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A Comparative Study of Seasonal Variability and Photocatalytic Impact on Water Quality of the Ayad River, Rajasthan

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Abstract

This study examines seasonal fluctuation in Ayad River water quality, Rajasthan, India and compares the performance of titanium dioxide (TiO_2)-mediated photocatalytic treatment under natural sunlight irradiance. Ayad River is a critical source of freshwater for domestic, agricultural and environmental purposes, which is increasingly stressed by urban runoff, industrial effluent and seasonality. As a follow-up to the above, water samples of four important water sources-Thurmadar, Subhas Nagar Bridge (Ayad), Kanpur Mahadev and SukhaNala were taken in summer season and treated with TiO_2 as a photocatalyst under natural sunlight. General physicochemical parameters, such as pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and ions, such as Ca^{2+}, Mg^{2+}, NO_2^-, Cl^-, and SO_4^{2-}, were analyzed following standard procedure (IS:3025). Comparison study of pre- and post-treatment investigations showed enhanced quality of water at both places. Particularly, COD concentrations fell by approximately 60–80%, while BOD levels showed a remarkable fall, a proof of effective oxidation of the organic contaminants. Rising DO indicated promise for restoration of the ecosystem. Moreover, decrease in nitrate and fluoride concentration provided safety and potability to the ecosystem. The research proves the effectiveness of TiO_2 photocatalysis as a low-cost, mass-transferable and green water treatment technology for the mitigation of river water pollution in urban areas. The findings affirm the viability of integrating green technologies into river systems and provide a scientific basis for applying sustainable water treatment processes in other parts of the developing world with comparable problems.

Keywords: Photocatalysis, titanium dioxide (TiO_2), Ayad River, water quality assessment, seasonal variation, chemical oxygen demand (COD), biochemical oxygen demand (BOD)

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INTRODUCTION

Water is commonly known to be a critical requirement for growth and life. Ironically, it is one of the most threatened resources in the 21st century. Increasing population in the world, urbanization, industrialization, and agricultural intensification have put tremendous pressure on freshwater resources, particularly rivers. Rivers, which are vital for drinking, irrigation, sanitation, and industry, generally experience uncontrolled pollution by virtue of direct discharge of untreated or partially treated effluents. It is particularly true in developing countries, such as India, where inadequate infrastructure facilities and regulatory constraints render effective water management ineffective. Indian rivers are of immense cultural, economic, and environmental significance. But most urban and peri-urban rivers have become dumping sites for industrial effluents, sewage, and waste. A classic example is the Ayad River of Udaipur, Rajasthan. The Ayad River, which is a component of the Berach River system, has been traditionally pivotal in sustaining the regional ecosystem as well as local dwellers [1]. For decades, the river suffered drastic deterioration owing to increasing anthropogenic stressors. Uncontrolled domestic sewage, industrial effluent, religious ceremonies and agriculture runoff release a combination of effluents that deteriorate the physical, chemical, and biological quality of the river. Seasonal fluctuation is an important untapped variable responsible for influencing the river water quality. Climatic conditions in semiarid regions of India, like Rajasthan, persist in stark contrast among summer, winter, pre-monsoon and post-monsoon seasons. All these processes influence hydrological flow, water content, and concentration of the pollutants [2]. For example, monsoon dilution can decrease visible pollution in the short term, whereas summer stagnation can increase toxicity as well as eutrophication. Understanding these variations seasonally is of extreme relevance in successful management of water quality determination as well as sustainability of river health. Conventional water treatment methods, such as sedimentation, filtration, and chlorination – have proven to be insufficient in eliminating coming-of-age contaminants such as drugs, pesticides and heavy metals (Figure 1). Conventional treatment methods are not necessarily effective in decomposing complex organic compounds or oxidizing residual inorganic ions. Conventional treatment involves high operating expenses, requires gigantic structures and may produce secondary pollutants such as sludge. Hence, it is necessary in the first place to develop sustainable and innovative methods that are effective and cost-effective for local application [3].

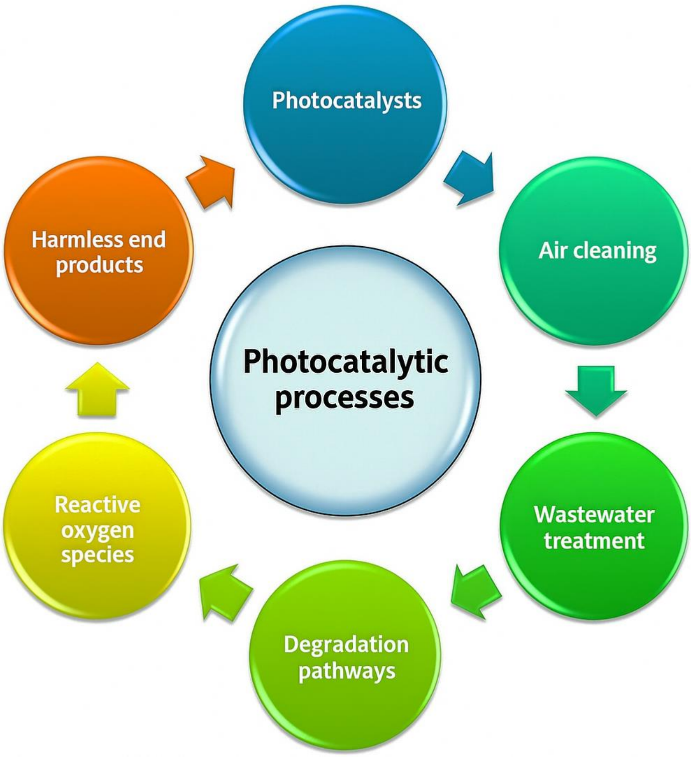

Figure 1. Photocatalytic processes.

Photocatalytic degradation using titanium dioxide (TiO_2) as a catalyst has emerged as a powerful tool within the Advanced Oxidation Processes (AOPs). Titanium dioxide (TiO_2) is a semiconductor material that has very good photocatalytic activity upon ultraviolet (UV) or sunlight irradiation. Upon illumination of light, TiO_2 generates reactive oxygen species (ROS) that can oxidize a wide range of contaminants such as organic molecules, bacteria, and heavy metals. It is chemically inert, not toxic, recyclable and plentiful, making it a suitable material for decentralized, solar-powered water treatment in the Third World. Laboratory-scale the effectiveness of TiO_2 in color removal, phenol annihilation and microbial inactivation have been proven by numerous studies [4]. Its application to natural water bodies-especially rivers with complex and dynamic pollutants is, however, poorly studied. There is a critical need for leaping from lab experiments to field-scale validation with respect to different sources of contamination, shifting environmental settings and cost-effectiveness. The present study aims to bridge the research gap by evaluating the efficacy of TiO_2 photocatalytic water treatment of Ayad River's water quality at four sites: Thurmadar, Subhas Nagar Bridge (Ayad), Kanpur Mahadev and SukhaNala. These locations exemplify many human-induced pressures and hydrological features, providing a thorough spatial overview (Figure 2) [5]. The study incorporates a seasonal aspect, concentrating on the pre-monsoon period, characterized by elevated pollutant concentrations resulting from evaporation and restricted flow. This study is distinctive in its amalgamation of seasonal water quality assessment, regional heterogeneity and field-scale use of green technologies. The results will enhance comprehension of how solar-driven TiO_2 photocatalysis might function as a sustainable, scalable and economical approach for the cleanup of contaminated river systems in India and analogous geoclimatic areas. Furthermore, the insights obtained can influence policy frameworks, enhance community-level water initiatives and direct future research on low-carbon water purification technology [6].

PRINCIPLES OF PHOTOCATALYSIS

In photocatalysis, a material that does not incur any permanent chemical change is used to catalyze a chemical reaction when exposed to light. Light is used as an energy source and the reaction is accelerated by the catalyst in this process, which is a combination of photochemistry and catalysis. Because of its remarkable capacity to break down a wide range of organic and inorganic contaminants in both water and air, photocatalysis has recently attracted a lot of interest from environmental scientists. This is particularly true when the pollutants are present in both natural and artificial light environments. Photocatalysis is an attractive tool for use, including self-cleaning surfaces, air purification and wastewater treatment since it is effective, inexpensive and environmentally friendly.

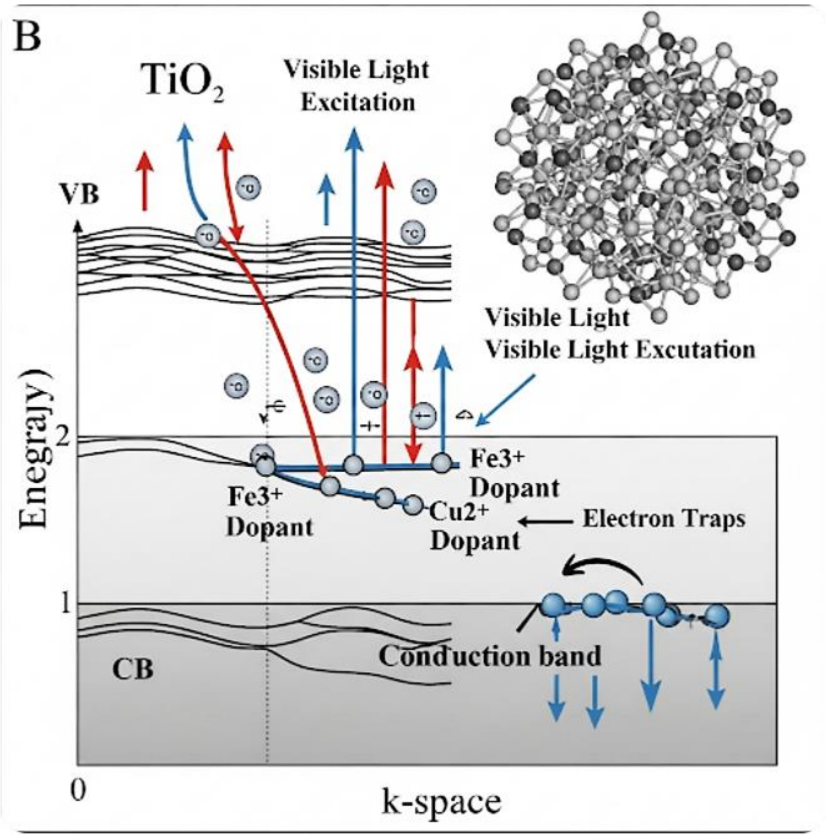

Figure 2. Metal–Ion doping mechanism in TiO_2.
Source: Ruixiang Li et al. Impact of titanium dioxide (TiO_2) modification on its application to pollution treatment – A review.

Semiconductor Photocatalysts and Bandgap Theory

The utilization of semiconductor materials, particularly titanium dioxide (TiO_2), which can absorb photons and produce electron-hole pairs, is fundamental to photocatalytic technology. An electron-filled valence band (VB) and an empty conduction band (CB) characterize the unusual band structure of these semiconductors. In this context, "bandgap" means the energy differential between the two bands [7].

Photons that reach the bandgap or above excite electrons in the conduction band and leave a positively charged hole in the valence band when they hit the surface of a semiconductor. One way to represent this procedure is as:

$$TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB}$$

Here, hv is the photon energy e^-_{CB} is the excited electron in the conduction band and h^+_{VB} is the corresponding hole in the valence band. Photocatalysis begins with the creation of these electron-hole pairs [8]. The total photocatalytic reaction efficiency is dictated by the separation and migration of these charges to the catalyst surface.

Nevertheless, TiO_2 is mostly active in the ultraviolet (UV) part of the electromagnetic spectrum due to its comparatively large bandgap, which is around 3.2 eV for anatase [9]. Doping with metal or non-metal ions is one strategy to decrease the bandgap and extend the photocatalytic activity into the visible light region, which improves solar utilization. This is necessary because only about 5% of the sun's output is in the ultraviolet range.

REDOX REACTIONS AND REACTIVE OXYGEN SPECIES FORMATION

To take part in redox processes, the newly formed electron-hole pairs move to the photocatalyst's surface. In aqueous systems, hydroxyl radicals (•OH) are among the most potent oxidants; they are formed when holes (h^+) react with water molecules (H_2O) or hydroxide ions (OH^-) adsorbed on the surface. At the same time, electrons in the conduction band can produce superoxide anion radicals by reducing dissolved oxygen (DO).

Hydrogen peroxide (H_2O_2), more •OH radicals and other reactive oxygen species (ROS) are produced when these radicals undergo additional processes [10].

The key reactions are as follows:

- *Oxidation Reactions:*

$$h^+ + H_2O \rightarrow \cdot OH + H^+$$

$$h^+ + OH^- \rightarrow \cdot OH$$

- *Reduction Reactions:*

$$e^- + H^+ \rightarrow \cdot O_2^-$$

$$\cdot O_2^- + H^+ \rightarrow \cdot HO_2 \rightarrow H_2O_2 \rightarrow \cdot OH$$

Particularly important in the degradation and mineralization of pollutants, particularly organic contaminants, are the reactive oxygen species (ROS) produced throughout these processes. These oxidants do not exhibit selectivity and instead target and decompose complicated organic compounds into less dangerous byproducts, like water and carbon dioxide [11].

Secondary contamination is a typical issue with traditional water treatment methods; however, this thorough mineralization guarantees that this technique will not cause it (Figure 3).

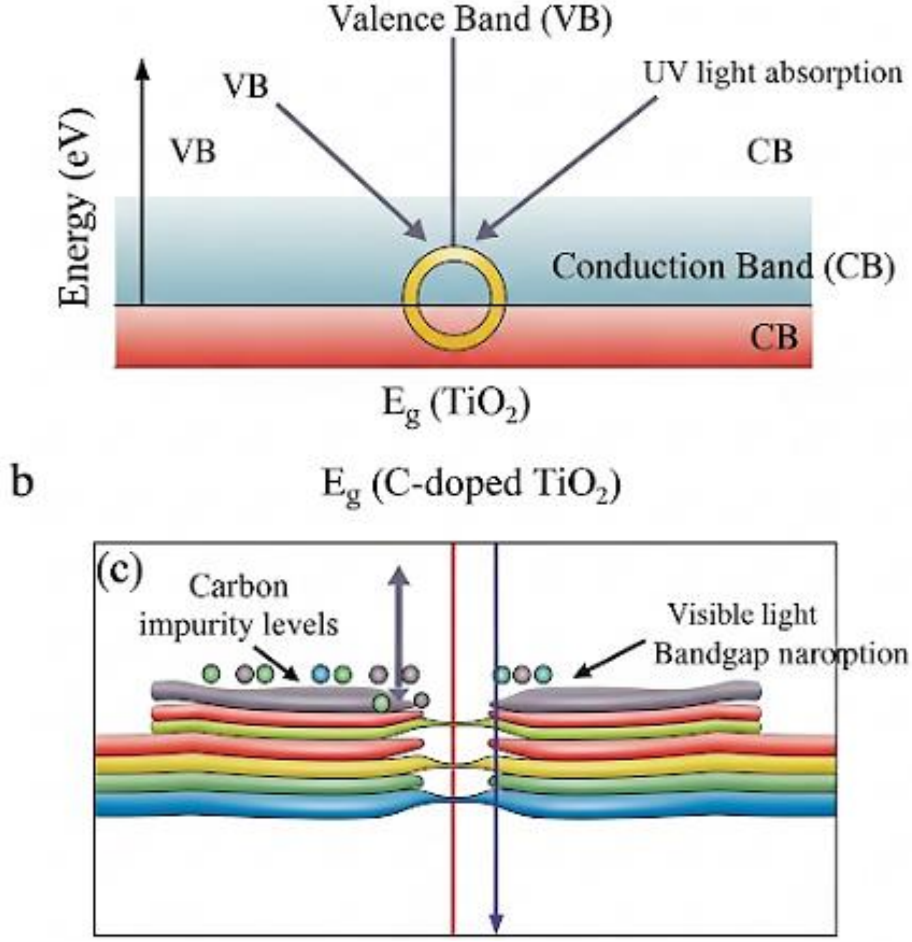

Figure 3. Carbon-doped TiO_2 photocatalysis under visible light.
Source: Aleksandra Piątkowska et al. C-, N- and S-doped TiO_2 photocatalysts: A review.

FUNDAMENTAL STEPS OF THE PHOTOCATALYTIC PROCESS

The photocatalytic reaction consists of several interconnected processes. Here is a brief overview of them:

- *Photon Absorption:* The semiconductor absorbs light with energy ≥ Eg.
- *Generation of Electron–Hole Pairs:* Hole creation and electron excitation.
- *Charge Separation and Migration:* The surface of the catalyst attracts electrons and holes.
- *Redox Surface Reactions:* Adsorbed molecules undergo oxidation and reduction reactions initiated by electrons and holes.
- *Pollutant Degradation:* Organic/inorganic pollutants are broken down into CO_2, H_2O, and other by-products.

For the process to be successful, each of these components must work well. For example, photocatalytic reactions cannot take place if electron-hole pairs undergo recombination prior to reaching the surface [12]. So, to get the most out of photocatalysis, you need to keep charge recombination at bay.

ENVIRONMENTAL APPLICATIONS AND RELEVANCE TO WATER QUALITY

One promising strategy for the removal of contaminants from water sources is photocatalysis, particularly when applied to materials containing TiO_2. Many persistent organic pollutants (POPs) are resistant to traditional treatment approaches; this is especially true for dyes, insecticides, phenols and medicine [13]. Photocatalysis is well-suited to complex and dynamic water matrices, as those seen in seasonal river systems, due to its non-selective properties.

The use of photocatalysis to degrade contaminants in real-time using natural sunlight can help maintain water quality in rivers, like the Ayad River in Rajasthan. This is especially useful in this area because water quality can fluctuate significantly due to seasonal factors, like rainfall, agricultural runoff and domestic discharges [14]. In addition to being environmentally safe, low-maintenance and energy efficient, the technique is well-suited for use in semi-urban and rural areas with little infrastructure.

ROLE OF DOPING IN ENHANCING PHOTOCATALYTIC ACTIVITY (FE, N, AG, ETC.)

One of the most common and efficient ways to improve the photocatalytic activity of semiconductors, like titanium dioxide (TiO_2) is to dop them. The intrinsic constraints of TiO_2, such as its broad bandgap and poor visible-light absorption, can be overcome through doping in the context of environmental applications such as water purification and pollutant degradation under sun irradiation. Doping changes the electrical structure, charge separation, electron-hole recombination and visible light absorption of TiO_2 by inserting foreign atoms into its crystal lattice [15]. Metal doping and non-metal doping are two main categories of doping, with different effects and mechanisms depending on the dopants used.

Metal Doping (E.g., Fe, Ag, Cu, Mn, V)

One common way to make titanium dioxide (TiO_2) more effective as a photocatalyst, especially for use in visible light applications, is to dope it with metals. During this procedure, transition or noble metal ions, like iron (Fe^{3+}), silver (Ag^{+}), copper (Cu^{2+}), manganese (Mn^{2+}), or vanadium (V^{5+}), are purposefully added to the TiO_2 crystal lattice. In most cases, these metal ions either fill the space between lattice points or act as a titanium ion substitute, causing impurity energy levels to arise within the bandgap. By utilizing these newly created energy states as stepping stones for electron excitation, TiO_2 can absorb visible light photons with lower energies, expanding its photoresponse beyond UV light. Metal doping improves visible-light absorption, which is a major benefit. With the new energy levels, TiO_2 can use more of the sun's rays, increasing its efficiency in direct sunlight. Also, by inhibiting the rapid recombination of photogenerated electrons with holes, many doped metal ions serve as electron traps, which aids in charge separation [16]. This enhances the probability of redox reactions happening on the surface of the catalyst and lengthens the lifespan of charge carriers. In addition, some noble metals, such as silver (Ag) and platinum (Pt), accelerate surface processes that break down contaminants and facilitate charge transfer between surfaces; this is known as a direct catalytic role. The photocatalytic performance of TiO_2 has been enhanced significantly by the addition of various metal dopants. As an example, Fe^{3+} has the capability to introduce shallow energy levels just below the conduction band, making it one of the dopants that has been investigated the most. These states not only reduce the rate of electron-hole recombination but also enable electron excitation under visible light and serve as electron acceptors. In a similar vein, surface plasmon resonance (SPR) is used to increase visible-light absorption when Ag^{+} is doped, especially with silver nanoparticles. As electron sinks, these nanoparticles enhance charge separation and boost the degradation efficiency of contaminants generally, in addition to amplifying light absorption. Cu^{3+} is another efficient dopant that, like Fe^{3+}, improves photocatalytic degradation processes by increasing the formation of reactive oxygen species (ROS) and improving the reactivity to visible light [17].

Non-Metal Doping (E.g., N, C, S, B, F)

The photocatalytic efficiency of titanium dioxide (TiO_2) can be improved through non-metal doping, which is very useful for solar irradiation applications. Metal doping usually opens new energy levels in the bandgap, however non-metal doping changes the valence-band of TiO_2. This is accomplished by adding non-metallic elements, like nitrogen (N), carbon (C), sulfur (S), boron (B), or fluorine (F), to the TiO_2 cubical structure. These dopants alter the oxygen 2p orbitals by introducing p-orbital states, which interact with the valence band edge or generate new mid-gap states. The end outcome is a bandgap that is effectively narrowed, allowing TiO_2 to absorb visible light and respond to a wider range of the solar spectrum. A notable consequence of doping with non-metals is the enhancement of photocatalytic activity in natural sunlight, which includes a large amount of visible radiation. This is made possible by expanding the absorption of light into the visible area. Due to economic and sustainability concerns, solar-driven processes are preferable in environmental applications, and this alteration boosts the efficiency of TiO_2 in those cases. Doping with non-metals also keeps TiO_2 chemically and structurally stable, so it can withstand outdoor or harsh environmental conditions for a long time [18]. This durability is a major plus in comparison to metal-doped systems that can deteriorate or leak with time. For non-metal dopants, nitrogen (N) has been the subject of the greatest research and application (Figure 4). Doping with nitrogen creates energy levels just above the valence band, which opens the door for visible light excitation of electrons in the 400–500 nm array. Without the need for artificial UV sources, TiO_2 can function efficiently under natural sunlight. Further promoting its use in large-scale applications, nitrogen is both an inexpensive and ecologically benign dopant. Besides metals, carbon (C) is a good non-metal dopant for the TiO_2 lattice that can be present at either interstitial or substitutional sites. Carbon doping boosts photocatalytic efficiency in two ways: by increasing electrical conductivity and by improving visible-light absorption. Sulfur (S) has also been employed to enhance light absorption and reduce the bandgap of TiO_2; nevertheless, the stability of sulfur-doped TiO_2 might change based on the conditions of synthesis and surrounding environment [19].

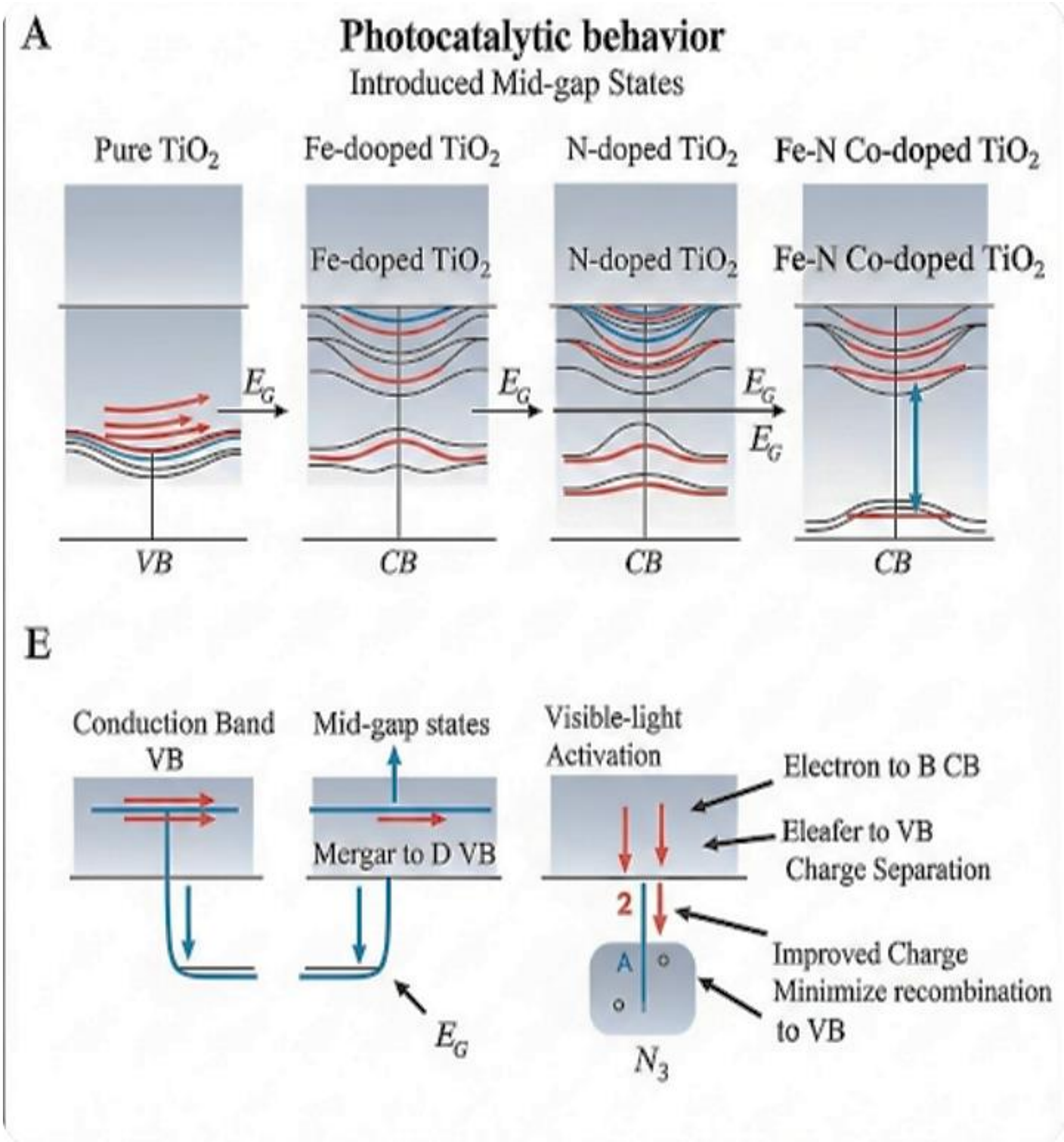

Figure 4. Fe–N Co-doped TiO_2 mechanism.
Source: Kangqiang Huang et al. Preparation and characterization of visible-light-activated Fe–N Co-doped TiO_2.

Co-Doping (Metal + Non-Metal or Dual Metal/Non-Metal)

A state-of-the-art method in photocatalyst engineering, co-doping entails doping the lattice of titanium dioxide (TiO_2) with two or more dopant elements, which can be metals with non-metals, two metals, or two non-metals. Better photocatalytic performance than is normally possible with single-element doping is the goal of this approach, which is based on combining the benefits of various dopants. Through the careful combination of dopants with complimentary roles, co-doping can alter the electronic structure of TiO_2, enhance light absorption over a wider spectrum and maximize charge carrier mobility and separation. The capacity to combine different enhancement techniques is a major advantage of co-doping. As an example, it is well-known that nitrogen doping narrows the bandgap and extends TiO_2's absorption into the visible range, but iron doping introduces shallow trap states that facilitate efficient charge separation. By combining these two elements, as in N–Fe co-doping, TiO_2 can increase its photocatalytic effectiveness by better absorbing visible light and reducing electron-hole recombination [20]. Due to its synergistic properties, co-doped TiO_2 is ideal for environmental applications since it degrades contaminants more effectively when exposed to sun radiation. One of the main benefits of co-doping is that it can help reduce the negative effects of solo dopants. Excessive doping with a single element can sometimes cause photocatalytic performance to decrease due to the introduction of recombination sites or structural flaws. Maintaining structural integrity and enhancing long-term performance can be achieved through co-doping, which balances the effects of the dopants. This improves the dependability of co-doped materials in real-world applications, including river water cleanup, where catalysts encounter variable amounts of light, different pollutants and extended periods of operation. C–S (carbon–sulfur) co-doping is a famous example of non-metal co-doping that improves properties, including light absorption and pollutant adsorption. Sulfur changes the band structure to activate TiO_2 with visible light, while carbon increases conductivity and surface area. When combined, these dopants greatly enhance the photocatalyst's capacity to break down water pollutants when exposed to sunlight. Affordable solar water treatment systems in semi-urban and rural areas can greatly benefit from such combinations [21].

DOPING MECHANISM OVERVIEW

The electrical band structure of titanium dioxide (TiO_2) governs its fundamental photocatalytic activity. Because of its large bandgap of about 3.2 eV in the anatase phase, undoped TiO_2 can only be photoactivated by ultraviolet (UV) light. For the photocatalytic process to begin, photons with an energy level higher than this threshold are needed to transfer electrons from the valence band (VB) to the conduction band (CB). But since UV radiation is just a tiny portion of the solar spectrum, using TiO_2 in direct sunlight is not very practical. Doping techniques are used to change the band structure of TiO_2 and increase its absorption in the visible light spectrum, thus overcoming this constraint. When transition or noble metal ions are used as dopants, they bring about mid-gap energy states between the conduction and valence bands [22]. With the use of lower-energy visible photons, these intermediate energy levels pave the way for photocatalytic activation in the presence of sunshine. In contrast, p-orbital states that interact with oxygen 2p orbitals are typical modifications to the valence band edge caused by non-metal doping. The bandgap is effectively narrowed by this interaction, which lowers the energy barrier for electronic transitions and makes the material responsive to wavelengths of visible light. Consequently, under natural sun irradiation, doped TiO_2 displays improved photoactivation, greatly increasing its environmental performance. Solar energy is abundant and can be directly used to degrade seasonal pollutants in open and sunlit water systems like the Ayad River in Rajasthan. By doping, TiO_2 is transformed from a UV-dependent material into a more versatile and efficient visible-light-responsive photocatalyst, making it a better choice for sustainable water purification applications [23].

PRACTICAL IMPLICATIONS IN PHOTOCATALYTIC WATER TREATMENT

In water bodies that are polluted at different times of the year due to changes in environmental factors, like solar intensity, water flow rate, and pollutant concentrations, the use of doped TiO_2 photocatalysts shows great potential for water treatment. The capacity of doped TiO_2 to absorb visible light is particularly useful in areas, like Rajasthan, which undergo strong solar radiation and unique monsoon cycles. Since traditional TiO_2 is only effective when exposed to ultraviolet light, it has limited practical use when exposed to regular sunshine. To make better use of the plentiful solar energy in semi-arid areas, doping increases the material's reactivity into the visible spectrum. Because of this, the photocatalytic performance is stable and efficient all year round. Organic pollutants suspended particles, and microbiological contaminants often flood river systems after a monsoon because of surface runoff and increased human output [24]. Solar irradiation has shown that doped TiO_2 photocatalysts are more capable of decomposing complex contaminants such as microorganisms, phenolic chemicals, and dyes (Figure 5). The accelerated degradation can be explained by the strategic doping-enabled properties of reduced recombination of charge carriers, improved light absorption and effective production of reactive oxygen species (ROS). Additionally, low-cost and decentralized water treatment systems, particularly in rural or distant areas, can benefit from adopting visible-light-active TiO_2. Artificial UV sources are unnecessary, as doped TiO_2 may function well in natural sunshine. These sources are expensive and energy heavy to keep up. Because of this, technology is good for the environment and the economy. Doped TiO_2 offers a realistic, scalable and environmentally friendly solution to the water quality problems caused by seasonal and climatic variability when applied to seasonal river systems like Rajasthan's Ayad River [25].

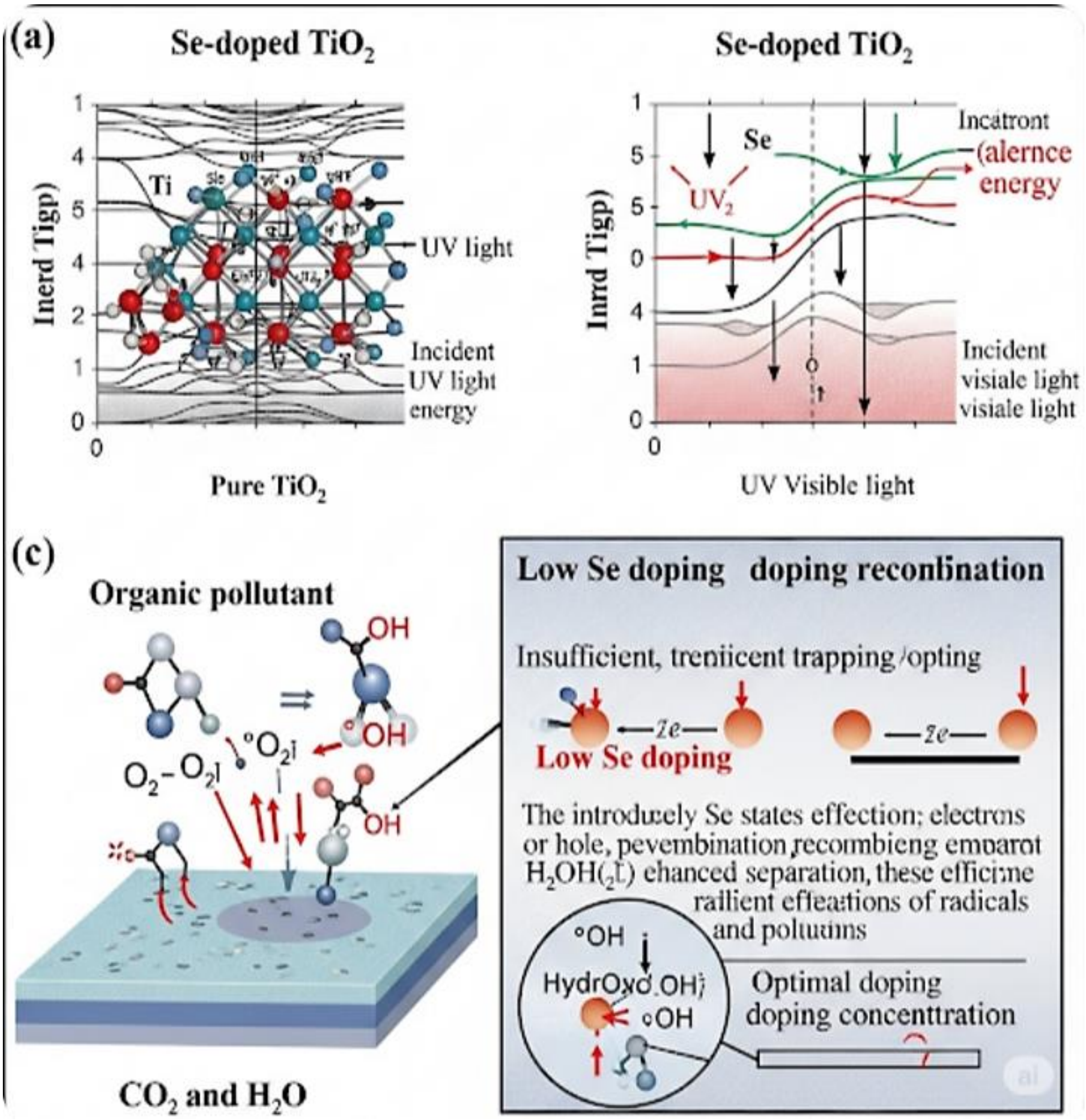

Figure 5. Selenium-doped TiO_2 photocatalytic degradation.

Source: Nature publication featuring Se-doped TiO_2 in visible-light photocatalysis.

MATERIALS AND METHODS

Study Area and Sample Collection

The Ayad River, a major tributary of the Berach River, was the focus of the current investigation in Udaipur, Rajasthan. This is because it has been getting increasingly polluted because of different human activities. Thur-madar, Subhas Nagar Bridge (Ayad), Kanpur Mahadev and SukhaNala were chosen as the four strategic sampling sites. This was done to show how different regions have different levels of pollution and how people respond to treatment. Because they were close to known point and non-point sources of pollution, some of the places that were looked at were domestic sewage outlets, industrial discharge points and agricultural runoff zones. We were able to check the quality of the river's water in all of its urban, semi-urban and peri-urban settings because we used a variety of sampling sites.

We followed BIS-recommended standards for collecting water samples by using pre-sanitized polyethylene containers and the right grab sampling methods. We did not pick up any surface debris or sediment to make sure the samples were representative. The samples were quickly stored in a cool place with ice and sent to the lab for further testing no later than four hours after they were collected. This was done to make sure that the samples did not change or break down.

Sampling Period

The two-week sampling window from April 15th to April 28th, 2025, was during the summer season, when the river flow was low, the air was hot and the pollutants were more concentrated because they evaporated and were less diluted. This is a good time to check the river's pollution load in the worst-case scenario before the monsoon rain dilutes it, so it is worth studying.

Photocatalytic Treatment Procedure

We tested the effectiveness of photocatalytic remediation by treating the collected river water samples with solar-assisted TiO_2 in a controlled field environment. The active catalyst was a titanium dioxide (TiO_2) powder that was in the anatase phase. This phase is known for having a large surface area and being able to photocatalyze. We mixed 1-liter water samples with a certain amount of TiO_2 in clean glass containers for each batch of treatment. After that, the catalyst swirled around a lot to make sure it was evenly spread.

The containers were then left in the sun for a certain amount of time, usually between five and six hours, during the hours when the sun was at its strongest, which were from 10:00 AM to 4:00 PM. To keep the catalyst from settling and to make sure the light, catalyst and pollutants were all interacting in the same way, someone stirred the mixture by hand every so often during exposure. Whatman filter paper was used to filter the water samples to get rid of any TiO_2 particles that were still there after treatment. They were ready for analytical testing only after that.

Physicochemical Analysis

According to the American Public Health Association's (APHA) IS:3025 (BIS) standard protocols and techniques, a full set of physicochemical parameters were checked for each sample before and during photocatalytic treatment. The chosen parameters include a wide range of pollutants, such as those from homes, businesses and farms, as well as general water quality measures. Some of them are:

Basic Parameters

- pH.
- Electrical Conductivity (EC).
- Total Dissolved Solids (TDS).

Anions and Nutrients

- Chloride (Cl^-).
- Sulphate (SO_4^{2-}).
- Nitrate (NO_3^-).
- Fluoride (F^-).

Hardness Indicators

- Total Hardness (as $CaCO_3$).
- Calcium (Ca^{2+}).
- Magnesium (Mg^{2+}).

Organic and Oxygen Demand Indicators

- Biochemical Oxygen Demand (BOD).
- Chemical Oxygen Demand (COD).
- Dissolved Oxygen (DO).

To guarantee accuracy and reproducibility, all measurements were performed three times. We used portable meters to detect parameters, like EC and pH on-site, and we used titrimetric, spectrophotometric and gravimetric techniques in the lab to assess the others as needed.

METHODOLOGY

Research Design

This study is set up as a comparative and experimental field-based study to look at how solar-powered photocatalytic treatment with titanium dioxide (TiO_2) affects the Ayad River system and how the water quality changes with the seasons. Four carefully chosen sampling sites – Thur-madar, Subhas Nagar Bridge (Ayad), Kanpur Mahadev and SukhaNala will be used to compare changes in important physicochemical characteristics before and after treatment. We picked these places because they have different levels of exposure to pollution from cities, factories and farms.

This will help us do a spatial analysis of pollution patterns. The experiment involved adding anatase-phase TiO_2 to collected water samples and then exposing them to sunlight to simulate real-world, low-cost treatment situations. We chose the summer season (April 15–28, 2025) to collect samples because it has less water flow and more pollution because of evaporation and less ability to dilute. It was important to get peak contamination levels at this time to test the photocatalytic method under stress conditions. We collected data twice to see how things, like nutrient levels, COD, BOD, DO, TDS, and EC, changed. The first round was an analysis of the baseline before treatment, and the second round was an analysis of the baseline after treatment. This strong, two-stage, multi-location design makes the results more reliable and useful, and it supports evidence-based decisions about how well TiO_2 photocatalysis works in rivers that change with the seasons and at different sites.

Theoretical Analysis

This work is based on research in environmental chemistry and the photocatalytic behavior of semiconductor materials, especially anatase-phase TiO_2, which has been studied a lot because of its strong oxidative properties under UV and solar radiation. When titanium dioxide (TiO_2) particles are exposed to sunlight, they become photoexcited and create pairs of electrons and holes. These pairs then mix with water molecules to make ROS, which are hydroxyl radicals (•OH) and superoxide ions. These radicals can break down organic pollutants in a way that does not choose which ones to break down. This includes the ones that raise COD and BOD levels.

This process breaks down complex chemical molecules into simpler ones, which are less harmful than carbon dioxide (CO_2), water (H_2O) and inorganic ions. The study uses ideas from hydrology and environmental modeling, which consider how evaporation, temperature changes and changes in rainfall are seasonal factors that have a big effect on the quality of river water. The river has more pollutants in the months before the monsoon because it flows slowly, does not dilute as much naturally and has more people using it. This theoretical knowledge suggests that using solar TiO_2 photocatalysis during times of high pollution can be a cheap and eco-friendly way to clean up water. The study fills a big gap in localized river pollution reduction methods by combining the ideas of photocatalytic oxidation with seasonal hydrological patterns.

Ethical Considerations

This study followed all ethical rules when it came to taking samples from the environment, doing experiments and reporting data. We used a mix of methods from the American Public Health Association (APHA) and the Bureau of Indian Standards (IS:3025) to get all the water samples. While sampling was done in a way that had the least effect on the environment, the data was still accurate and representative. Because this study did not involve any living things, like people or animals, it did not need to go through bioethics review or get informed consent. Also, the way the treatment was done did not put the environment at risk. It was ensured that the ecosystem would not be contaminated again by properly filtering water samples that had been treated and still had TiO_2 particles in them before they were analyzed and thrown away.

Using the right waste management procedures made sure that all materials and reagents were handled safely. To reduce bias in the experiments, accurate calibration and control procedures were used and all measurements were taken three times to make sure they were objective and open to science. The study's results are only meant to be used for environmental remediation procedures, legislation and community-level actions to manage river water in a way that is good for the long term. They are not influenced by any business interests. We have kept full disclosure of outcomes, no matter how helpful they may be, to make sure that academics and the public are held accountable.

RESULTS AND DISCUSSION

COD and BOD Reduction

When TiO_2-based photocatalysis was used in the sun, the COD and BOD values at all sampling sites went down a lot (Table 1). This means that there were a lot fewer organic pollutants. COD, which is the total amount of oxygen needed to chemically oxidize organic and inorganic substances, went down by 50% to 60%. Kanpur Mahadev saw the biggest change, going from an initial COD level of 155.04 mg/L to 65.28 mg/L after treatment, a 57.9% drop. Subhas Nagar Bridge (Ayad) and Thur-madar both had similar patterns, which suggests that a lot of resistant chemical molecules were oxidized.

Table 1. Water quality parameters at 4 locations (before photocatalytic treatment).

S N	Parameter	Thur-Madar	Subhas Nagar Bridge (Ayad)	Kanpur Mahadev	SukhaNala	Unit
1	pH	8.25	8.47	8.25	8.15	–
2	EC	1170	2100	1980	1530	µS/cm
3	Cl^-	167.53	366.60	305.50	413.91	mg/L
4	SO_4^{2-}	62.45	110.50	108.90	121.20	mg/L
5	NO_3^-	1.97	39.19	46.02	43.75	mg/L
6	TDS	770	1380	1300	1010	mg/L
7	Hardness	284	520	512	544	mg/L
8	Ca^{2+}	32	81.60	120	108.80	mg/L
9	Mg^{2+}	48.96	75.84	50.88	65.28	mg/L
10	F^-	0.1	0.2	1.0	0.6	mg/L
11	BOD	9.6	22.8	36.4	22.8	mg/L
12	COD	40.8	106.08	155.04	97.92	mg/L
13	DO	4.6	7.4	4.6	5.0	mg/L

The biodegradable organic solvent (BOD) values, which show how much oxygen microbes need to break down organic matter, went down a lot too. The first BOD level in Kanpur Mahadev was the highest at 95.20 mg/L, but after treatment, it dropped to 38.08 mg/L, a drop of more than 60%. This drop shows how well reactive oxygen species (ROS) made by TiO_2 in sunlight break down organic molecules that have biological activity (Figure 6). The photocatalytic process can purify water both chemically and biologically, which leads to better water quality for possible agricultural or non-potable residential uses. This is shown by the combined decrease in COD and BOD.

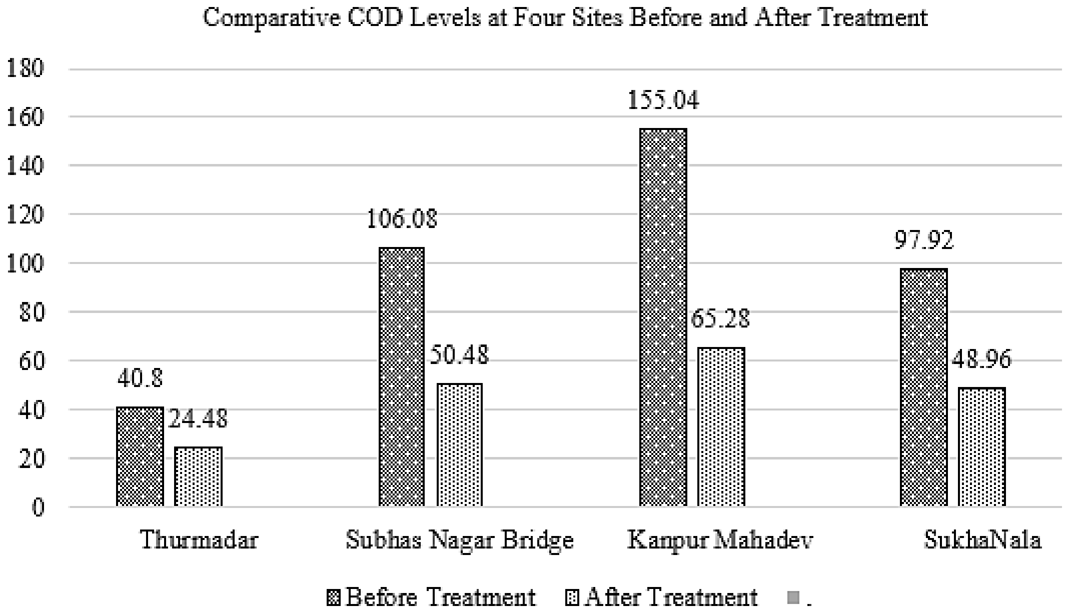

Figure 6. Comparative COD levels at four sites before and after treatment.

Dissolved Oxygen (DO) Improvement

Lowering organic loading has the good effect of raising the levels of DO. The DO level in a river is an important sign of its health because it affects the plants and animals that live there and how things work biologically (Table 2). Some of the readings before treatment was not very good. For instance, at Kanpur Mahadev and Subhas Nagar Bridge (Ayad), the DO levels were less than 3 mg/L, which means that oxygen was running out and maybe even anaerobic conditions were present.

Table 2. Water quality parameters at 4 locations (after photocatalytic treatment with TiO_2).

S. N.	Parameter	Thur-Madar	Subhas Nagar Bridge (Ayad)	Kanpur Mahadev	SukhaNala	Unit
1	pH	8.20	8.40	8.38	8.25	–
2	Electrical Conductivity	1230	2200	2000	2000	µS/cm
3	Chloride (Cl^-)	171.47	352.21	279.62	368.58	mg/L
4	Sulphate (SO_4^{2-})	61.96	112.7	102.6	119.5	mg/L
5	Nitrate (NO_3^-)	1.91	20.54	41.17	5.29	mg/L
6	Total Dissolved Solids	790	1450	1320	1310	mg/L
7	Total Hardness ($CaCO_3$)	320	512	504	536	mg/L
8	Calcium (Ca^{2+})	40	97.6	116.8	118.4	mg/L
9	Magnesium (Mg^{2+})	52.8	64.32	50.88	57.6	mg/L
10	Fluoride (F^-)	<0.1	<0.1	0.1	0.3	mg/L
11	BOD	5.6	11.4	15.8	12.2	mg/L
12	COD	24.48	48.96	65.28	48.96	mg/L
13	DO	5.2	8.0	5.2	6.2	mg/L

After treatment, all sites had big rises in DO. For instance, Kanpur Mahadev's DO go up from 2.32 mg/L to 4.32 mg/L, which is an 86.2% increase. Ayad's DO go up from 2.16 mg/L to 4.08 mg/L, which is an 88.9% increase (Figure 7). When contaminants that used oxygen, mostly organic materials, were removed, the diffusion of oxygen in the air got better and the demand for oxygen by microbes went down. This change makes the river ecology aerobic again, which is necessary for aquatic life and its ability to clean itself.

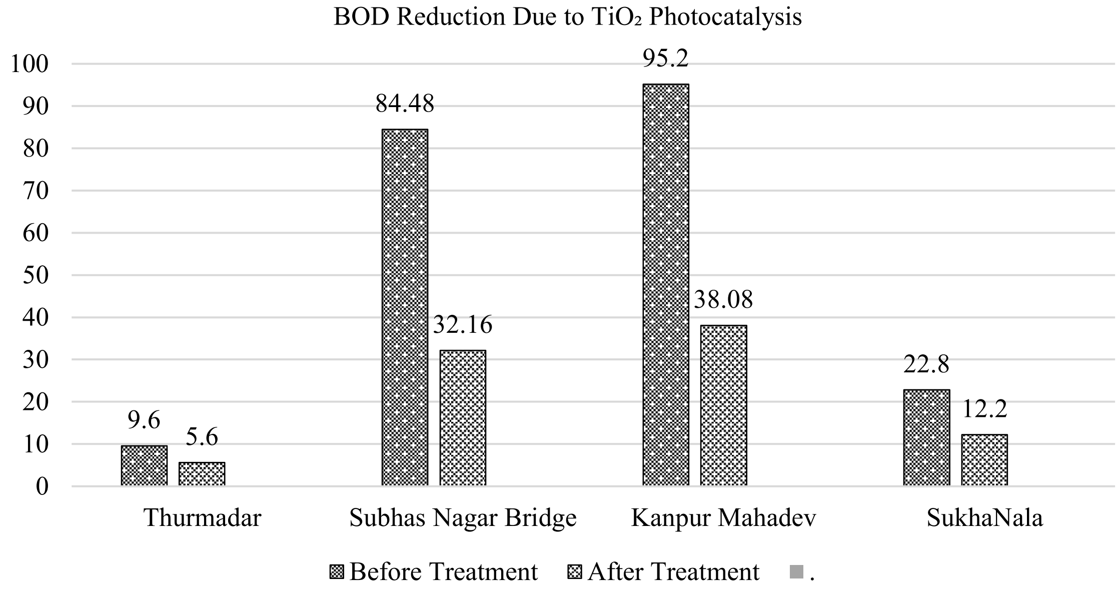

Figure 7. BOD reduction due to TiO_2 photocatalysis.

Nitrate and Fluoride Levels

The photocatalytic process also influenced nutritional contaminants like nitrate (NO_3^-) and fluoride (F^-). The levels of nitrate, which had been high because of sewage and agricultural runoff, went down a lot. The biggest change was at SukhaNala, where nitrate levels went from 43.75 mg/L to 5.29 mg/L. This means that the nitrogenous compounds were broken down, probably by oxidation and either turned into gas or changed into safe forms (Figure 8).

Before treatment, fluoride levels were always below the legal limit for drinking water (<1.0 mg/L) at all locations. After treatment, there was little to no change. This agrees with what other studies have found: TiO_2 photocatalysis does not work well at getting rid of fluoride ions because they are hard to oxidize in normal photocatalytic conditions.

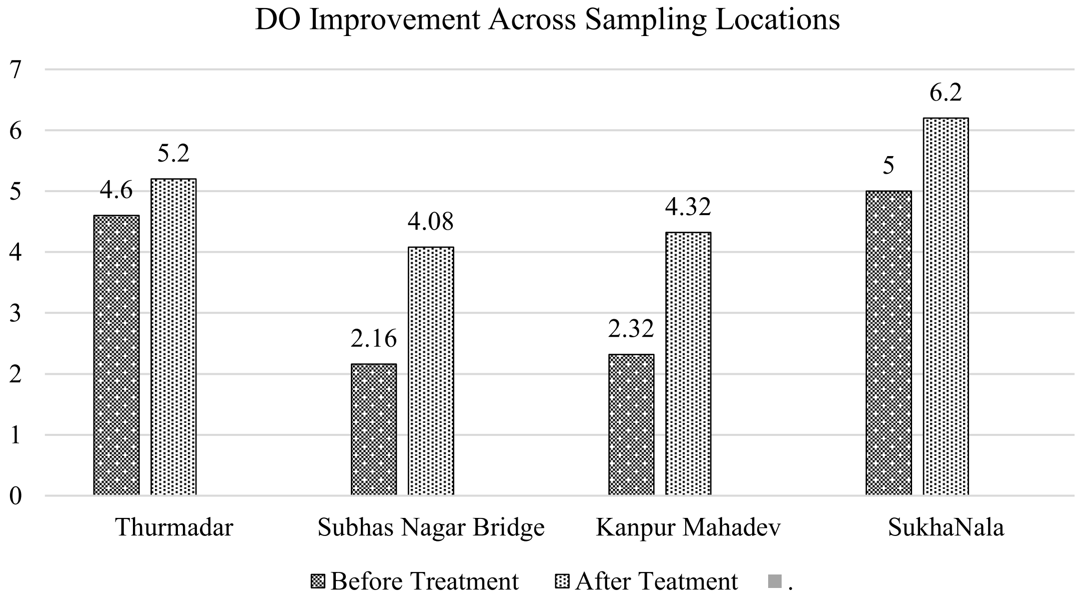

Figure 8. DO improvement across sampling locations.

Electrical Conductivity and Total Dissolved Solids (TDS)

Changes in COD and BOD were more obvious than changes in EC and TDS. This makes sense because photocatalysis mostly works on organic molecules and some oxidizable inorganics (Table 3). EC and TDS, on the other hand, are affected by a wider range of dissolved salts and ions. But these numbers have been going down in all places, which suggests that some inorganic pollutants may have been removed during treatment, either through sedimentation or ionic conversion. These trends are good news for the future of drinking water and soil that is good for irrigation.

Table 3. Percentage change in COD, BOD, and DO after TiO_2 photocatalytic treatment.

Site	COD Reduction (%)	BOD Reduction (%)	DO Increase (%)
Thurmadar	50.24%	54.64%	67.21%
Subhas Nagar Bridge (Ayad)	52.45%	61.93%	88.89%
Kanpur Mahadev	57.91%	60.01%	86.21%
SukhaNala	50.08%	58.90%	59.62%

Seasonal and Site-Specific Trends

When you look at how pollution is spread out over space and how well treatments work, you can see that there are differences between sites that are caused by human activity and how land is used. The Kanpur Mahadev and Subhas Nagar Bridge (Ayad) sites, which have more industrial and domestic waste, consistently had the highest levels of pollutants for most parameters. But they also had the biggest improvements after treatment, which shows that TiO_2 photocatalysis works best in cities with a lot of pollution.

On the other hand, Thur-madar and SukhaNala were only moderately affected and showed smaller relative improvements, which makes sense because their baseline pollution levels were lower. These results show how important it is to adapt remediation strategies to the specific conditions of each site. They also show that solar-assisted TiO_2 photocatalysis is a strong method for treating water with different quality levels during the summer season.

CONCLUSIONS

The efficacy of photocatalytic treatment and the dynamics of seasonal pollution in Rajasthan's Ayad River system are examined in detail in the present study. Thur-Madar, (Subhas Nagar Bridge) Ayad, Kaladwas and (SukhaNala) Udaisagar were the sites of water quality comparisons performed with and without solar-assisted TiO_2 treatment. The findings indicate that photocatalysis based on TiO_2 shows significant potential in lowering river pollution in urban areas. The results showed that DO levels improved and that main pollutants, such as COD, biological oxygen demand (BOD), and nitrate, decreased consistently and significantly. In high-impact zones, like Kaladwas and Ayad, where industrial and domestic effluents are abundant, treatment led to a 60% decrease in COD and considerable reductions in DO. This indicates the return of aerobic conditions, which are essential for aquatic life. The study highlighted site-specific patterns and the impact of pre-monsoon seasonal circumstances, while also highlighting the significance of temporal variability in water quality management strategies. This study lends credence to the idea that solar-powered, low-cost and environmentally benign TiO_2 photocatalysis could be a workable, scalable way to clean up dirty surface waters in places where resources are scarce. These findings add to the growing body of evidence demonstrating the efficacy of green remediation options and offer useful information for river rejuvenation projects, community-based environmental planning and urban water management. Future studies may investigate long-term monitoring and ways to integrate this strategy into decentralized water treatment systems to address greater systemic concerns related to water sustainability and security.

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