SYNTHESIS, CHARACTERIZATION, AND PHOTOCATALYTIC DEGRADATION ACTIVITIES OF TiO_2/GO AND ZnO/GO IN AQUEOUS MEDIUM

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by

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LIST OF SYMBOLS

Ag	Silver
pH_{ZPC}	pH at zero point of charge
•OH	Hydroxyl radical
$O_2^{\bullet -}$	Superoxide radical
t	Time
C	Concentration of the pollutant
k	Rate constant
n	Order of reaction
%	Percentage
M	Molar
nm	Nanometer
mL	Millilitre
h	Hours
g	Gram
Rpm	Revolutions Per Minute
W	Watt
eV	Electron volt
λ	Wavelength
O_2	Oxygen
Fe_2O_3	Iron (III) oxide
Bi_2O_3	Bismuth oxide
SnO	Tin (II) oxide
CeO	Ceric oxide
TiO_2	Titanium dioxide
ZnO	Zinc oxide

GO	Graphene oxide
$NaNO_3$	Sodium nitrate
H_2SO_4	Sulphuric acid
$KMnO_4$	Potassium manganate
H_2O_2	Hydrogen peroxide
$TiCl_4$	Titanium tetrachloride
NaOH	Sodium hydroxide
HCl	Hydrogen chloride
CO_2	Carbon dioxide
H_2O	Water
WO_3	Tungsten trioxide
ZrO_2	Zirconium dioxide
V_2O_5	Vanadium pentoxide
Nb_2O_5	Niobium pentoxide
$BiVO_4$	Bismath vanadate
Cu	Copper
Cd	Cadmium
N	Nitrogen
S	Sulfur
F	Fluorine
C	Carbon
B	Boron
I	Iodine
Al	Aluminium
Cr	Chromium
Fe	Iron
V	Vanadium

Au	Gold
rGO	Reduced graphene oxide
Mt	Million tons
kg	Kilogram
K	Potassium
CB	Conduction band
VB	Valence band
Mn	Manganese
Pt	Platinum
Na	Sodium
Co	Cobalt
CdS	Cadmium sulphide
CeO_2	Ceric dioxide cerium dioxide
COOH	Carboxyl group
$C_{16}H_{18}ClN_3S$	Methelene blue
N_s	Substitutional nitrogen state
N_i	Interstitial nitrogen state
E	Electron
h^+	Positive hole
ZPC	Zero point of charge
C_o	Concentration of methylene blue before irradiation
C_t	Concentration of methylene blue at ‘t’ minutes
λ_{max}	Maximum wavelength

LIST OF ABBREVIATIONS

AOP	Advance Oxidation Process
EDX	Energy dispersive X-ray
FTIR	Fourier Transform Infrared
HOMO	Highest occupied molecular orbital
HTC	Hydrothermal carbonisation
LUMO	Lowest unoccupied molecular orbital
MB	Methylene blue
OPEFB	Oil Palm Empty Fruit Bunch
OPF	Oil palm fronds
OPKC	Oil palm kernel cake
OPKS	Oil palm kernel shells
OPT	Oil palm trunks
PL	Photoluminescence
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscope
UV	Ulraviolet
Vis	Visible
XRD	X-ray Diffraction

SINTESIS, PENCIRIAN DAN AKTIVITI DEGRADASI FOTOKATALITIK TiO_2/GO DAN ZnO/GO DALAM MEDIUM BERAKUES

ABSTRAK

Penyelidikan ini melibatkan penyediaan fotomangkin TiO_2 dan ZnO menggunakan kaedah mesra alam sekitar menggunakan ekstrak kulit limau nipis sebagai agen penurunan dan penukupan. Untuk meningkatkan sifat TiO_2 dan ZnO, grafena oksida (GO) digabungkan ke dalam TiO_2 dan ZnO untuk membentuk nanokomposit TiO_2/GO dan ZnO/GO dengan komposisi GO yang berbeza (i.e. 1, 3, 5, 7 and 10 %). GO diperbuat dari sisa biojisim iaitu serat tandan buah kosong kelapa sawit (OPEFB), melalui tindak balas karbonisasi diikuti dengan kaedah Hummer. Pemangkin yang disintesis dicirikan secara menyeluruh menggunakan pelbagai teknik, termasuk mikroskop pengimbasan elektron (SEM), mikroskop elektron transmisi (TEM), penyerakan sinar-X (XRD), fotopendarcahayaan (PL), spektroskopi inframerah jelmaan Fourier (FT-IR), dan spektroskopi ultralembayung-sinaran nampak. Analisis FT-IR mengesahkan bahawa TiO_2 dan ZnO yang disintesis menunjukkan pola yang mirip dengan TiO_2 dan ZnO komersial sekaligus mengesahkan kejayaan kaedah sintesis mesra alam sekitar. Perantaramukaan GO menyebabkan pengurangan tenaga jalur jurang bagi bahan komposit (3.19 kepada 2.8 eV untuk komposit TiO_2/GO dan 3.28 kepada 2.97 eV untuk komposit ZnO/GO) serta memperlambatkan kadar penggabungan semula pasangan lubang elektron yang bertanggung-jawab ke atas aktiviti fotomangkin yang tinggi. Untuk penilaian prestasi fotomangkin, TiO_2, ZnO, TiO_2/GO dan ZnO/GO yang dihasilkan digunakan untuk degradasi metilena biru (MB) di bawah pencahayaan cahaya nampak. Komposit TiO_2/GO dan ZnO/GO menunjukkan aktiviti fotomangkin yang lebih tinggi dibandingkan dengan TiO_2 dan ZnO tulen. Keputusan menunjukkan bahawa degradasi MB masing-masing mencapai 74 dan 66% menggunakan TiO_2 dan ZnO yang disintesis. Sementara itu, dalam kes komposit TiO_2/GO (7%) dan ZnO/GO (7%), degradasi dicapai masing-masing adalah 93 dan 87%. Degradasi MB menggunakan parameter yang berbeza seperti kepekatan pewarna, dos mangkin dan pH awaldikaji menggunakan fotomangkin terbaik i.e. TiO_2/GO dan ZnO/GO (7%). Kecekapan degradasi fotomangkin didapati sangat dipengaruhi oleh semua parameter di atas dan kecekapan degradasi terbaik diperolehi pada kepekatan pewarna 0.03 mM, dos mangkin 1 g L^{-1} dan pH 13 bagi TiO_2/GO manakala bagi ZnO/GO, kepekatan pewarna 0.03 mM, dos mangkin 1.5 g L^{-1} dan pH 12. Kecekapan degradasi berkurangan masing-masing daripada 93 dan 87% kepada 43 dan 38% selepas kitaran ke-10 masing-masing bagi nanokomposit TiO_2/GO dan ZnO/GO (7%). Bagi ujian pengaut, pengurangan maksimum dalam kecekapan degradasi didapati adalah dengan kehadiran isopropil alkohol sekaligus menunjukkan peranan radikal hidroksil dalam proses fotodegradasi. Seterusnya, kinetik degradasi fotopemangkinan MB dapat diterangkan dengan baik melalui model kinetik tertib pseudo pertama dengan pekali regresi (R^2) masing-masing adalah 0.9867 dan 0.9906 untuk TiO_2/GO dan ZnO/GO (7%).

SYNTHESIS, CHARACTERIZATION, AND PHOTOCATALYTIC DEGRADATION ACTIVITIES OF TiO_2/GO AND ZnO/GO IN AQUEOUS MEDIUM

ABSTRACT

This research covers the preparation of TiO_2 and ZnO photocatalysts using environmental friendly methods that involved the use of lime peel extract as a reducing and capping agent. To enhance the properties of TiO_2 and ZnO, graphene oxide (GO) was interfaced into TiO_2 and ZnO to form TiO_2/GO and ZnO/GO nanocomposites with different GO compositions (i.e. 1, 3, 5, 7 and 10 %). The GO was prepared from biomass waste, oil palm empty fruit bunch fiber (OPEFB), through a carbonization reaction followed by Hummer's method. The synthesized catalyst was thoroughly characterized using various techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), photoluminescence (PL), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and UV-Visible spectroscopy. The FT-IR analysis confirmed that the synthesized TiO_2 and ZnO exhibited a similar pattern to commercially available TiO_2 and ZnO, thereby validating the success of the environmentally friendly synthesis method. The interfacing of GO led to a reduction in the band gap energy of the composite material (3.19 to 2.8 eV for TiO_2/GO composite and 3.28 to 2.97 eV for ZnO/GO composite) as well as the slow down the recombination rate of electron hole pairs which was responsible for the high photocatalytic activities. To evaluate the photocatalytic performance, the synthesized TiO_2, ZnO, TiO_2/GO and ZnO/GO photocatalysts were employed for the degradation of methylene blue (MB) under visible light illumination. The TiO_2/GO and ZnO/GO composites demonstrated higher photocatalytic activities as compared to pure TiO_2 and ZnO. The results indicated that the degradation of MB reached 74 and 66% using synthesized TiO_2 and ZnO, respectively. Meanwhile, in the case of TiO_2/GO and ZnO/GO (7%) composites, 93 and 87% degradation was achieved, respectively. The degradation of MB using different parameters such as dye concentration, catalyst dosage and initial reaction pH was studied using the best photocatalysts i.e. TiO_2/GO and ZnO/GO (7%). The degradation efficiency of the photocatalysts was found to be strongly influenced by all the above parameters in which the best efficiencies of degradation were found at dye concentration of 0.03 mM, catalyst dosage of 1 g L^{-1} and pH 13 for TiO_2/GO while for ZnO/GO, dye concentration of 0.03 mM, catalyst dosage of 1.5 g L^{-1} and pH 12. The reusability test revealed the degradation efficiencies were reduced from 93 to 43 % and 87 to 38 % after tenth cycle for TiO_2/GO and ZnO/GO nanocomposite, respectively. The scavenger test revealed the maximum reduction in degradation efficiency was found to be in the presence of isopropyl alcohol and this indicates the primary role of hydroxyl radical in the photocatalytic degradation process. Furthermore, the kinetics of the photocatalytic degradation of MB are best described by the pseudo first-order kinetics model having regression coefficients (R^2) of 0.9867 and 0.9906 for TiO_2/GO and ZnO/GO, respectively.

CHAPTER 1

INTRODUCTION

1.1 Research background

Water is an essential part for living organism to survive on this earth. Over 70 % of the Earth's surface consists of water, which is certainly the most important natural resource that exists on it, as there would be no life on Earth without water. (Dhivya et al., 2019). Water pollution occurred when harmful chemicals enter into water bodies such as seas, lakes, and oceans and cause various dangerous effects towards the health of both humans and animals. As the water is essential for the survival of livings beings specially for human beings on this Earth (Lin et al., 2022). Further, clean water is one of the major need for human beings and living organisms to sustain life. Moreover, as the world’s population continues to expand, the demand for fresh water has grown exponentially, placing an enormous strain on existing water resources. Further, the water resources are being polluted due to the rapid growth of industrialization, and agricultural activities (Parris 2014). The primary cause of this pollution is the discharge of untreated wastewater from various sources, such as industries, agricultural fields, pharmaceuticals, and households (Jun et al., 2018). Major categories of organic pollutants which are generally found in the water stream include dyes, pesticides, antibiotics, analgesics, herbicides, and stimulants. The presence of these contaminants in the environment adversely affects the human health, aquatic life and disrupting the natural ecosystem balance (Hejna et al., 2022). Therefore, it is imperative to implement measures to treat the wastewater and control the sources of these pollutants to safeguard human health and maintain environmental balance. Among them the largest group of organic pollutants is constituted by dyes, which are used to colour natural and man-made fibres that produce wastewater in a very large amount. Hence, the degradation of dye effluent is needed to reduce water pollution (Umar et al., 2012). This polluted coloured water is neither useful for irrigation nor for domestic purposes. Therefore, degradation of dye effluents has been attracting the attention of many researchers since the last decade that is not only because of the potential toxicity of certain dyes but also due to their visibility in water resources.

Researchers have proposed a number of techniques for the removal of these compounds including dyes from wastewater such as adsorption, biodegradation, coagulation, treatment with ozone and filtration (Umar et al., 2012). Though, various restrictions such as difficulties in operations, time-consuming nature, high operational costs and aggregate loam generation hinder their potential application (Raizada et al., 2020). Given the limitations associated with existing methods, there is an urgent need to develop water treatment technologies that proved more efficient to remove persistence organic pollutants from wastewater. In this regards, there is an increasing interest in the development of innovative approaches using advance oxidation process (AOP) (Cardoso et al., 2021).

AOP is considered to be one of the most suitable techniques for effective wastewater treatment. Photocatalysis is one example of AOP technique, for the removal of organic contaminants due to its ability to mineralize the pollutants completely (Chiu et al., 2019). Photocatalysis is a reaction that occurs using light in the presence of a photocatalyst. The reaction of photocatalysis generally utilizes non-toxic and low-cost semiconductors as catalysts to degrade the pollutants. The use of light sources initiate chemical reactions that can break down the pollutants to produce byproducts which are less harmful in nature. Several advantages are related to this technology, namely complete degradation of organic pollutants and not to produce any secondary pollution (Zhang et al., 2019). Further, this method typically operates at or near ambient temperature and pressure reducing the need for traditional and often expansive treatment methods.

Moreover, the selection of suitable catalyst material for the degradation of pollutants from water is an important aspect to consider. The use of semiconductors as catalysts is considered due to the abundance of these materials and their low environmental impact. Several metal oxide semiconductors have been investigated as a heterogeneous photocatalyst for wastewater treatment (Yaqoob et al., 2020). Few examples are Fe_2O_3, Bi_2O_3, SnO, CeO, TiO_2 and ZnO etc. Amongst all of these, TiO_2 and ZnO are the priroity metal oxides for their use as photocatalysts to treat wastewater. Both TiO_2 and ZnO possess high chemical stability, excellent photosensitivity and has reasonable cost (Mullani et al., 2020). Owing to these facts, TiO_2 and ZnO have been used in the photocatalysis to remove organic pollutants.

1.2 Problem statement

Dyes are widely used in various industries such as textiles, paper, printing, leather tanning, plastic, food, cosmetics, pigment, and many others and the discharge of dyes and dye-containing wastewater into the environment can lead to severe pollution and ecological imbalance/damage (Ramzan et al., 2022). Dye pollution is a significant environmental concern as it can affect both aquatic and terrestrial ecosystems. The presence of dyes in water bodies can reduce sunlight penetration and disrupt the balance of aquatic life. Some dyes are toxic, carcinogenic, and mutagenic, posing a significant threat to human health (Alsukaibi, 2022). Furthermore, it is estimated that about 1–15% of dyes is wasted through the dyeing procedure and is discharged in the effluents of textile industries which is a major threat to the environment (Umar et al., 2012). Therefore, development of effective and sustainable approaches for treating dye-containing wastewater is essential. As continues research going on, photocatalysis is considered as an effective approach to degrade these pollutants (dyes) (Saeed et al., 2021). In this study, methylene blue (MB) was taken as a pollutant for degradation which represents a common cationic dye and frequently employed in various sectors within the textile manufacturing domain. It has the capacity to generate aromatic amines, which have the potential to be carcinogenic and have an impact on human health through drinking water as well as the aquatic river biota (Al-Tohamy et al., 2022; Moorthy et al., 2021). Methylene blue (MB) is one of the most consumed substances utilized within the dye sector and widely used to color silk, cotton, paper and wool (Khan et al., 2022). Thus, it is necessary to find an environmental friendly and efficient method for the degradation of this dye (MB).

In the photocatalysis process, the use of semiconductors like TiO_2 and ZnO as the catalyst is widely investigated to degrade dye pollutants. Despite their excellent qualities, they have some drawbacks in terms of wide bandgap energy and a high recombination rate. These limitations cause a reduction in photodegradation efficiency (Chen et al., 2020). A high band gap energy restrict their use only with UV radiation and, thus, significantly increase their expenses by providing the light sources using electrical energy, because solar light constitutes only ~5-10% UV radiation; Hence, there is a requirement to tune the band gap energy of photocatalyst which can work in visible region, mean can use solar energy (Moma and Baloyi, 2019; Umar et al., 2019). Secondly, low catalytic activity of TiO_2 and ZnO is also due to fast recombination of photogenerated charges. In order to resolve this problem, the interfacing of graphene oxide will be proved a better option and further improve the degradation performance. Some functional groups containing oxygen such as hydroxyl (-OH) and carboxylic (-COOH) groups, are bonded covalently on the surface of graphene oxide (GO). With the help of unpaired pi-electrons and the free electrons which are available on the surface graphene oxide forms a Ti-O-C structure with TiO_2, which shifted up the valence band edge and reduce the band gap (Timoumi et al., 2018). Additionally, the interfacing of GO increases the separation of electron-hole pairs on the catalyst's surface and improves the photocatalytic activites of nanocomposite in the visible region.

Traditionally, graphite is used as the precursor material for the preparation of graphene oxide (Torres et al., 2021). Recently, there has been a rising interest in developing more sustainable and environmentally methods, including the use of bio-based sources such as biomass waste. In Malaysia, as the cultivation of oil palm is accounted for the largest area under industrial tree crops (Shevade et al., 2019) and also produces a huge amount of waste after the extraction of oil which create a burden on our environment (Hamzah et al., 2019). In this regards, oil palm empty fruit bunch fiber (OPEFB) is an excellent source of raw material due to its wide availability and low-cost for its utilization to produce a valuable product. This alternative has the potential to reduced environmental impact of the GO production process at the same time providing a more sustainable source of graphene oxide. Moreover, the synthesis of semiconductors like TiO_2 and ZnO are generally use some chemicals which also pollute the environment, cause water pollution. Therefore, in this study, green photocatalyst synthesis of TiO_2/GO and ZnO/GO produce by were presented and their properties and photocatalytic effectiveness on the degradation of methylene blue (dye) in wastewater were investigated.

1.3 Research Objectives

The primary goal of this study is to synthesise graphene oxide interfaced metal oxide nanocomposites photocatalysts for methylene blue dye (pollutant), to be efficiently degrade under the presence of visible light. To achieve this goal, there are four specific objectives have been addressed as follows:

i) To prepare graphene oxide from carbonized oil palm empty fruit bunch fibres (OPEFB).

ii) To prepare TiO_2, ZnO, TiO_2/GO and ZnO/GO via green route and characterize the as-prepared photocatalysts using various techniques.

iii) To determine the photocatalytic performance of the synthesised photocatalysts for the degradation of methylene blue dye under visible light.

iv) To determine the optimal photocatalytic condition for the degradation of methylene blue dye such as substrate concentration, catalyst dosage, pH and investigate the reusability and the kinetics of the photocatalytic reaction.

1.4 Scope of Research

The scope of this research covers the preparation of graphene oxide (GO) from carbonized oil palm empty fruit bunch fiber by using Hummer's method, and the synthesis of TiO_2 and ZnO photocatalysts using green and environmental friendly routes i.e extract of lime peel. Additionally, the prepared GO was interfaced with TiO_2 and ZnO to form TiO_2/GO and ZnO/GO nanocomposites. Subsequently, the surface morphology and physicochemical properties of the photocatalysts were then evaluated using various techniques such as transmission electron microscope TEM, Scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), X-Ray diffraction analysis (XRD), PL (Photoluminescence Spectroscopy) Raman and UV-Visible spectroscopy. The photocatalytic degradation of the prepared photocatalysts was also determined for the degradation of MB dye under visible light. The study also determine the effects of various variables such as initial concentration, catalytic dosage, pH and reusability properties of the photocatalyst on the photocatalytic degradation of MB dye. The scavenger study, reaction kinetics, and pHpzc were also be performed in order to determine the optimal degradation condition, which is helpful for the practical application of photocatalytic degradation.

CHAPTER 2

LITERATURE REVIEW

2.1 Water Pollution

Water stream can be polluted by various types of contaminants including toxic chemicals, sediments, oil, fertilizers, pesticides, radioactive substances, pathogenic microorganisms, and other materials (Singh et al., 2020). This will cause the water unsafe for human use and disrupts environmental balance especially the aquatic ecosystems. Due to this concern, water treatment methods are continuously and actively being research by the academic world and industries.

2.2 Organic Pollutants

There are various types of organic pollutants, which generally responsible for water pollution for example pesticides, drugs (antibiotics), polycyclic aromatic hydrocarbons, Polychlorinated biphenyls and dyes. Among them, industrial textile dyes and other stuffs belongs to coloring materials form one of the most extensive categories of organic based compounds. Dyes utilized to color paper, plastic, and both natural and synthetic fibers. During the dyeing process, approximately 1–15% of the dyes are lost and discharged into textile effluents, posing a significant environmental challenge (Lallis et al., 2019; Galindo et al., 2001; Tehrani-Bagha et al., 2010). This colored wastewater is not suitable for irrigation or domestic use. Therefore, many researchers have focused on decolorizing dye effluents over the past few decades. This is not only because certain dyes may be toxic but also because their presence in receiving waters is highly visible.

2.2.1 Pesticides

Pesticides encompass a range of substances utilized in various forms such as herbicides, rodenticides, fungicides, insecticides and nematicides to avoid, eradicate, manage pests, predominantly in agriculture and domestic purposes (Tudi et al., 2021). Based on their chemical composition, pesticides are grouped so organochlorines, organophosphates, carbamates, synthetic pyrethroids, and inorganic pesticides, with another category derived from natural sources known as biopesticides. Agriculture stands as the primary sector employing pesticides, with an annual consumption more than two million tonnes (Mt) globally (Sharma et al., 2019). Nevertheless, according to literature, global pesticide consumption reaches around 2 Mt annually, with 24% utilized in the USA, 45% in Europe, and the remaining 25% distributed across the rest of the world (Abhilash et al., 2009; Sánchez-Bayo, 2011; Mahmood et al., 2016; Ali et al., 2021). Although some pesticides have been prohibited since decades ago due to their prolonged persistence in the environment, however, they were still exist in agricultural soil, sediments deposit, and groundwater (Parween et al., 2014). The extensive and regular application for these chemicals has resulted their accumulation in soil, from where they leached to ground water sources. Owing to the slow degradation process, their limited solubility and structural stability hinder degradation using chemical and biochemical mechanisms with plants and microbes, potentially leading to groundwater contamination (Bala et al., 2022). Factors influencing their persistence include microbial diversity, rainfall, soil temperature, sunlight exposure, application rate, as well as solubility and mobility in water.

2.2.2 Dyes

Numerous textiles, pharmaceutical, and printing industries utilize a significant quantities of azo-dyes, a class of artificial organic colorants derived from toluene, phenol, benzene, and aniline, containing nitrogen as the azo group (Benkhaya et al., 2020). Due to their extensive utilization in various industries, these dyes become a common component of industrial wastewater (Yaseen et al., 2019). A notable portion of azo-dyes employed in textile industries fails to joint to fabrics and is consequently discharged into wastewater (Dihom et al., 2022). Indeed, out of one million tons of organic dyes produced per annum worldwide, about 15% lost in effluents during manufacturing and different application processes (Umar et al., 2012). The presence of dyes within water reflects color, which is obstruct penetration of sunlight and the dissolution oxygen which are crucial elements intended for aquatic life (Pierce, (1994; Berradi et al., 2019). Thus, there is a significant necessity to treat these colored wastewater before releasing them into different water reservoirs. Additionally, few dyes are combined with heavy metals such as chromium and copper to impart specific shades and enhance resistance to washing (Velusamy et al., 2021). Consequently, wastewater from textile industries, if not adequately treated, poses a significant environmental threat due to both organic and metal pollutants. Various varieties of azo-dyes and their degradation byproducts are poisonous and carcinogenic to aquatic and terrestrial life including mammals (Bafana et al., 2011; Chung et al., 2016). Moreover, numerous dyes exhibit resistance to degradation and necessitate advanced treatment methods under natural conditions. Therefore, there is need to develop an efficient method to degrade these dyes.

2.2.3 Drugs (Antibiotics)

Antibiotics are substances that hinder activity of microorganisms and eukaryotic cells, they are commonly employed in human and veterinary medicine for curing infections. The benefits of antibiotics also extend to various sectors such as agriculture, aquaculture, beekeeping, and livestock farming, where they serve as growth promoters. Additionally, a considerable amount of antibiotics is regularly employed as a dietary supplement toward enhance the growth of food-producing animals and to prevent subclinical infections, ultimately boosting productivity. Antibiotics come in various types, categorized based on their chemical composition, mode of action, spectrum of activity, and route of administration. Despite being designed to be effective at low concentrations, higher doses are often required when administering antibiotics due to their limited effectiveness in reaching to the marked pathogens. Most of the antibiotics which administered to humans, animals are inadequately absorbed in the gastrointestinal tract, leading to a significant portion being excreted through urine and faeces which ultimately produces water pollution (Polianciuc et al., 2020).

2.3 Impacts of Organic Pollutants

Although the use of pesticides, dyes and drugs is essential nowadays for the betterment of life. However, they have very harmful effects on human beings, invertebrates, plants, aquatic life as well as the microbial diversity in soil.

2.3.1 Pesticides

The accumulation of pesticides can reduce the populations of both macro and micro flora and fauna species present in soil, including earthworms, fungi, bacteria and other organisms (Miglani et al., 2019). These organisms play vital roles in various ecosystem. It was revealed that pesticides adversely affect organism at all levels of organization within ecosystems. These chemicals disrupt enzymatic activities and growth, alter individual behaviors such as feeding rates, and decrease the overall biomass and density of micro-organism communities (Pelosi, et al. 2014). Similarly, pesticides also affect other soil invertebrates, with extent of impact varying depending on the type and accumulation levels of pesticides and the species of invertebrates. The toxic pesticides can lead to reduced reproductive rates and biochemical disruptions in the body regarding the birds, and in severe cases, direct mortality at high doses. Water typically hosts diverse groups of microorganisms, mainly unicellular and of prokaryotic or eukaryotic origin, including bacteria (eubacteria and archaebacteria), cyanobacteria, actinomycetes, fungi, and algae, if the concentration of pesticide goes to beyond the acceptable limit, can cause some dangerous impact on the aquatic life (Albuquerque et al., 2016). Pesticides have been studied to impact human health, with the effects varying depending on the type of pesticides, their dosage, and the time intervened after application (Sabarwal et al., 2018).

2.3.2 Dyes

Dyes exhibit varying levels of stability in water bodies, ranging from days to several weeks, depending on chemical composition. For instance, Direct-Red 81 proved to be more resilient to microbial degradation compared to Reactive-Black 5 and Acid Yellow 19 (Imran et al., 2015). Due to the irrigation with effluent from dye industries, there is a significant buildup of total organic dyes in cultivated soil. Various azo dyes demonstrated toxicity to soil microorganisms, with greater toxicity observed on Gram-negative bacteria compared to Gram-positive bacteria (Imran et al., 2015). Specific azo-dyes discovered to negatively impact the growth of the atmospheric nitrogen-fixing cyanobacterium Anabaena sp. The presence of reactive-black 5 dye significantly decreased the population of ammonia oxidizing bacteria and the rate of the nitrification process. These findings highlight the substantial toxicity of dye pollutants to soil microorganisms and essential nutrient cycling processes in agriculture.

Azo dyes represent notable aquatic pollutants that pose harmful effects on both humans and ecological species. Exposure to the textile dyes can lead to acute toxicity through oral ingestion and inhalation, causing skin and eye irritation in humans and other species. The acute toxicity associated with textile dyes is concerning. The genotoxic effects as a result of textile dyes, along with several instances of mutagenicity, are significant contributors to cancer development. Disposal of aromatic amines may result in allergic dermatitis. The adoption of environmentally friendly technologies in the textile industry is imperative to mitigate environmental damage and safeguard human health (Hemashenpagam et al., 2023).

2.3.3 Drugs

It is believed that up to 90% of certain antibiotics may be released in their original form through excretion, thereby polluting the environment. Sulfamethazine, ciprofloxacin, amprolium ofloxacin, monensin, cetirizine penicillin, and nicarbazine are among the most frequently detected antibiotics. Various researchers have documented contamination of soil, sludge, groundwater, tap water, wastewater, surface water (lakes, sea, rivers), plants, and aquatic animals with antibiotics (Hamscher et al., 2002; Fick et al. 2009; Gothwal et al., 2015). The pharmaceutical sector has been found to heavily pollute surface water, groundwater, and drinking water with antibiotics such as ciprofloxacin, ofloxacin, and cetirizine. The wastewater discharged from a shared effluent treatment facility, which receives process water from about 90 bulk drug manufacturers, contained numerous antibiotics at significantly elevated levels (Fick et al., 2009).

The existence antibiotics in surface water, groundwater, seawater, soil, and sludge may have some very harmful effects on ecosystem, especially for human beings. Typically, contamination transfers from polluted soils to water bodies or plants through processes such as retention to the root surfaces, root absorption, translocation, and foliar absorption. While there are reports suggesting negative impacts of antibiotics on the growth and yield of plants, the doses causing toxicity in plants are considerably higher than those affecting soil microorganisms. The extent of phytotoxicity varies depending on the plant species and the type of antibiotic.

2.4 Various Wastewater Treatment Methods

Currently, various types of methods are available and can be categorized into three classes which are biological, physical, and chemical methods as illustrated in Figure 2.1. Biological methods are widely being applied for the elimination of pollutants. Some example biological treatment includes the use of fungi (Alothman et al., 2020), algae (Arun et al., 2020), bacteria (Barathi et al., 2020) and enzyme degradation (Bachosz et al., 2022) to remove or degrade the pollutants. Some limitation related to this method is the way biological process is hard to control and it cannot degrade persistent and high concentration levels of pollutants (Chen et al., 2020).

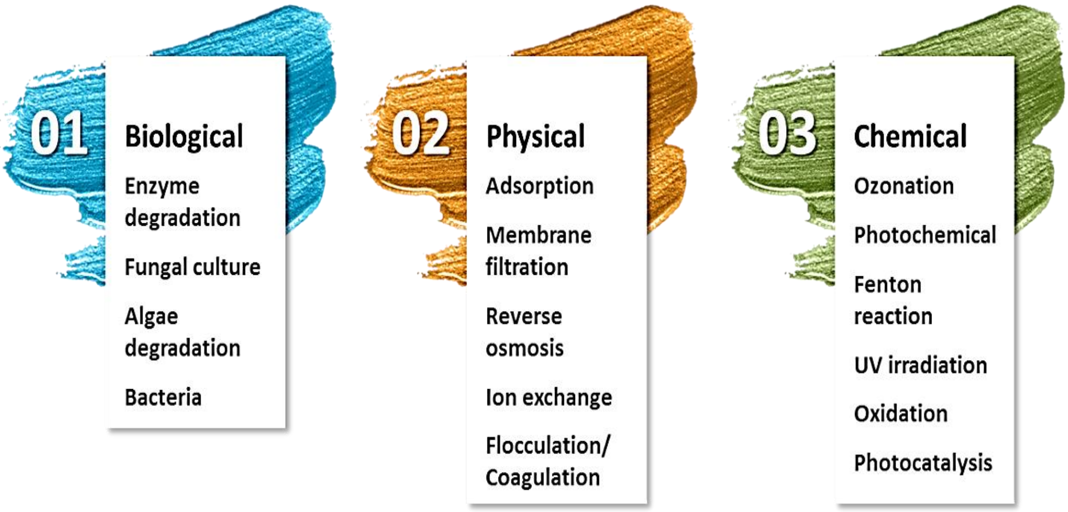

Figure 2.1 Available methods for wastewater treatments

The second category of water treatment method is based on physical techniques. A few examples of this method are adsorption (Georgouvelas et al., 2021), purification using membrane (Liang et al., 2021), reverse osmosis (Park et al., 2020), ion exchange (Can et al., 2020) and flocculation and coagulation (Rajala et al., 2020). Among all, flocculation and coagulation is perhaps the most widely used method. Despite its wide applicability, this method has the drawbacks of using non-reusable chemical like coagulants, flocculants and aid chemical, besides difficult sludge disposal, and thus creating secondary pollution. Meanwhile, membrane filtration is not practical for large scale as it usually involve expansive materials and high operational cost. Various wastewater treatment methods for the degradation of dyes such fenton reaction (Yan et al., 2021), ozonation (Yang et al., 2020) and photocatalysis reaction (Gopalakrishnan et al., 2021) are shown in Table 2.1.

Table 2.1 Various wastewater treatment methods for the degradation of dyes

No.	Wastewater treatment method	Pollutant	Ref.
1	Ozonolysis	Azo dye	(Muniyasamy et al., 2020)
2	Fungal degradation	Azo dye	(Sen et al., 2016)
3	Adsorption	Anthrquinone dye	(Lei et al., 2016)
4	Adsorption	Azo dye	(Birniwa et al., 2022)
5	Fenton degradation	Dye waste water	(Wang et al., 2021)
6	Fenton degradation	Azo dye	(Fernandes et al., 2021)
7	Fenton degradation	Textile dye	(Dias et al., 2016)
8	Photocatalytic degradation	Azo dye	(Shandilya et al., 2021)
9	Photocatalytic degradation	Textile dye	(Dodoo-Arhin et al., 2021)

These techniques are referred to as advance oxidation processes. In particular, photocatalysis is considered as a very promising technology because its simplicity, high efficiency and good reproducibility. Consequently, photocatalysis has received enormous attention in the search for an effective water treatment process because this process generally lead to complete mineralisation of pollutants into water and carbon dioxide.

2.5 Mechanism of heterogeneous photocatalysis

Photocatalysis in water treatment is a simple and green process that can degrade organic pollutants into carbon dioxide, water and other intermediates, and reduce or oxidize inorganic pollutants to harmless substances (Ren et al., 2021). The terminology of photocatalysis is derived from a Greek words; “phos” meaning light and “katalyo” meaning breaking apart or deteriorate (Gupta & Mondal, 2021). The catalyst alters or speeds up the pace of chemical reactions without undergoing any change or being depleted in the process. The term photocatalyst refers to a chemical reaction influenced by the absorption of ultraviolet (290 to 400 nm), and visible light

(400 to 800 nm) (Wu et al., 2017). During photocatalytic reaction, the catalyst generated powerful oxidizing and reducing agents while being irradiated to light source that will reacts and subsequently degraded the pollutants (Zhu & Zhou, 2019).

Principally, photocatalytic reactions take place on the catalyst's surface, triggering a sequence of redox reactions. There are several steps involve in this reaction, i.e., (1) generation of electron-hole pairs (e^{-} and h^{+}) by photocatalyst irradiation; (2) charge separation; (3) electrons and holes transfer to the outer surface of photocatalyst to avoid recombination reaction; (4) active species generation and (5) degradation of the targeted pollutants by the active species (Nasikhudin et al., 2018; Qiu et al., 2021). Figure 2.2 illustrates the photocatalytic mechanism involved in degradation of organic contaminants. Initially, the catalyst absorbed energy in the form of light source (referred as photons, hv). It's important to highlight that for the process of exciting electrons from the valence band to the conduction band, the absorbed energy needs to meet or exceed the band gap energy of the catalyst for electron excitation to occur. Therefore, the excitation results in the generation of positive holes (h^{+}) in the valence band, leading towards to the formation of electron-hole pairs. These pairs may travel to the catalyst’s outer surface to mediate redox reactions. When the h^{+} reacts with water molecules, a powerful hydroxyl radical will be formed. At the same time, the exited electron at the conduction band reduced the adsorbed oxygen to produce superoxide radical anion. These radicals with react with pollutants and degrade them to water (H_2O) and carbon dioxide (CO_2) molecules (Thirunavukkarasu et al., 2020). In that case, where sunlight (visible light) is the source to irradiate reactants, there are possibility degradation might occur via both photooxidation and photosensitizing mechanism (Hadnadjev-Kostic et al., 2020; Thirunavukkarasu et al., 2020).

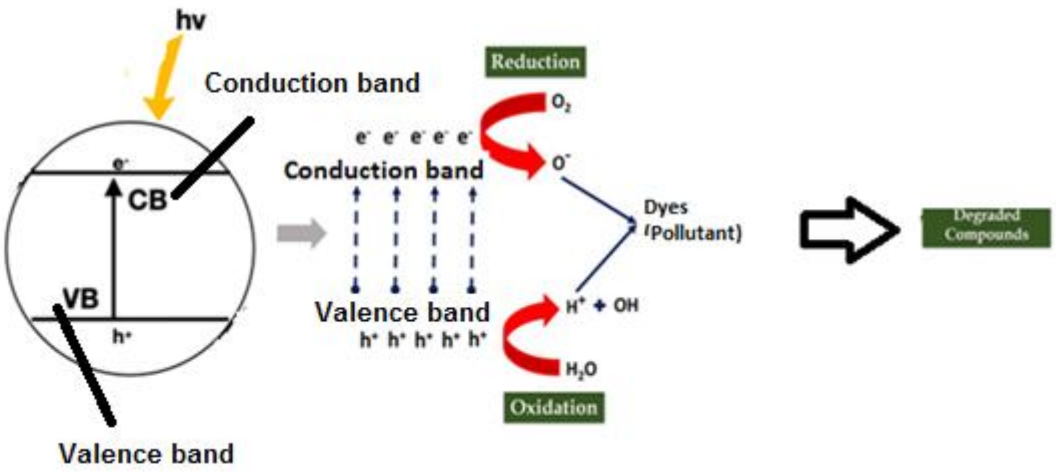

Figure 2.2 Pictorial representation of photocatalytic mechanism for degradation of organic dyes.
Adapted from (Thirunavukkarasu et al., 2020) Springer Publisher with permission

Such photocatalysis reaction can be either homogenous or heterogeneous, depending on the type of catalyst used. Homogenous refers to the reactants and catalysts existing in the same phase. A typical example of homogeneous photocatalysts utilized in water treatment includes ozone and photo-Fenton systems. The downside of homogenous catalysis is the stringent operating pH and heavy power consumption (Shukla et al., 2021). Conversely, heterogeneous catalysis involves the catalysts and reactants being in a different phases, for instance, the reactants are in liquid phase while the catalyst are in solid phase. One of the advantages of using a heterogeneous catalyst is that the separation process from a reaction mixture can be conducted straightforwardly. To date, the most commonly reported heterogeneous photocatalyst is from metal oxides semiconductors. Various types of semiconducting materials like TiO_2, ZnO, WO_3, ZrO_2, V_2O_5, Nb_2O_5, $BiVO_4$, SnO_2, CdS, CeO_2, and Fe_2O_3 have been successfully degraded organic compounds by photocatalytic reaction (Lama et al., 2022). Table 2.2 is also showing different types of metal oxides for the degradation of respective pollutants.

Table 2.2 Different types of metal oxides for the degradation of respective pollutants

No.	Metal oxides (semiconductor)	Pollutants	Ref.
1	V_2O_5	Drugs	(Armaković et al., 2023)
2	Nb_2O_5	Drugs	(Bi et al., 2021)
3	$BiVO_4$	Herbicide	(Chang et al., 2015)
4	SnO_2	Dyes	(Elango et al., 2016)
5	CeO_2	Dyes	(Sane et al., 2018)
6	Fe_2O_3	Pesticides	(Fu et al., 2018)
7	TiO_2	Pesticides	(Umar et al., 2019)
8	ZnO	pharmaceutical micro-pollutants	(Sabouni et al., 2019)

Moreover, for the selection of suitable materials as photocatalysts, it is essential to consider their availability, chemical and physical stability, cost wise and non-toxicity properties. Other specific criteria for these materials to be effective catalysts include preferred band gap energy, higher surface area, possess stability and potential reutilization (Roy & Chakraborty, 2019).

2.6 Metal oxide semiconductors

Metal oxide semiconductors are considered as versatile materials that have been successfully integrated in many applications. These materials are being used in the bio-sensing (Şerban & Enesca, 2020), energy conversion (Wrede & Tian, 2020), microelectronics (Li et al., 2020) and photo-degradation of organic pollutants in water/air. Metal oxides are garnering significant interest in the field of photocatalysis for water treatment due to their ability to absorb light, facilitate charge transport, and possess distinctive electronic structural arrangements. They are relatively inexpensive, safe, possess chemical and photo-stability, and widely available. Under appropriate irradiation, they have the ability to form oxidizing and reducing agents that promote degradation of pollutants. Additionally, due to their insoluble nature, they can be easily separated from the reaction media during catalytic processes. As presented in Figure 2.3, metal oxides semiconductors are usually characterized by a large band gap energy (>3.0 eV) (Riente & Noël, 2019). Depending on the band gap energy, these materials are activated when irradiated either with UV light, visible light or a combination of both, to produce electron/hole pairs. Metal oxides with energy near 3.2 eV are UV-light active and those with energy near to 2.7 eV are visible-light active (Díaz et al., 2022). Among all types of metal oxide semiconductors, TiO_2 and ZnO stand out as the leading materials for their application as photocatalysts in wastewater treatment.

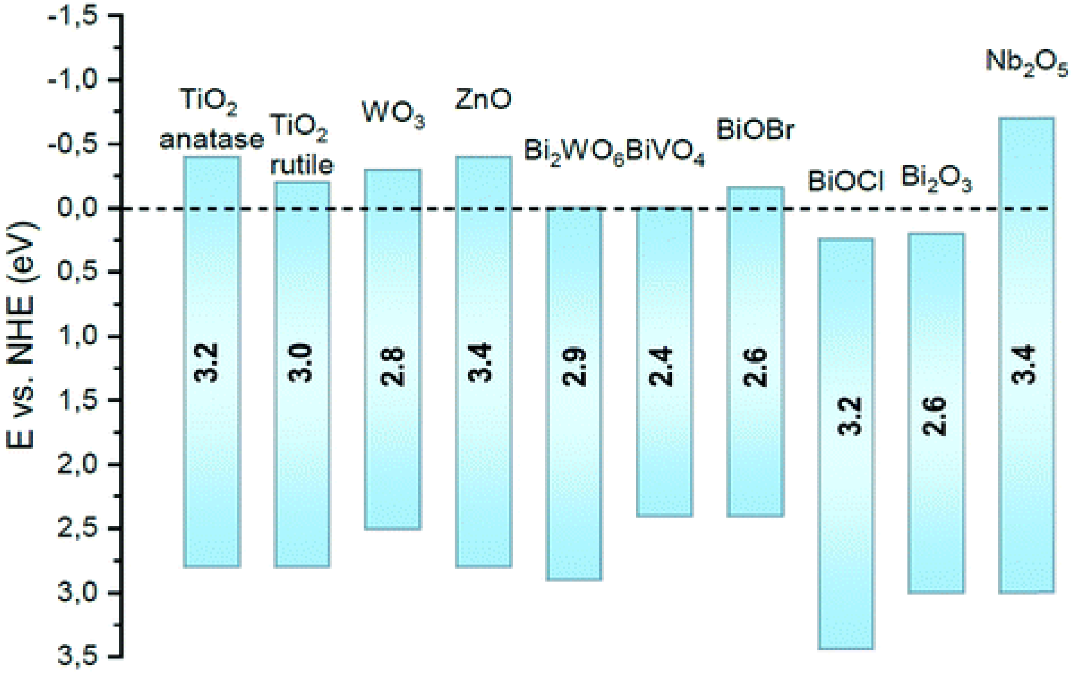

Figure 2.3 Diagram of redox potentials and band gaps energy of some metal oxide semiconductors at pH 7.
Adapted from (Riente and Noël, 2019) with RSC Publisher permission

2.6.1 Titanium dioxide as a photocatalyst

Titanium dioxide (TiO_2) or Titania has been recognized as an efficient semiconductor for photocatalysis. Titania is a naturally occurring oxide that can be employed in a broad range of industrial and consumer products such as paints, plastics, paper, printing inks, fabrics and textiles, cosmetics, electronics and others (Wu, 2021). Other than being low-cost, TiO_2 is considered as an inert, safe, non-toxic and highly stable material (Chen et al., 2018). The interest of TiO_2 as photocatalyst was started to gain attention in 1972 after Fujishima and Honda reported in document on electrochemical photolysis of water using a semiconductor electrode (Fujishima & Honda, 1972). Since then, a rapid growth of studies has been reported on utilizing TiO_2 photocatalyst especially for water treatment purpose. TiO_2 can exist in various forms and the prominent polymorphs structure is the naturally-occurring anatase, rutile and brookite as depicted in Figure 2.4. The most common type of TiO_2 polymorphs studied in photocatalysis is anatase and rutile (Haggerty et al., 2017). In nature, rutile is the most abundant, whereas anatase is consider the utmost photoactive form of TiO_2. TiO_2 with anatase structure (E_g: 3.2 eV) expressed better photocatalytic performance compared to rutile structure (E_g: 3.0 eV) despite having a higher band gap energy. This finding is attributed to the rapid rate of electron-hole recombinant in rutile phase, and the conduction band in anatase is more reductive than in rutile (Shoneye et al., 2022). Alternatively, complex combination procedure of brookite makes it the least favoured for selection as photocatalyst despite having higher performance than anatase and rutile polymorphs. Interestingly, the combination of anatase and rutile produced better photocatalytic activity than their own individual component, for example, a commercial Degussa TiO_2 powder (P-25) containing about 1:3 ratio of rutile and anatase phase (Žerjav et al., 2022). The combine structure can align the conduction and valence band and improve the electron-hole separation subsequently improve the photocatalytic performance than single component (Wang & Saitow, 2020).

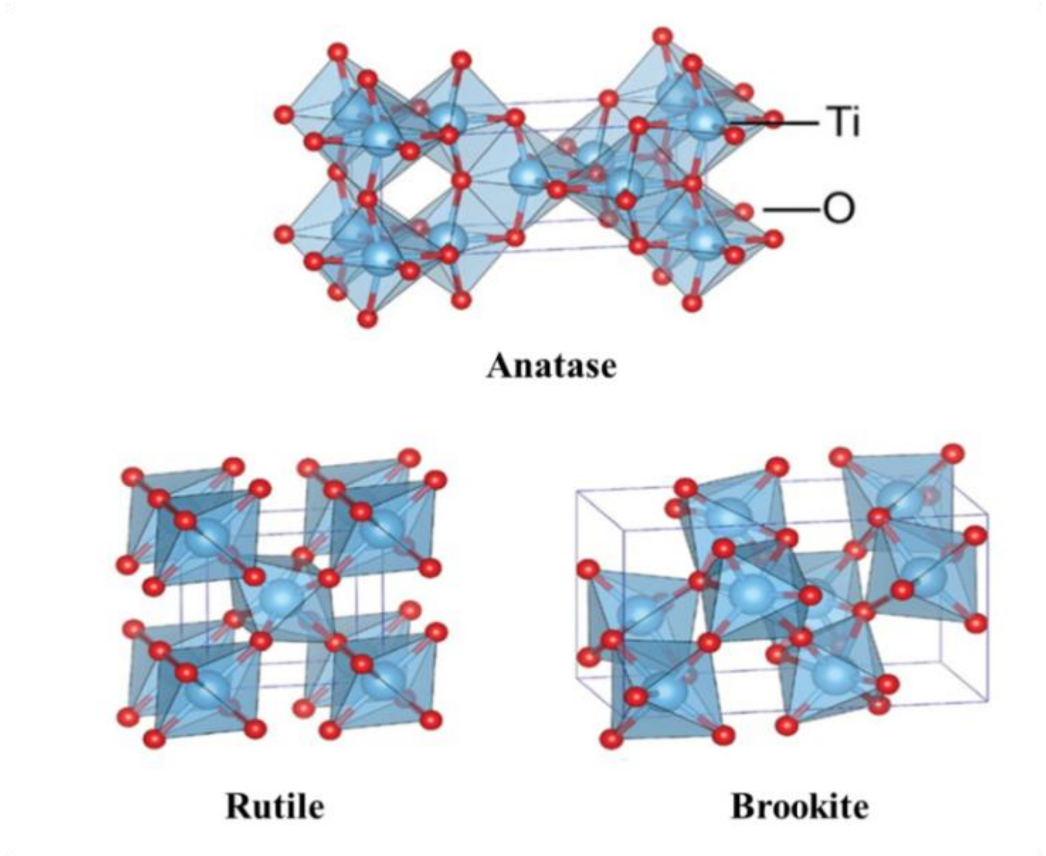

Figure 2.4 Different crystal structures of TiO_2 polymorphs.
Adapted from (Haggerty et al., 2017) with Nature Publisher permission

2.6.2 Zinc oxide as a photocatalyst

Zinc oxide (ZnO) is a multifunctional material that found application in a variety of fields. In fact, ZnO is one of the most widely synthesized metal oxides. ZnO has been used in painting, pigments, coating, rubber, ceramics, food, pharmaceutical, and cosmetic industries (Rahman et al., 2021). ZnO is drawing attention due to its affordable cost and distinctive attributes, including non-toxicity, excellent chemical stability, potent oxidation capabilities, remarkable photosensitivity, biocompatibility, satisfactory photocatalytic performance with some exceptional pyroelectric and piezoelectric properties (Mullani et al., 2020; Lee et al., 2016). ZnO possesses a significantly large surface area with sharp edges, which plays a crucial role in producing charge carriers and reactive oxygen moieties such as hydroxyl radicals. These facilitate the adsorption degradation and mineralization of pollutants while exposed to light sources. ZnO exists in three different crystalline forms; zinc blend, wurtzite and rock-salt as shown in Figure 2.5. The prevalent and enduring phase of ZnO under room conditions is the wurtzite structure, but it can change to rock-salt structure at high pressure (Mustapha et al., 2020).

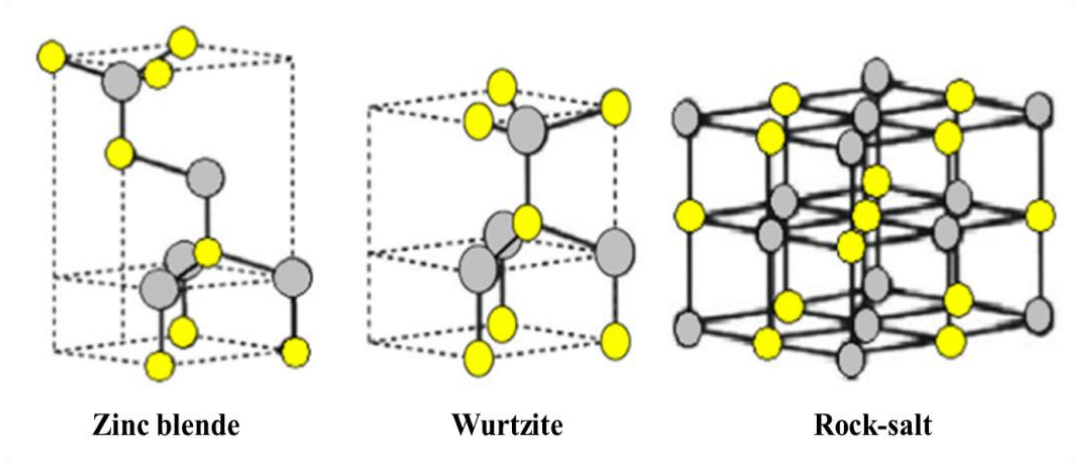

Figure 2.5 Crystal structures of ZnO polymorphs.
Reprint from (Mustapha et al., 2020) with Springer Publisher permission

2.6.3 Synthesis of metal oxide semiconductors

TiO_2 can be synthesized through various chemical and physical methods such as via hydrothermal, microwave, solid-state, solution route method, sol-gel, chemical vapour decomposition, co-precipitation, electrodeposition, solvothermal, crystallization and ultrasonic irradiation (Aravind et al., 2021). The use of chemicals during the production stage is known to have adverse effects to the environment. Therefore, nowadays there is an increasing interest of using green synthesis method to produce TiO_2. Other than being low-cost and non-toxic, such method is gaining attention due to its simple and environmental friendly procedure (Fall et al., 2019). The green synthesis or biosynthesis method utilized biomaterials such as plant extract and other microorganism like fungi and enzyme during the reaction (Nabi et al., 2021). In this context, the biomediator, for instance the one obtained from plants acts as an oxidizing, reducing and capping agents, and at the same time used to control aggregations and agglomerations of the TiO_2. For this purpose, different parts of the plants can be used i.e. stem, leaf, flower, peel and their waste. Since organic wastes are being generated daily globally, it is a smart move to revaluate the waste for the synthesis of TiO_2. Residues from citrus fruit like lime, tangerine, lemons, oranges etc. have been investigated. These biomediators contain soluble sugar and insoluble polysaccharides, polyphenols that serve as reducing agents, whereas carboxylic groups, amino acid and citric acid acts as stabilizer (Mobeen Amanulla & Sundaram, 2019; Rueda et al., 2020).

Similarly to TiO_2, ZnO can be synthesized using chemical and physical methods. Physical methods include radio-frequency magnetron sputtering, arc discharge, pulse laser deposition and molecular beam epitaxy, whereas chemical synthesis by electrochemical deposition, combustion, hydrothermal synthesis, chemical vapour deposition, spray pyrolysis, etc. (Sulciute et al., 2021). The physical methods are expansive and required high usage of energy during the process. The chemical methods own distinct advantages in terms of ability to control the size of ZnO, mass production and reproducibility (Davar et al., 2015). Despite these advantages, chemical syntheses usually use solvents and toxic reducing agents which can harm the environment. Therefore, numerous studies explored the green synthesis of ZnO using biomediators. In one study, synthesis of ZnO using via orange fruit peel and investigated its antibacterial properties for biomedical applications (Doan Thi et al., 2020). In another literature report,pomegranate peel and solid coffee ground extract were used as capping agents for the synthesis of ZnO (Abdelmigid et