Investigation on water pollution scenario of Damodar river basin and treatment of organic contaminants in wastewater by the heterogeneous photocatalyst

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

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August, 2022

Synopsis

Water is coined as the phrase "elixir of life". The progress of human civilisation and the development of a country depend highly on its freshwater resources and their proper utilisation. However, presently, the crisis of freshwater resources throughout the globe has become a severe threat to the environment, ecology and human civilisation. The critical scenario may be due to the long term exposure of the freshwater resources to anthropogenic and geogenic contaminants caused by socio-economical modernisation, rapid urbanisation and industrialisation. Water pollution is one of the major concerns in the present day in highly populated developing countries like India and China. India's rapidly growing economy, industrialisation, and urbanisation significantly threaten the environment and human health. Eleven major rivers are scattered around India, and most industrialisation happened on these rivers' banks. In the present thesis, we have chosen the Damodar river basin (one of India's largest polluted industrial provinces in eastern India, having a dense and high population) to examine the water pollution scenario as a case study. The present thesis emphasises two significant concepts that complement each other and are highly interdisciplinary. Firstly, the present work includes the (a) physicochemical analysis of the Damodar river basin's water bodies to assess the water pollution profile through geochemical experiments and statistical analyses and (b) estimation of overall possible health hazards due to water pollution. Secondly, this report focused on the possible remediation of water pollution, namely removing organic contaminants using eco-friendly and cost-effective techniques (nanomaterial-based photocatalyst). This thesis work is organised into **five chapters** as follows:

Chapter I [INTRODUCTION] conveys the primary introductory section of the entire thesis work. The first part covers the recent literature survey on global and Indian scenarios on water pollution. The objectives of this thesis work are clearly stated in this section. Water pollution status in several industrial zones of India and the water contamination of India's major rivers are discussed here. This thesis comprises a detailed survey of the water pollution profile at the study area and its geological and hydrological setup. Moreover, the second part consists of a comprehensive discussion on nanotechnology's intervention in dealing with the observed pollutants in the water

bodies. This chapter reports a literature review on the recent advancement of semiconductor metal oxide materials as photocatalysts in water treatment applications. Titania based materials are chosen in this thesis as a cost-effective solution for removing organic pollutants from the wastewater. Further, supporting literature surveys on titania material synthesis and the associated science and engineering of the titania-based nano-photocatalyst is discussed here.

Chapter II [METHODOLOGIES] explains the necessary methodologies used in (i) water quality measurements and (ii) synthesis and characterisation of nano TiO_2 photocatalyst used in the removal of organic pollutants of water bodies. The entire methodology is organised into (a) experimental methodology and (b) analytical procedure. The sampling protocols for measuring water quality parameters, i.e. physical parameters, inorganic ions, heavy metals, organic compounds etc., are discussed in detail. Moreover, comprehensive experimental methods are proposed to remove the pollutants found in the analysed water samples. The present thesis reports the synthesis of titania-based nanomaterials to remove identified organic contaminants in the wastewater. One-step easiest solvothermal methods are adopted by varying the reaction temperature and pH of the synthesis solution. Details of the experimental procedures relating to numerous characterisation techniques like electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) analysis, BET analysis, Raman Spectroscopy, Infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), UV-Vis spectroscopy and diffuse reflectance spectroscopy (UV-Vis and DR spectroscopy), Fourier Transform Infrared Spectroscopy (FTIR), Photoluminescence Spectroscopy (PL), Electron paramagnetic resonance (EPR) of the prepared titania photocatalyst materials are well explained to comprehend the catalytic efficiency of prepared TiO_2 photocatalyst for removing organic compounds. Details of the photocatalytic degradation experiment and its kinetic study are well explained. Moreover, experimental details for detecting the by-products are included. Additionally, this chapter explores the charge carrier mechanism during the catalytic reaction and band structure of synthesised TiO_2 through an electrochemical test. Furthermore, the essential and associated analytical methodologies and relevant equations, including statistical analyses, are discussed in this chapter.

Chapter III [DAMODAR RIVER'S WATER POLLUTION AND ITS IMPACT ON HUMAN HEALTH] comprises, first of its kind, a complete report on the water pollution status of the Damodar river basin in terms of the conventional water quality parameters. The physicochemical characteristics of the groundwater (bore-well, dug-well), surface water (rivers/ponds/lakes), industrial effluents and mining discharges from several sampling locations of the Damodar river basin are analysed. Pollution scenarios at the upper and lower Damodar river basin are evaluated separately. All polluted industrial cities of this basin are identified. Moreover, a detailed comparative study of the pollution profile is performed by considering the historical database (1980-2018) to the current dataset (data obtained in 2019). On the other hand, a comparison study is made among the water quality parameters of the other most polluted eleven rivers in India and the Damodar river. Among all water quality parameters, the heavy metal pollution profile of the study area is mainly emphasised in this chapter as heavy metals have adverse effects on the environment and human health. The hazardous zones around the entire Damodar river basin are identified in terms of the heavy metal pollution index. Moreover, both cancer and non-cancer health risk are estimated via. ingestion and dermal pathways for adults and children. The spatial analysis of the variations of health risk factors is also reported. Since most of these identified pollutants are non-biodegradable and persistent in the environment, this thesis attempts to take a cost-effective solution for their removal. In this background, the following chapters deal with a detailed discussion on the removal mechanism of selected organic pollutants only among other identified toxicants, and their possible outcomes are included.

Chapter IV [HETEROGENEOUS PHOTOCATALYST FOR REMOVING THE ORGANIC CONTAMINANT IN WASTEWATER] introduces a primary photocatalytic mechanism for the degradation of organics in the water media using TiO_2 photocatalyst. New observations and associated fundamental science relating to the synthesis of TiO_2 photocatalyst by varying the reaction temperature and pH of the synthesis solution are discussed here. Solvothermal alcoholysis reaction is chosen to synthesise TiO_2 photocatalyst as the easiest solution. Numerous effecting factors are investigated involved in solvothermal reactions during the synthesis, and this report explores the science of photocatalytic effectivity that depends on these factors. This

chapter shows the effect of reaction temperature, i.e., solvothermal temperature, on the nucleation process during the TiO_2 synthesis. The report includes the study for developing a hierarchical TiO_2 nanoflower photocatalyst due to its three-dimensional morphology. Benefits of hierarchical nanoflower morphology of TiO_2 is incorporated. Microscopic, macroscopic, and spectroscopic analysis of all prepared TiO_2 reveals a remarkable change in the crystalline phase, crystalline size, morphology, porosity, etc. The report shows that the catalytic efficiency is varied at different solvothermal temperatures (e.g., 130 °C, 140 °C, 150 °C, 160 °C, 180 °C and 200 °C). This chapter enlights optimising the reaction temperature for TiO_2 to obtain the highest catalytic efficiency for the degradation of organic compounds.

Further, Chapter IV also explores the effect of another vital parameter in the nucleation process of solvothermal alcoholysis reaction TiO_2 synthesis, i.e., solution acidity (pH of the synthesis solution). This chapter strongly emphasises brookite phase dominated TiO_2 photocatalyst obtained at four varied pH (e.g., 1.0, 2.5, 4.0 and 5.5) of the reaction solution. Associated literature studies on the utility of brookite phase enriched TiO_2 are discussed in this chapter. Necessary observations relating to various techniques of material characterisations are discussed here. The present work explores that the solution acidity highly affects the ratio of three polymorphs of TiO_2 (anatase, rutile and brookite), morphology, crystalline size, defects states, surface area, pore size, UV absorbance capacity, bandgap and structures. An evolutionary morphological change (nanoflower to microsphere) is observed at high pH, and a high brookite phase is obtained. This part of this thesis investigates the effect of the crystalline coherence phenomenon on the morphological anisotropy features of brookite TiO_2. The change in the crystalline size of three polymorphs explained a clear vision of the morphology change.

Chapter V [SUMMARY AND CONCLUSION] is the last and final chapter that embraces the overall summary, conclusions, outcomes, and future plan concerning our theoretical and experimental observations of water pollution status in India's Damodar river basin, based on past and present reports. Zone wise human health risk assessment is estimated due to long term exposure to polluted water, and frequent monitoring of medical diagnosis is proposed. Imposing strict pollution control rules and frequent

water quality monitoring is highly recommended at Damodar river with the help of the pollution control regulatory board.

Moreover, this chapter summarises our observation and recommendation about the science of photocatalyst in developing new material for removing organic pollutants from the water bodies. The reaction mechanism of solvothermal alcoholysis shows the effect of the adsorption phenomenon of anions on the identified crystallographic planes, which helps to explore final morphological change, i.e., nanoflower (at low pH) to microsphere TiO_2 (at high pH). The ratio of used reagent seems to be a controlling factor for adjusting the solution pH as no external acid is used. Nevertheless, enhanced defect states and high surface hydroxylation at high pH conditions are appeared to be significant features for exceptionally high catalytic efficiency, as shown in this thesis. The required photocatalytic test, kinetics study and identification of intermediates are discussed through mass spectrometry analysis. However, several radical trapping experiments of photocatalytic reactions are performed to observe the role of quenchers in the photocatalysis reaction. The electrochemical test includes impedance spectroscopy analysis and chronoamperometry to reveal the charge transfer mechanism.

Finally, this chapter includes the **future plans** as follows:

- Seasonal variation (pre-monsoon and post-monsoon) data must be recorded and analysed with proper statistical tools.
- Detailed medical surveys need to be performed to understand the impact of water pollution on the possibility of cancer among the dwellers in the areas.

For a better water treatment process, the following points need to be addressed:

- The synthesis methods need to be optimised to obtain the Brookite phase in any titania-based photocatalytic system.
- On a commercial scale, a photocatalytic membrane reactor can be fabricated using prepared nanoflower and microsphere TiO_2 material to purify the wastewater.