalytic performance were discussed. The basic principles of the instrumental characterisation methods by Fourier transform infrared (FTIR), X-Ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), digital microscopy, ultraviolet-visible (UV-Vis) spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence (PL) spectroscopy, gas chromatography-mass spectroscopy (GS-MS), total organic carbon (TOC) and zeta potential analyses were also explained. The scavenging and reusability studies of the optimised C, N-TiO_2/sodium alginate buoyant photocatalyst were described. The steps for validation analysis of this study were indicated.

Chapter 4 discusses the synthesis and the characterisation results obtained for TiO_2 NPs and C, N-TiO_2 NPs. The synthesis and optimisation studies of C, N-TiO_2 NPs and C, N-TiO_2/sodium alginate buoyant photocatalyst through sol-gel and ionotropic gelation methods, respectively were carried out. Characterisation of C, N-TiO_2 NPs and C, N-TiO_2/sodium alginate buoyant photocatalyst were identified. The possible formation mechanism of the fabricated C, N-TiO_2/sodium alginate beads buoyant photocatalyst was studied. The adsorption, photocatalytic and reusability studies of C, N-TiO_2/sodium alginate beads buoyant photocatalyst against diazinon were elucidated. The possible mechanism of diazinon degradation was expressed clearly.

Chapter 5 gives a conclusion to the study and valuable recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Contamination of water

Safe water is required for the entire ecosystem and it can be a major worldwide challenge for ensuring it is maintained. As such, this fact emphasises that water is vital in our life. However, to meet the water demand, water supply has been restrained by high levels of water pollution (Boltz & Daigger, 2022). This water pollution is linked to the various activities that originated from the agricultural, textile and pharmaceutical industries (Krakowiak et al., 2021; Rafiq et al., 2021; Wang et al., 2022). Water pollution is caused by the presence of toxic substances in the aqueous system which can degrade the quality of water (Kotilainen et al., 2020). It does not only affect the aquatic ecosystems, but the toxic pollutants that seep through and reach the groundwater may end up in our households as contaminated water. The contaminated water will disrupt the usage of water in our daily lives.

Furthermore, UNESCO 2024 World Water Development Report highlighted 2.2 billion people lacked safe drinking water access, with progress mainly in cities but rural areas still facing significant shortages where four out of five people lacking at least basic drinking water services in 2022. Therefore, it leads to the poor quality of water which has severe impacts on human health causing gastrointestinal illness, inhibiting nutrient absorption and malnutrition in humans and poisoning aquatic life (Lin et al., 2022).

The quantity of generated wastewater depends on the type of industry, consisting of both non-biodegradable materials (such as dyes, pesticides and antibiotics) and biodegradable substances (such as paper, leather and wool) (Khairnar & Shrivastava, 2019; Varma et al., 2020). However, non-biodegradable wastes are the most harmful compared to biodegradable wastes. This is because non-biodegradable wastes cannot be decomposed by microorganisms or naturally and will harm humans and animals when exposed to them (Ajmal et al., 2014). Whereas biodegradable wastes can be decomposed and degraded by microbes or microorganisms. Therefore, it is crucial to eliminate non-biodegradable wastes from wastewater.

2.2 Types of water pollutants and their effects

Currently, types of water pollutants include dyes, pesticides and antibiotics are given high attention by researchers due to their rapid increase in wastewater generated which possesses a severe public health and environmental protection concern (Krakowiak et al., 2021; Rafiq et al., 2021; Wang et al., 2022).

2.2.1 Dyes

Dyes represent significant sources originating from various industries, including textile, cosmetic, and paint sectors (Ahmad et al., 2021). The exposure of this industrial waste to the aqueous system threatens human health and the environment. Dyes are divided into various types including acid, basic, direct, vat, disperse, nitro, mordant, reactive, sulphur and azo dyes as listed in Table 2.1.

Table 2.1: Type, examples, applications and effects of dyes.

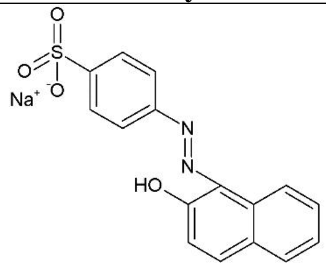
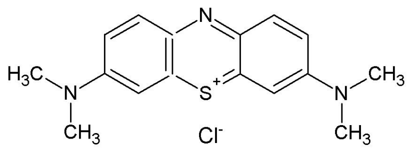
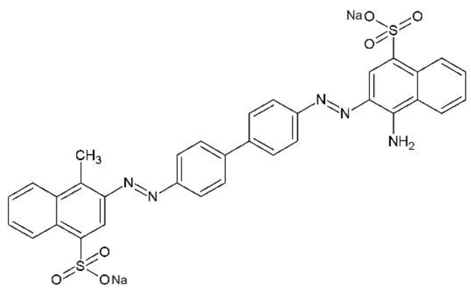
Type of dyes	**Example of dyes**	**Example of the chemical structure of the dye**	**Applications**	**Effects**	**Reference**
Acid dye	Acid yellow 36, Acid orange 7, Acid blue 83	 Acid orange 7	Textile, leather and pharmaceutical industries	Vomiting, nausea, diarrhea, carcinogenic and mutagenic effects	(Benkhaya et al., 2020)
Basic dye	Methylene blue, Basic red 1 or rhodamine 6G, Basic yellow 2	 Methylene blue	Paper and polyacrylonitrile-modified nylons	Detrimental effects on the flora and fauna	(Abhilash et al., 2019; Abbad et al., 2020)
Direct dye	Congo red, Direct red 28, Direct black 38	 Congo red	Coloring paper products	Toxic to aquatic animals and plants; and dermatitis	(Ali et al., 2020)

Table 2.1: Type, examples, applications and effects of dyes.

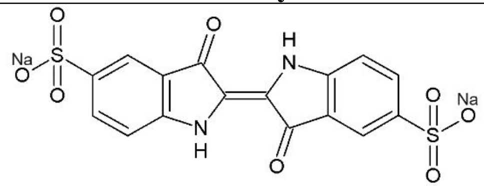
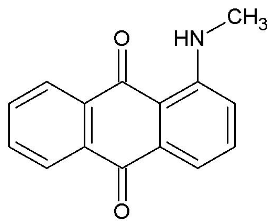
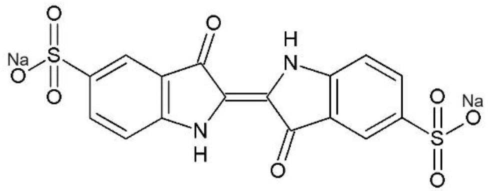
Type of dyes	Example of dyes	Example of the chemical structure of the dye	Applications	Effects	Reference
Vat dye	Vat blue 1, Vat acid blue 74	 Vat acid blue 74	Insoluble pigment, indigo and natural fibres	Affects the quality and clearness of water resources such as lakes and rivers; dermatitis, allergic conjunctivitis and rhinitis	(El Jabbar et al., 2019)
Disperse dye	Disperse red 9, Disperse violet 1, Disperse red 60	 Disperse red 9	Polyester, nylon, cellulose acetate and acrylic fibres	Mutagenic, carcinogenic	(Jamil et al., 2020; Setthayanond et al., 2022)
Nitro dye	Naphthol yellow (II)	 Naphthol yellow (II)	Dye wool	Decreases light penetration and photosynthetic activity; carcinogenic and mutagenic	(Darzi & Bastami, 2022)

Table 2.1: Type, examples, applications and effects of dyes.

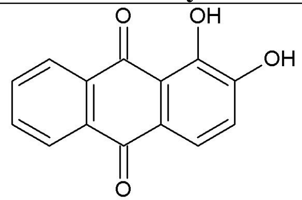
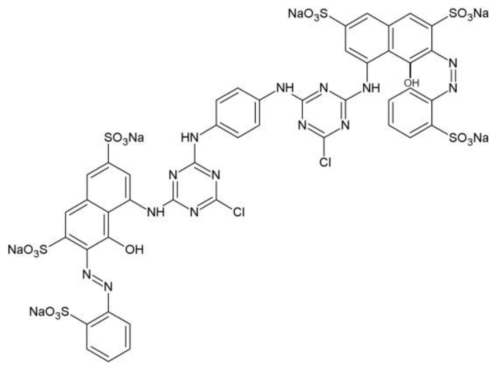
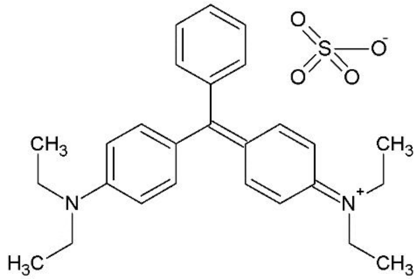
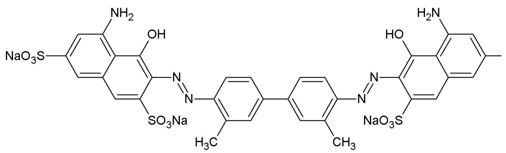
Type of dyes	Example of dyes	Example of the chemical structure of the dye	Applications	Effects	Reference
Mordant dye	Mordant red 11, Mordant black 17	 Mordant red 1	Textile fibres such as wool, silk and leather	Allergic reactions	(Ćirković et al., 2021)
Reactive dye	C.I. reactive red 120, C.I. reactive red 147, C.I. reactive blue 19	 Reactive red 120	Dyeing cellulosic, silk and wool fibres	High and unwanted levels of dissolved solids in the effluent	(Rodrigues et al., 2021)

Table 2.1: Type, examples, applications and effects of dyes.

Type of dyes	Example of dyes	Example of the chemical structure of the dye	Applications	Effects	Reference
Sulphur dye	Sulfur brilliant green, Sulfur blue, Sulfur black 1, Leuco sulfur black 1	 Sulfur brilliant green	Dyeing cellulosic fibres and cotton	Skin irritation; itchy or blocked noses; sneezing and sore eyes; carcinogenic	(Bhattacharya et al., 2019; Ajibade & Oluwalana, 2021)
Azo dyes	Direct black 22, Methyl orange, Trypan blue	 Trypan blue	Textile industry for dyeing process and food colouring	Carcinogenic; if inhaled or swallowed, affecting the eye, skin and digestive tract. Affects aquatic life if present in excess	(Dihom et al., 2022)

2.2.2 Pesticides

Pesticide is any substance used to kill, repel or control certain forms of plant or animal life (pests) which composes of herbicides, insecticides and fungicides in the agricultural field (Islam et al., 2020; Wang et al., 2022). The type of pesticides, examples and their application are shown in Table 2.2 (Khairnar & Shrivastava, 2019). In addition, the pesticides can be classified into three major synthetic organic groups, including organochlorine, organophosphorus and organonitrogen pesticides. The United Nations Environmental Program (UNEP) has listed the organochlorine pesticides (OCPs) including dichlorodiphenyltrichloroethane (DDT), aldrin and chlordane which are chlorine-containing organic compounds as persistent organic contaminants (POPs) (Wang et al., 2022). POPs are stable for longer time and can be transported in water and air to pollute areas far from the point sources (Wang et al., 2022). As such, the agricultural industry has switched usage of pesticides to organophosphorus and organonitrogen pesticides.

For instance, herbicides such as atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) act as selective herbicides, targeting photosynthesis in susceptible plants. However, in humans, exposure to atrazine has been associated with cardiovascular issues, retinal degeneration, and cancer (Islam et al., 2020). In contrast, diazinon is an example of a widely employed organophosphorus pesticide

(OPPs). Diazinon has been classified by World Health Organization (WHO) as one of the ‘’moderately hazardous’’ Class II organophosphorus pesticides and the maximum acceptable concentration of diazinon in water is 0.17 mg/L (Phuong et al., 2019). The hazard occurs in its acute toxicity which is the inhibition of the acetylcholinesterase (AChE) enzyme. Consequently, OPPs can prevent the action of enzymes in the nervous system, resulting in several neurobehavioral side effects (Phuong et al., 2019).

Even though the residual level of OPPs in drinking water is at a very low concentration (the permitted maximum concentration in drinking water for a single compound and total pesticides are 0.1 and 0.5 μg/L, respectively), it possesses a major concern (World Health Association, 2007). Hence, the elimination or treatment of pesticides from contaminated water is critical.

Table 2.2: Type, examples and application of pesticides (Khairnar & Shrivastava, 2019).

Type of pesticides	**Chemical group**	**Examples**	**Application**
Insecticides	Organochlorines, Organophosphates	Diazinon, Parathion, Aldrin	To control and kill various insects
Herbicides	Carbonates, Pyrethroids, Phenylureas, Amides	Carbofuran, Cypermethrin, Diuron, Alachlor	To destroy weeds and other unwanted vegetation
Fungicides	Thio-carbanates, Mercurial	Ferbam, Maneb, Ceresin	To prevent the growth of molds and mildew

2.2.3 Antibiotics

On the other hand, antibiotics are applied to treat or prevent some types of bacterial infection, whereby they kill bacteria or prevent them from reproducing and spreading. Antibiotics are also one of the most widely used pharmaceuticals in veterinary care and medicine (Shokri et al., 2013). It has been reported that the annual usage of antibiotics is measured between 100,000 and 200,000 tons worldwide (Davies et al., 2021). Several different types of antibiotics can be classified into six groups which are penicillins, cephalosporins, aminoglycosides, tetracyclines, macrolides and fluoroquinolones as depicted in Table 2.3 (Bai et al., 2022). However, antibiotics are non-biodegradable wastes and can survive in aquatic environments for long periods (Davies et al., 2021). Even though antibiotics present at residual levels, they can retain in bacterial populations, causing them inactive in the treatment of several diseases (Wei et al., 2020). Moreover, antibiotics can cause endocrine-disrupting effects once exposed to living organisms, which can impede the synthesis, transport and elimination of hormones in the human body (Alam et al., 2022). Thus, the detected residual antibiotics in the water are required to be removed to ensure that human health and the environment are in good condition.

Table 2.3: Type, examples and application of antibiotics (Bai et al., 2022).

Type of antibiotics	Examples	Application
Penicillins	Penicillin, amoxicillin, flucloxacillin	To treat a variety of infections, including skin infections, chest infections and urinary tract infections
Cephalosporins	Cefalexin	To treat more serious infections such as septicaemia and meningitis
Aminoglycosides	Gentamicin, tobramycin	To treat more serious infections such as septicaemia
Tetracyclines	Tetracycline, doxycycline and lymecycline	Commonly used to treat acne and a skin condition called rosacea
Macrolides	Azithromycin, erythromycin and clarithromycin	To treat lung and chest infections; as an alternative for people with a penicillin allergy; to treat penicillin-resistant strains of bacteria
Fluoroquinolones	Ciprofloxacin and levofloxacin	To treat respiratory and urinary tract infections

2.3 Treatment of wastewater

In order to eliminate the pollutants from the wastewater system, adequate techniques are vital to ensure that safe water is obtained. For example, the various conventional methods for wastewater treatment are present for a long time ago (Dutta et al., 2021). Conventional wastewater treatment is a combination of physical, chemical and biological processes as well as their operations to remove solids, organic matter and nutrients from wastewater. These nutrients come from sources like agricultural fertilisers, animal manure, and untreated sewage, primarily nitrogen and phosphorus. This can lead to algal blooms, eutrophication, and oxygen depletion, resulting in fish kills and harmful effects on aquatic ecosystems. The methods involve chemical precipitation, adsorption and ion exchange processes. Conventional wastewater treatment consists of four steps which are pre-treatment, primary treatment, secondary treatment and tertiary treatment as described in Table 2.4 (Ranjit et al., 2021).

Table 2.4: Step and type of conventional wastewater treatment (Ranjit et al., 2021).

Step	**Type of treatment**	**Description**
1	Pre-treatment	Consists of course solids removal of any large objects such as cans, sticks, sand as well as fats and oils; or anything that can cause clogging in pumps and pipelines
2	Primary treatment	Consists of the removal of thick solids in the form of sludge. The sedimentation process allows heavy solids to sink to the bottom, whereas grease and oils rise to the top
3	Secondary treatment	Degradation of any biological elements using aerobic biological processes such as a fixed film-activated sludge process. This treatment uses bacteria, enzymes and protozoa to consume the biological material in the solution
4	Tertiary treatment	In some cases when there is still matter that should not be released into the environment. The contaminants could be toxins, nitrogen, phosphorus or microorganism. As such, UV disinfection, specialised electrocoagulation, enhanced biological phosphorus removal and filtration are required in this treatment

Conventional methods for wastewater treatment are very costly and not economical (Dutta et al., 2021). The treatment requires a large space for setup and the use of bacteria makes the plant smelly. Furthermore, the treatment will take a longer period and be complicated during the process of treatment (Ranjit et al., 2021).

Therefore, the advanced oxidation processes (AOPs) are proposed as an innovative and effective way to treat wastewater due to their environmentally friendly, high reaction rates and efficiencies offering green chemistry aspects (Dihom et al., 2022).

Among the AOPs, photocatalysis is the most efficient and popular technique compared to the UV-hydrogen peroxide process; Fenton and photo-Fenton; sonolysis and ozone-based process (Lee & Park, 2013; Cui et al., 2020; Jamil et al., 2020). Photocatalysis is a chemical reaction that occurs in the presence of light and a semiconductor (photocatalyst) (Piątkowska et al., 2021). This efficient technique possesses several benefits, including cost-effectiveness, the creation of harmless end products (such as water and carbon dioxide) and the formation of nonhazardous secondary pollutants only (Wang et al., 2017). Further description of the AOPs such as UV-hydrogen peroxide process; Fenton and photo-Fenton; sonolysis and other zone-based process is shown in Table 2.5.

Table 2.5: Type and further description of advanced oxidation process (AOPs).

Type of AOPs	Descriptions	Reference
Ultraviolet (UV)-hydrogen peroxide (H_2O_2) process	The reaction with the presence of UV light irradiation and hydrogen peroxide, whereby UV light acts as a natural disinfectant agent for wastewater treatment	(Cui et al., 2020)
Fenton and photo-Fenton	Fenton is the reaction with the presence of a ''Fenton reagent'' which is known as a mixture of H_2O_2 and Fe^{2+} ions to degrade the pollutants into harmless compounds (such as water and carbon dioxide). Meanwhile, photo-Fenton is the reaction with the combination of UV radiation with Fe^{2+} or Fe^{3+} to enhance the rate of degradation of the pollutants	(Jamil et al., 2020)
Sonolysis	The degradation of molecules via the formation, growth and collapse of a bubble in a liquid based on acoustic cavitation using ultrasonic irradiation	(El Hakim et al., 2021)
Ozone-based process	Involving ozone in aqueous reactions may produce various unwanted byproducts due to its high redox potential	(Kotilainen et al., 2020)
Photocatalysis	The reaction that takes place by applying light and a semiconductor (photocatalyst) for degrading the pollutants into harmless products such as water and carbon dioxide	(Piątkowska et al., 2021)

2.4 Photocatalyst

A photocatalyst is a material that speeds up a chemical reaction when exposed to light, without undergoing any permanent change itself. It works by absorbing photons from light, which energise electrons in the material, creating electron-hole pairs that can drive chemical reactions. Photocatalysts are used in various applications such as environmental remediation, water purification, air purification, and solar energy conversion.

2.4.1 Semiconductor as a photocatalyst

Fujishima and Honda's pioneering work on water splitting using a TiO_2 electrode under UV light and a mild external electric field garnered significant attention in the field of photocatalysis (Fujishima & Honda, 1972). Semiconductor can be employed in various applications ranging from environmental remediation to energy conversion, including pollutant degradation and water splitting. As such, there have been over 130 inorganic materials, involving metal oxides, nitrides or sulfides that have been evaluated to be promising photocatalysts (Osterloh, 2008; An et al., 2019). The metal oxide semiconductors consisting of d^0 or d^{10} elements such as Ti, V and Gr have high efficiency in photocatalytic processes (An et al., 2019; Ma et al., 2020; Poornaprakash et al., 2021). Meanwhile, the valence band is served by the 2p orbitals from nitrogen or the 3p orbitals from sulphur atoms for the metal nitride or sulfide, respectively (Kumar et al., 2021; Zhang et al., 2022).

Besides, the utilisation of semiconductors in photocatalytic reactions is favored for its capability to remove pollutants, as it can produce benign compounds like carbon dioxide (CO_2), water (H_2O) and mineral acids (Li & Yang, 2018). This reaction using semiconductors involves two steps which are photoexcitation of the semiconductor, leading to the separation of electrons (e^-) and holes (h^+) as charge carriers and the migration of charge carriers with the emission of heat or light as shown in Figure 2.1 (Hasim et al., 2023). Due to the surface defect sites on the crystal lattice TiO_2 NPs, photogenerated electrons can become trapped by Ti^{4+} and generate Ti^{3+} species which act as the recombination center, slowing the recombination of electron-hole pairs (Zhang et al., 2022).

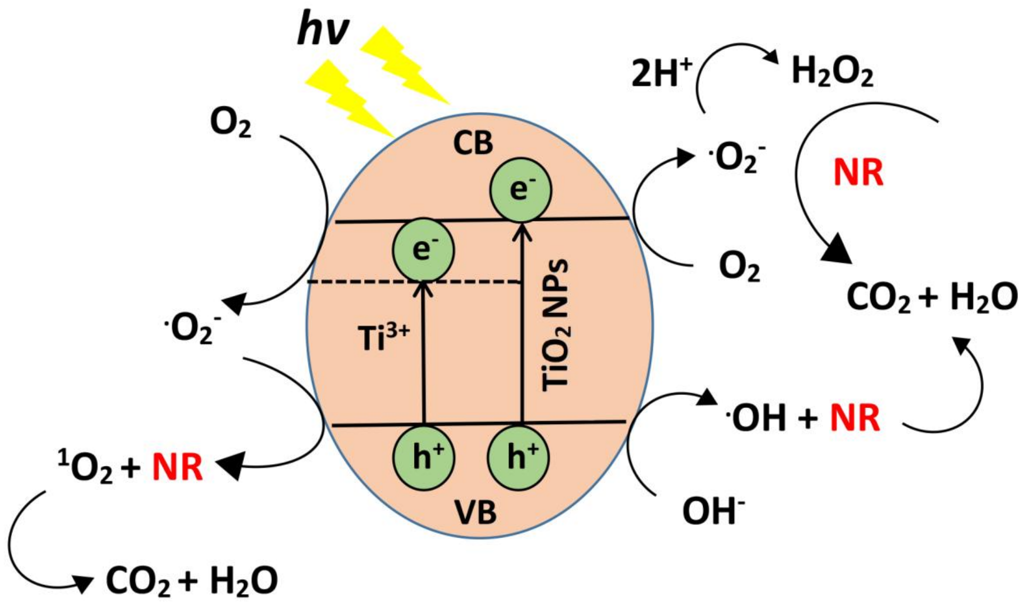


Figure 2.1: Basic principles of photocatalytic reaction using semiconductors, whereby TiO_2 as an example of a semiconductor to degrade neutral red dye (NR) (Hasim et al., 2023).

2.4.2 Titanium dioxide (TiO_2) as an effective photocatalyst

Titanium dioxide (TiO_2) is an n-type metal oxide semiconducting material (An et al., 2019). In contrast with p-type semiconductors, TiO_2 contains electron acceptors, whereby the charge carriers are holes rather than electrons (Aziz et al., 2021). Furthermore, TiO_2 has three crystalline phases including anatase, brookite and rutile with bandgap of 3.2, ~3.3 and ~3.0, respectively, as depicted in Figure 2.2

(Aziz et al., 2021). The anatase phase is the most used and studied for photocatalytic applications due to its high photocatalytic performance when compared to the brookite or rutile phase (Vequizo et al., 2017).

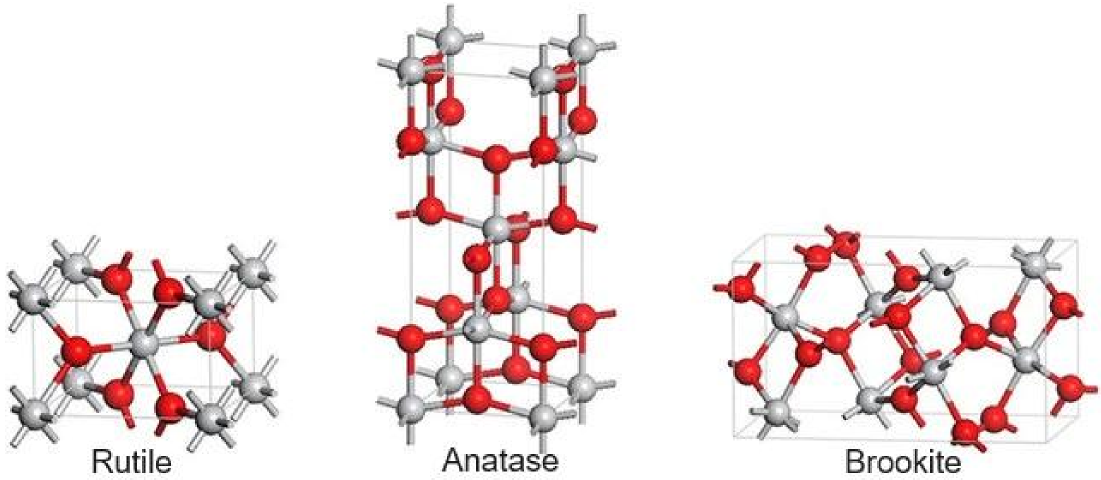


Figure 2.2: The crystal structure of titanium dioxide phases of rutile, brookite and anatase (Aziz et al., 2021).

Despite all the unique properties, anatase TiO_2 has some drawbacks including its large bandgap energy of 3.2 eV, making it the most active under ultraviolet (UV) light with a shorter wavelength below 388 nm (An et al., 2019). As such, about 3-5 % of the energy of the solar spectrum would be used, suggesting that the need to tackle the challenge seems not over. In addition, it also has rapid recombination of electron-hole pairs that eventually decrease its photocatalytic performance. Thus, the modification of TiO_2 is crucial to generate an effective based-TiO_2 photocatalyst with enhanced photocatalytic performance.