

HARNESSING THE POWER OF SURFACE-MODIFIED NANOPARTICLES FOR SUSTAINABLE WASTEWATER REMEDIATION

Abstract

Wastewaters refer to the combination of solid and liquid substances that are released into water bodies, encompassing the byproducts generated from both community activities and industrial processes. The treatment of wastewater has become a significant concern in relation to its impact on the environment and the organisms that inhabit it. Typically, the process of wastewater treatment involves the integration of several physical, chemical, and biological procedures and activities aimed at eliminating insoluble particulates and soluble pollutants from effluent streams. In order to enhance the efficacy of the materials and procedures employed in various waste water treatment systems, it is advisable to consider certain measures. These measures may include the utilization of non-toxic chemicals for the eradication of hazardous microorganisms, as well as the optimization of disinfectant concentrations, among others. This chapter focuses on the utilization of surface modified nanoparticles for the purpose of wastewater cleanup. Surface-modified nanoparticles refer to nanoparticles or nanoscale materials that have undergone modifications to their surface properties. These alterations serve various purposes, including enhancing stability, functionalizing the nanoparticles, improving biocompatibility, or augmenting barrier capabilities. Different types of nanoparticles can be employed in the treatment of wastewater, including iron oxide nanoparticles, carbon nanotubes, titanium dioxide nanoparticles, zinc oxide nanoparticles, aluminium oxide nanoparticles, and polymeric nanoparticles.

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The selection of these nanoparticles is based on their unique characteristics and significant surface area. In this context, the focus is on the investigation of the role of TiO₂ nanoparticles due to its positive properties such as photocatalytic activity, high surface area, and chemical stability, among others, which have been extensively covered in the preceding chapter. The objective is to assess their effectiveness in alleviating the issue of wastewater pollution. This chapter provides a concise overview of the overall framework of wastewater treatment, while also examining the merits and drawbacks of various methods applicable to diverse contexts.

Keywords: Surface modified nanoparticles, Waste water treatment, Biocompatibility, TiO₂

I. INTRODUCTION

- 1. Overview- Wastewater:** In the context of a global population of 8 billion individuals, characterized by a significant growth rate and corresponding increase in societal needs, the provision of clean water has emerged as a pressing requirement. The demand for enhanced water treatment technology is steadily rising.

Wastewater, a by-product generated by both human activities and industrial processes, plays a crucial role in maintaining environmental health and promoting sustainability. Wastewater can be categorized into two main types, namely industrial wastewater and household wastewater, based on the presence of contaminants¹.

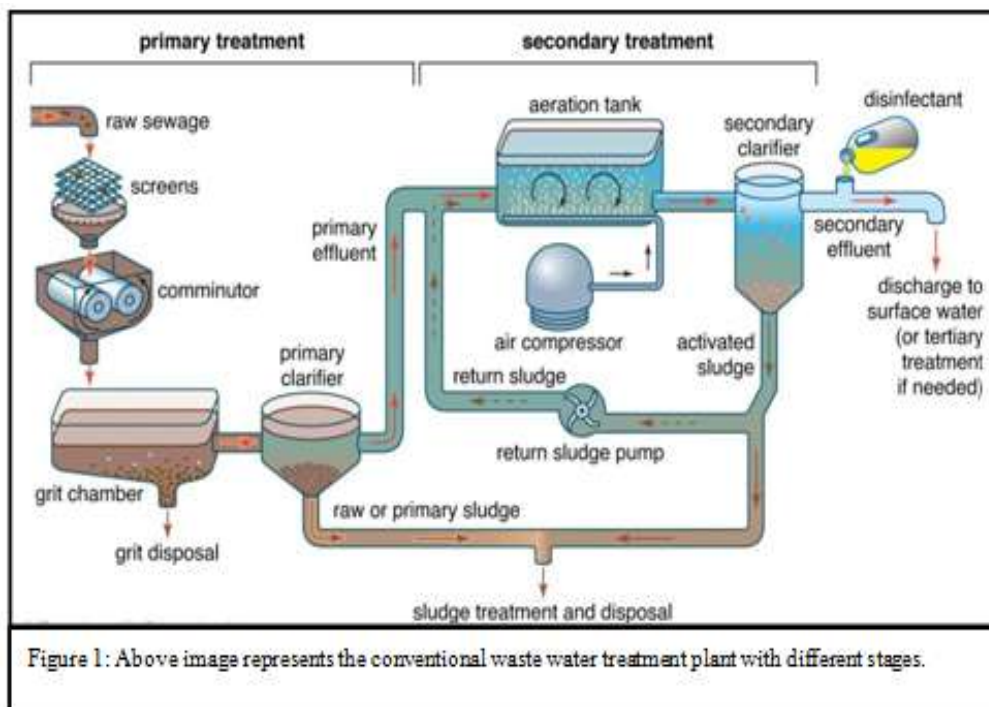
- 2. Harmful Effects of Wastewater:** The involuntary production of wastewater is released into water bodies, either partially or entirely, resulting in significant water-related issues such as the degradation of marine life and disruption of the aquatic ecosystem. This poses risks to both aquatic flora and fauna, as well as to human beings, who may be exposed to various waterborne diseases such as cholera, typhoid, and diarrhoea, among others. The effluent has the potential to contain several hazardous substances, such as poisonous compounds, oil and grease, acids and bases, as well as heavy metals like mercury, cadmium, lead, and arsenic. These substances can have both chronic and acute deleterious impacts on various species. Therefore, it is imperative to appropriately treat the wastewater prior to its release into aquatic ecosystems².

- 3. Importance of Wastewater Treatment:** The principal objective of wastewater treatment is to effectively remove all impurities that render it unsuitable for reuse and mitigate any potential hazards associated with its presence. Eutrophication occurs when water bodies become excessively contaminated with toxins, leading to a reduction in the concentration of dissolved oxygen. This decrease in oxygen levels poses a significant threat to the survival of aquatic organisms³. The ongoing natural process of water purification is significantly outpaced by the rate of contamination due to the substantial volume of pollution generated. Thus, treating wastewater is an inevitable step in getting clean water.

4. Conventional Wastewater Treatment Process There are eight stages to treat wastewater

- **Bar Screening:** The initial stage of wastewater treatment is bar screening, which is the physical process of removing big impurities. This step is necessary to prevent damage to the pumps and blockage of the pipelines, which can hinder the flow of water⁴. In order to eliminate the significant pollutants, present in the influent, a bar screen is employed.
- **Screening:** Screening is a crucial phase in the wastewater treatment process. While the initial stage effectively eliminates the majority of big contaminants, the subsequent screening process is necessary to remove small grit that may have entered the influent⁵. This step is essential to prevent any potential harm to the treatment system. A grit chamber is utilized due to the inability to screen out the fine particles of grit. The collected grit is physically extracted from the lower portion of the chamber and afterwards disposed off.

- **Primary Clarifier:** The removal of solids, specifically organic matter or sludge, is achieved by introducing the influent into sizable primary clarifiers. The process involves the sedimentation of heavy metals or sludge, causing them to settle at the bottom, while the cleaner influent is discharged. The effectiveness of the clarifying process is contingent upon the movement of water⁶. Insufficient time for heavy contaminants to settle may occur if the flow rate is excessively rapid, while conversely, an excessively sluggish flow rate may adversely affect the upstream process.
- **Aeration:** The major purpose of the aeration tank is to facilitate the decomposition of organic materials through the activity of bacteria⁷. Oxygen or air is introduced into the tank in order to facilitate the proliferation of bacteria.
- **Secondary Clarifier:** The primary clarifier exhibits a high degree of similarity to the aforementioned concept. In this phase, little solid or particulate matter precipitates to the lowermost region of the container referred to as activated sludge, predominantly composed of active bacteria, while the purified influent is discharged⁸. Following this procedure, the organic matter undergoes a significant reduction.
- **Chlorination:** The utilization of this disinfection method proves to be very efficient and economically viable in preventing the discharge of bacterial concentrations that exceed regulatory limits in the treated wastewater. Prior to the introduction of chlorine into the environment, it is imperative to conduct an assessment of the levels of free-chlorine in order to ascertain their compliance with acceptable thresholds⁹.
- **Water Analysis and Testing:** The ultimate phase of testing is conducted in order to verify the suitability of the effluent discharged by industrial facilities for subsequent reuse. In order to ascertain the safety of the water, various tests are performed to determine the appropriate pH level, presence of ammonia, nitrates, and residual chlorine¹⁰.
- **Effluent Disposal:** Effluent disposal is the reintroduction of clean water into the environment following the completion of testing, provided that all requisite criteria have been met.



5. Chemical Risks Involved / Disadvantages: While wastewater treatment plays a crucial role in purifying contaminated water, it is important to acknowledge that conventional methods possess some limitations and potential hazards.

For example, the inherent volatility of chlorine, which is employed for disinfection purposes in treated wastewater, can result in the formation of disinfection by-products that may have adverse effects on organisms¹¹. Certain viruses, such as rotavirus and adenoviruses, have been found to exhibit resistance to chlorine treatment.

- After the completion of wastewater treatment processes, the generation of sludge is a common occurrence. This sludge is characterized by its high concentration of pollutants and particles, which have been effectively eliminated from the treated wastewater. The appropriate disposal of this sludge is of utmost importance due to its potential to cause environmental harm¹².
- After the process of wastewater treatment, it is common for the generation of sludge as a secondary product. The substance in question comprises a high concentration of contaminants and solid particles that have been extracted throughout the treatment process. The appropriate management of this sludge is of utmost significance due to its potential to inflict environmental harm.
- During the process of wastewater treatment, the treatment plants themselves have the potential to generate pollutants, hence giving rise to environmental problems. The entity in question has the potential to release gases, including odorous emissions.
- The efficacy of the treatment procedure is contingent upon the specific composition of pollutants within the wastewater as well as the technological approach employed¹³.
- In order to address these limitations, the implementation of surface modified nanoparticles has been proposed as a means to enhance overall efficacy.

II. SURFACE MODIFIED NANOPARTICLES

Surface modified nanoparticles are nanoparticles or materials at the nanoscale that have undergone alterations to their surface properties in order to fulfil several objectives, such as improving their stability, functionalizing them, enhancing their biocompatibility, or enhancing their barrier capabilities¹⁴.

1. Surface Modification Techniques: The different techniques used for surface modification are

- **Physical Modification:** This approach encompasses physical mechanisms aimed at modifying the surface characteristics of nanoparticles. Several commonly used physical methods for surface alteration include
 - **Physical Vapour Deposition:** The present methodology involves the deposition of a thin coating onto the surface. The process entails the sublimation of a solid substance, followed by its subsequent deposition onto the nanoparticle's surface. Methods such as sputtering, evaporation, and pulsed laser deposition are encompassed within this classification¹⁵.
 - **Chemical Vapour Deposition:** During this particular procedure, the occurrence of chemical reactions in the gaseous phase results in the deposition of a substance onto the surface of the nanomaterial. The solid substance that is obtained exhibits various forms, such as a thin film, powder, or single crystal¹⁶.
 - **Laser Ablation:** The aforementioned procedure entails the utilization of a laser with significant power output. The target material undergoes vaporization, resulting in the condensation of its particles onto the surface of the nanomaterial. This process leads to the formation of nanoparticles in the form of thin films¹⁷.
 - **Sputtering:** The technique involves the bombardment of a solid target with high-energy ions, resulting in the deposition of these ions onto the surface of the nanomaterial¹⁸.
- **Chemical Modification:** The process entails the utilization of chemical processes to modify the characteristics of nanomaterials. The phenomenon occurs through the alteration of the composition and configuration of the nanoparticle's surface. There exist a limited number of chemical techniques for the purpose of surface modification
 - **Esterification Reaction Method:** This technique is employed to modify the characteristics of a hydrophilic and oleophobic surface, rendering it lipophilic and hydrophobic¹⁹.
 - **Surfactant Modification Method:** Surfactants are employed to modify the structural characteristics of hydrophilic groups, hence enhancing the nanoparticles' attraction towards organic molecules²⁰.

- **Sol-Gel Process:** In this approach, the precursor molecule undergoes a process of hydrolysis and condensation, resulting in the formation of a robust network that can effectively encapsulate nanoparticles. This phenomenon leads to an increased surface area and a more stable surface²¹.
- **Biological Modification:** It involves the use of biological molecules, such as proteins, peptides, DNA, and other biomolecules, for surface modification. Some common biological methods are
 - **Bio-Conjugation:** In this approach, the process involves the immobilization of biomolecules onto the surface of nanomaterials. Nanoparticles can be chemically coupled with peptides, enzymes, and other biomolecules via targeted chemical processes²².
 - **Protein Adsorption:** The process of protein adsorption onto the surface of nanoparticles has the potential to modify the surface properties of the nanoparticles and influence their interactions²³.
 - **Enzymes-Mediated Modification:** The utilization of enzymes as catalysts for targeted reactions on the surface of nanoparticles has the potential to modify their properties through the creation of distinct functional groups²⁴.
 - **Bio-Fabrication:** The methodology described herein entails the direct integration of viable cells into nanomaterial architectures, resulting in the development of bio-hybrid systems that exhibit distinctive characteristics²⁵.
- 2. **Advantages of Surface Modification:** The alteration of nanoparticle surfaces by modification techniques results in the changing of nanomaterial properties, hence achieving the required attributes for improved outcomes. It presents numerous benefits across diverse disciplines and contexts
 - **Biocompatibility:** Surface modification techniques can be employed to mitigate the toxicity of nanomaterials and enhance their interactions with biological molecules and cells²⁶. Surface modification is frequently employed in the field of orthopaedic biomaterials to assure the continued functionality of implanted devices, hence preventing aseptic loosening or prosthetic joint infection.
 - **Selective Adsorption:** Engineered surfaces can be strategically constructed to selectively adsorb particular molecules or gases, rendering them highly advantageous for many purposes such as water purification and gas separation²⁷. One prevalent utilization involves customizing these nanoparticles to augment the discriminatory adsorption of carbon dioxide gas.
 - **Targeted Delivery:** Functionalized nanomaterials possess the ability to engage in selective interactions with specific cells or tissues, so facilitating the delivery of drugs to specified locations and mitigating the occurrence of adverse effects. The utilization of lipid nanoparticles containing stavudine, along with surface modification, presents

a promising approach for the development of a drug delivery system targeted towards anti-HIV chemotherapy²⁸.

- **Reduced Aggregation:** The implementation of surface modification techniques has the potential to mitigate the phenomenon of nanoparticle aggregation or agglomeration, hence resulting in enhanced dispersion characteristics within liquid media²⁹.

III. APPLICATIONS OF SURFACE MODIFIED NANOMATERIALS

Several techniques involve the application of surface-modified nanoparticles in the field of wastewater treatment

1. Adsorption of Heavy Metal and Other Impurities

- Magnetic nanocomposite materials, comprising many distinct nanomaterials, have been employed in the treatment of wastewater due to their ability to boost the adsorption capabilities of metal nanoparticles and mitigate agglomeration. For example, the inclusion of TiO₂ in MNPs is employed to enhance the photocatalytic characteristics of the latter, so facilitating their application in the purification of wastewater by eliminating pollutants.
- Synthesized ligands possessing exceptional chelating capabilities have the capability to establish strong interactions with MNPs, hence enhancing their adsorption capacities for the removal of both inorganic and organic pollutants from wastewater³⁰.
- Functionalized nano-adsorbents provide the capability to selectively target and capture trace pollutants, even when present in low concentrations. In the case of magnetic functionalized amidoxime nanoparticles (NPs), the inclusion of a nitrogen atom has been found to enhance the adsorption capacity of the functionalized NPs for pollutants present in environmental samples.
- Thiol-functionalized magnetic nanoparticles (MNPs) have been found to be effective in the removal of heavy metals from aqueous solutions. The efficacy of dimercaptosuccinic acid (DMSA) surface-functionalized magnetic nanoparticles in the removal of arsenic (As), mercury (Hg), lead (Pb), cadmium (Cd), silver (Ag), and titanium (Ti) was observed to be quite significant³¹.

2. **Improve Membrane Fouling:** The utilization of surface modification techniques proves to be advantageous in the context of membrane antifouling. Membrane fouling is a phenomenon that arises as a result of the accumulation of sludge flocs or particles on the surface of the membrane. Additionally, this phenomenon may arise as a result of the adsorption of solutes or colloids within membranes, as well as the creation of a cake layer on the surface of the membrane. The presence of membrane fouling leads to a decrease in both water permeability and separation efficiency, resulting in a shortened lifespan and reduced productivity of the membrane. During the separation process of oily wastewater, the membranes are obstructed by oil droplets and other organic pollutants³². In order to enhance the antifouling properties and eliminate the presence of contaminants, the hydrophobic membranes undergo a modification process wherein Al₃O₄, SiO₂, TiO₂, and Fe₃O₄ inorganic nanoparticles are incorporated into the membrane, resulting in the transformation of the membranes into highly hydrophilic structures.

- 3. Photo-Degradation:** The textile industry is responsible for the production of a significant amount of wastewater resulting from the process of textile dyeing. This wastewater is commonly released either into sewage treatment plants or directly into natural water sources. The efficacy of the standard treatment method in mitigating dye-induced pollution is limited, as it mostly involves the transfer of the pollutants into sludge, necessitating subsequent treatment measures. Therefore, the utilization of photo-degradation, a method that involves the interaction between UV light and catalysts such as TiO₂, has demonstrated efficacy in the reduction of organic contaminants in water³³.

The forthcoming section will comprehensively examine these applications by conducting an analysis of the characteristics of TiO₂.

IV. TITANIUM DIOXIDE NANOPARTICLES

Various types of nanoparticles can be utilized in wastewater treatment processes, such as iron oxide nanoparticles, carbon nanotubes, titanium dioxide nanoparticles, zinc oxide nanoparticles, aluminium oxide nanoparticles, and polymeric nanoparticles. These nanoparticles are chosen for their distinctive features and large surface area. In this section, we will specifically examine the role of TiO₂ nanoparticles in mitigating wastewater pollution³⁴.

- 1. Characteristics of TiO₂ Nanoparticles:** Titanium dioxide (TiO₂) nanoparticles are extensively employed in the field of wastewater treatment owing to their numerous advantageous characteristics that render them highly effective in the removal of various impurities³⁵.
- **Photocatalytic Activity:** When subjected to ultraviolet (UV) radiation, it exhibits robust photocatalytic properties. The process has the capability to produce reactive oxygen species (ROS) of significant reactivity, facilitating the degradation and oxidation of organic pollutants, resulting in the formation of by-products such as carbon dioxide (CO₂) and water (H₂O)³⁶.
 - **High Surface Area:** Titanium dioxide nanoparticles (TiO₂ NPs) exhibit a significant ratio of surface area to volume. This material offers a multitude of active sites that facilitate adsorption and catalytic processes³⁷.
 - **Chemical Stability:** TiO₂ has exceptional chemical stability and corrosion resistance, hence guaranteeing its long-lasting performance in various wastewater treatment applications³⁸.
 - **Biocompatibility:** The biocompatibility and safety of these nanoparticles are widely acknowledged in the context of water treatment applications. Harmful chemicals or by-products are not introduced into the treated water³⁹.
 - **Wide Applicability:** TiO₂ has demonstrated significant efficacy in the removal of a diverse array of contaminants, encompassing organic pollutants, bacteria, and viruses.⁴⁰

- **Minimal Sludge Production:** When employing TiO₂ particles in photocatalytic processes, it has been observed that they exhibit a propensity for generating negligible amounts of sludge. This practice effectively mitigates the expenses related to the disposal and handling of waste materials that are produced.⁴¹
- **Reusable:** TiO₂ has the potential to undergo regeneration and subsequent reuse inside certain wastewater treatment systems, hence providing an additional avenue for reducing operational expenses.
- **Low Cost:** TiO₂ is a cost-effective and easily accessible material.
- **Eco-Friendly:** TiO₂ is often regarded as an environmentally sustainable option due to its non-toxic nature, which ensures that no detrimental compounds are released into the environment throughout the treatment procedure⁴².

2. Application of TiO₂ Nanoparticles in Wastewater Treatment

- **Removal Of Heavy Metal From Wastewater**
 - The issue of heavy metal contamination poses a significant environmental concern, namely in relation to water and soil ecosystems, as well as the well-being of many organisms. These entities have the potential to present substantial hazards to both the natural ecosystem and the well-being of individuals. These substances have the potential to accumulate within sedimentary layers, as well as in various flora and fauna inhabiting aquatic environments, hence causing disruptions within ecological food webs and exerting adverse effects on overall biodiversity. The ingestion of water with heightened concentrations of heavy metals such as lead, mercury, and cadmium have the potential to result in a range of health complications, including renal impairment, organ dysfunction, and the development of cancer⁴³. Therefore, it is of utmost significance to ascertain efficacious approaches for mitigating the issue of heavy metal contamination.
 - Lajayer et al. conducted a study to assess the combined impacts of various parameters, including solution pH, nano-sized TiO₂ catalyst, and methanol, on the efficiency of Cu²⁺ and Cd²⁺ ion removal from wastewater using varied levels of gamma radiation. The impact of pH and additives on the elimination of these two ions was noted. The efficient removal of both Cu²⁺ and Cd²⁺ ions can be achieved with the simultaneous utilization of MeOH and TiO₂ nanoparticles in an acidic pH environment. The efficacy of gamma irradiation as a means of eliminating Cu²⁺ and Cd²⁺ ions from wastewater has been demonstrated in acidic solutions⁴⁴.

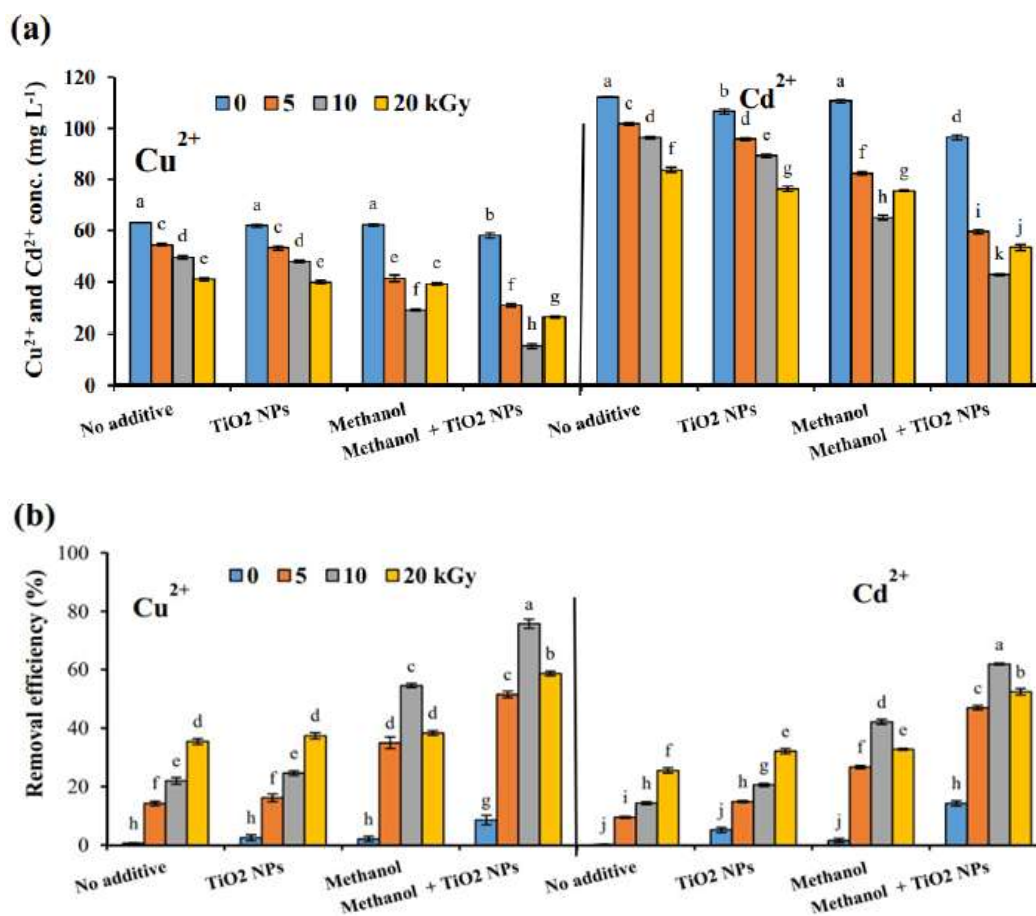


Figure 2: Effects of gamma, gamma+TiO₂ NPs, gamma + methanol and gamma+methanol+TiO₂ NPs treatments on: (a) Concentrations (b) Removal efficiency of Cd²⁺ and Cu²⁺ ions in acidic solution (pH 4.5)

- The study conducted by Maleki et al. focused on the utilization of poly-amidoamine dendrimer (PAMAM, G4) modified TiO₂ nanoparticles for the purpose of removing heavy metals from industrial effluent. The metal ions Cu²⁺, Pb²⁺, and Cd²⁺ were chosen as representative contaminants for the study. The study investigated the impact of many factors, including temperature, pH, and nano-hybrid dose. The findings of the study indicated that the augmentation of the nano-hybrid dosage resulted in a corresponding enhancement in the adsorption efficacy for each of the three metal ions. Additionally, the method was shown to be more favourable at higher pH levels⁴⁵. This is because higher pH values result in an increased negative charge, which is desirable for effectively removing metal ions.

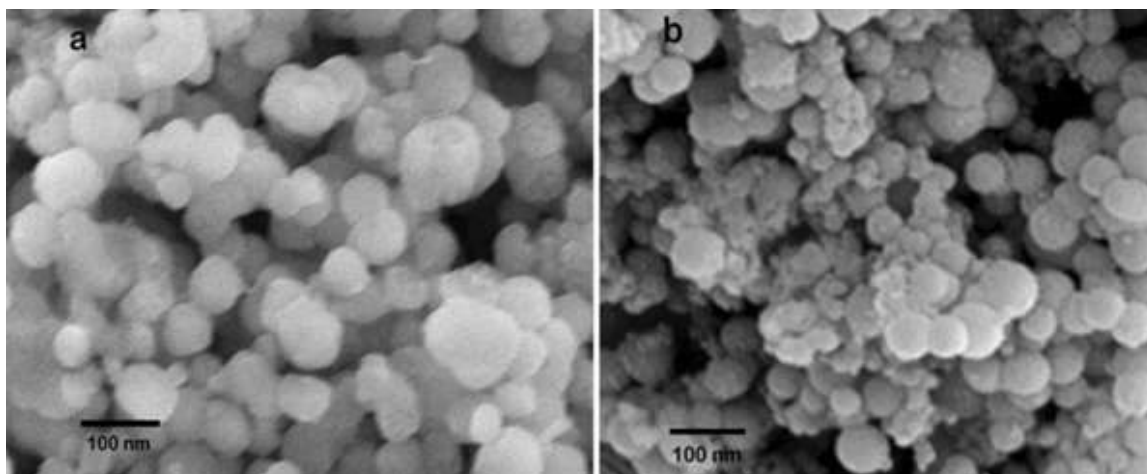


Figure 3: Represents SEM images of (a) TiO₂ nanoparticles and (b) PAMAM/TiO₂ nanohybrid

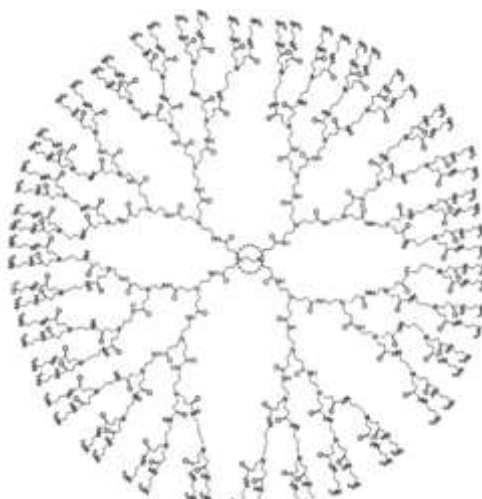


Figure 4: Chemical structure of PAMAM

- **Bacterial Inactivation**

- The demand for surface-modified nanomaterials arises from issues about the existing methods employed for water disinfection. Oxidation technologies, such as chlorination and ozonation, have been widely employed in the field of water disinfection for an extended period of time. Nevertheless, this approach is deemed unsafe as it gives rise to the production of potentially hazardous disinfection by-products (DBP) such as haloacetic acids. The release of treated wastewater that contains residual disinfection byproducts has the potential to cause detrimental impacts on aquatic organisms⁴⁶.
- TiO₂ photo-catalysis presents a viable alternative solution for the eradication of this issue. In addition to possessing a high level of photo-stability and being cost-effective, the catalyst also offers various additional benefits, such as its capacity to operate at ambient temperature and pressure settings, as well as its utilization of

air as an oxidant reactant. Despite exhibiting commendable characteristics, a notable limitation of TiO₂ photo-catalysis is the comparatively elevated band gap energy of the semiconductor⁴⁷. Therefore, doping is employed with the aim of enhancing performance.

- Among all metallic species, silver has demonstrated an augmentation in the separation of electrons and holes, as well as interfacial charge transfer. Consequently, there is an augmentation in the excitation of visible light in TiO₂⁴⁸.
- Grieken et al. conducted a study that focus on the advancement of Ag/TiO₂ materials in order to improve the photocatalytic efficiency for water disinfection purposes. The selection of Escherichia coli as a model microbe is mostly attributed to its extensive utilization as an indicator of fecal contamination. The Ag/TiO₂ particles were evaluated in three distinct reactor setups that had been previously examined using pure TiO₂ photocatalysts⁴⁹:
 - **Slurry Reactor:** The suspension of Ag/TiO₂ particles was evenly distributed across the entire liquid volume of the recirculation system.
 - **Wall Reactor:** The Ag/TiO₂ photo-catalyst was affixed as a thin layer onto the inner surface of the annular photo reactor's tube wall.
 - **Fixed-Bed Reactor:** The whole volume of the annular reactor was filled with glass rings that were coated with Ag/TiO₂ material.



Figure 5: Photograph of TiO₂ and Ag/TiO₂ Photocatalytic Wall Systems

- The bactericidal efficiency was shown to be boosted with higher levels of silver loading. Therefore, the considerable contribution to bacterial inactivation can be attributed to the bactericidal properties of silver. The observed increase in E. coli inactivation can perhaps be attributed to the enhanced bacterial adherence to the titania surface or, more plausibly, to the direct bactericidal effect of silver⁵⁰.
- In a separate experiment conducted by Suri et al., an investigation was carried out to examine the efficacy of Pt and Ag doped TiO₂ photocatalysts in the process of water disinfection. In this study, we examined the bacterial inactivation of

Escherichia coli in the presence of artificial irradiation. A control experiment, whereby the photocatalyst was absent, was undertaken and revealed no substantial alteration in the concentration of bacteria⁵¹. Nevertheless, the rate of inactivation exhibited an upward trend as the concentrations of photocatalyst were augmented, followed by a subsequent decline.

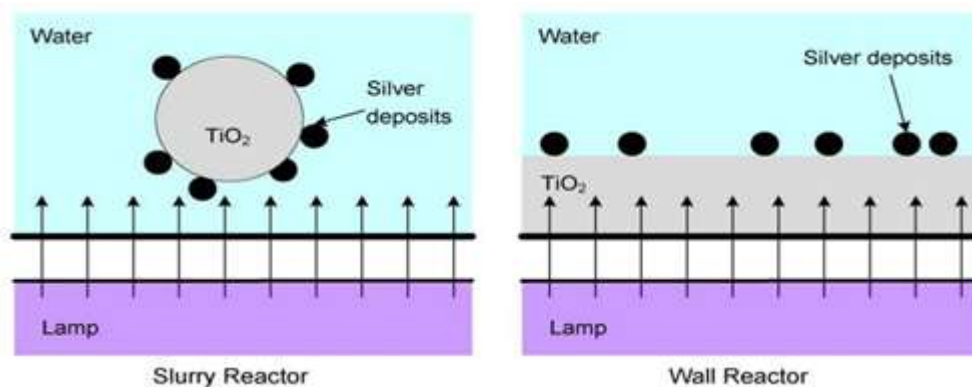


Figure 6: Schematic representation of the Irradiation Patterns in Slurry and Wall Reactors

- Ruth and colleagues conducted a study on the deactivation of fecal coliform bacteria found in actual urban wastewater obtained from the effluent of the sedimentation tank at a university sewage treatment facility. They employed photo electrolysis as a method, utilizing nano-particulated films of TiO₂ and TiO₂/Ag, while subjecting the samples to UV light irradiation and applied potential. The efficacy of the TiO₂/Ag photo-anode as a disinfectant for fecal coliform bacteria has been confirmed. The use of silver notably enhanced the efficacy of titanium dioxide in terms of bacterial inactivation. The researchers also conducted an examination of the structural deterioration of *E. coli* (DH5 α) as a result of the photo-electrocatalytic process in order to enhance comprehension of the mechanism behind its inactivation⁵².

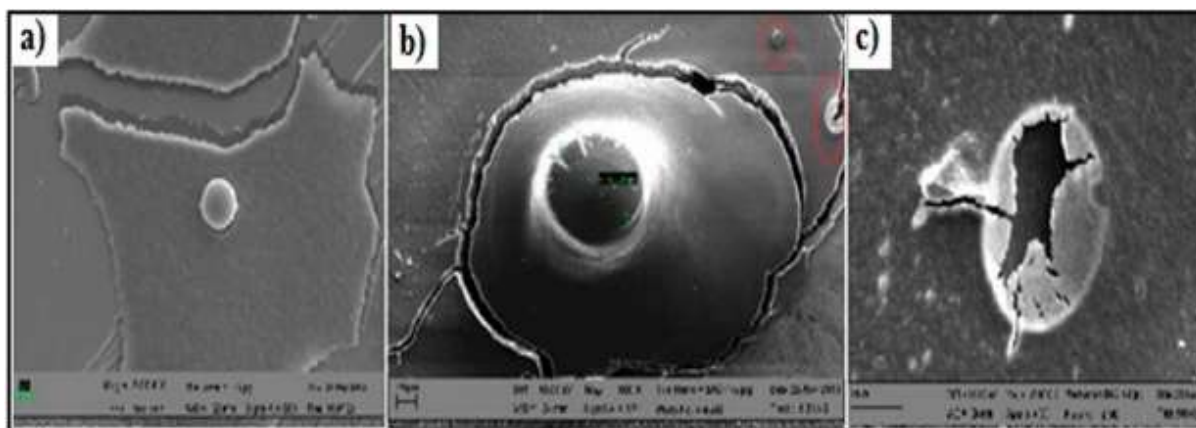


Figure 7: (a) Untreated *E. coli* (DH5 α) cells; (b-c) SEM images of *E. coli* after photo-electrocatalytic inactivation process using a TiO₂/Ag film annealed at 400°C using 1.5V and UV irradiation.

- **Membrane Fouling:** Surface modification is a widely employed technique in the field of wastewater treatment, specifically aimed at enhancing the performance of membranes that experience degradation as a result of fouling. Two primary strategies are employed to mitigate the impact of membrane fouling: nanoparticle decoration of the membrane and hydrophilic modification of hydrophobic polymers⁵³.

In cross-filtration experiments, hydrophobic polymers are often modified by including hydrophilic components. This is done to mitigate the potential for fouling, as hydrophobic surfaces possess a lower surface energy and are prone to serving as growth sites for foulants. In the field of membrane modification, titanium dioxide is commonly employed⁵⁴.

- Qin et al. successfully synthesized a novel hydrophilic ultrafiltration membrane using PVDF as the base material. This membrane was enhanced by the addition of TiO₂ nanoparticles and a Poly (vinyl alcohol) (PVA) layer, which were securely attached to the surface of the PVDF membrane. The TiO₂ nanoparticles exhibited strong cohesion through the formation of chemical bonds and adsorption crosslinking with PVA⁵⁵. The inclusion of TiO₂ nanoparticles in the PVA layer serves as a means of anchoring, so preventing the detachment of the PVA layer from the surface of the membrane.

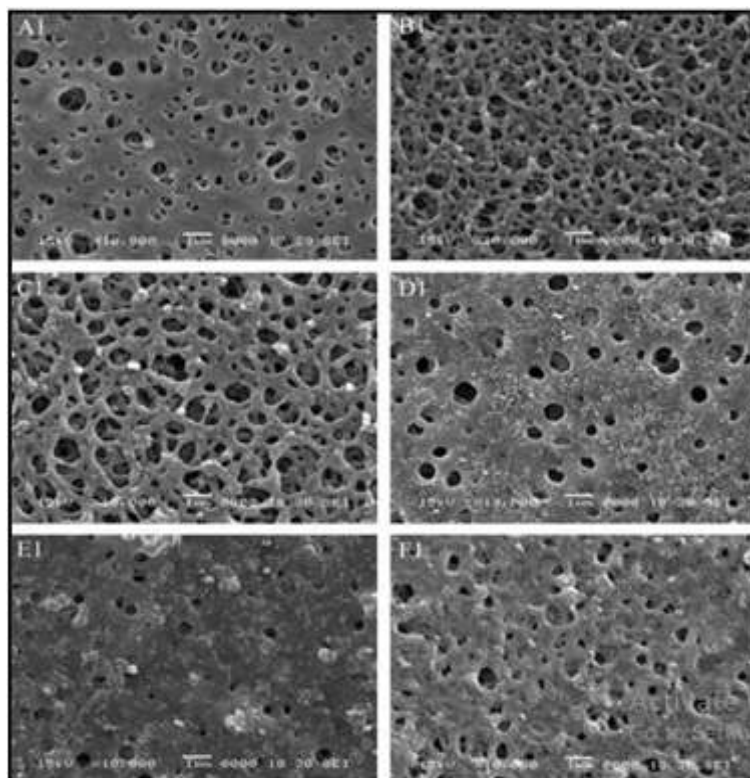


Figure 8: Electron micrograph of top morphology of the membranes with increasing TiO₂ content: (A1) 0 wt.%, (B1) 1 wt.%, (C1) 2 wt.%, (D1) 3 wt.%, (E1) 4 wt.% and (F1) 5 wt.%.

- A study conducted by Zhibiao Li examined the fouling properties of ultrafiltration membranes caused by transparent exopolymer particles (TEP). A comparative analysis was conducted on the fibre membrane, which consisted of conventional polyvinylidene fluoride (PVDF), and mixed matrix membranes incorporating titanium dioxide nanoparticles (PVDF/P25) or nitrogen-doped titanium dioxide (N-TiO₂) nanoparticles (PVDF/N-TiO₂) that were incorporated into the PVDF matrix. A notable improvement in fouling resistance was found for the PVDF/N-TiO₂ membrane when subjected to visible light radiation. The incorporation of titanium dioxide nanoparticles into the polyvinylidene fluoride (PVDF) matrix resulted in an enhancement of the surface hydrophilicity⁵⁶. This factor played a role in the improvement of the membrane's anti-fouling characteristics.
- Yi et al. conducted an experimental study to investigate the impact of key variables on the steady state permeate flux during the separation of oil from synthetic oily water with a low concentration. In this study, the researchers included nano-sized TiO₂/Al₂O₃ particles into PVDF ultrafiltration membranes as a modifier. This modification resulted in the fabrication of PVDF blend membranes with enhanced hydrophilicity and improved resistance to fouling by oil droplets. The researchers noted that the utilization of nano-sized TiO₂/Al₂O₃ resulted in a reduction in membrane fouling caused by oil droplets.⁵⁷
- **Photocatalytic Degradation:** Titanium dioxide undergoes photoexcitation when exposed to ultraviolet (UV) light, causing the movement of electrons from the valence band to the higher energy conduction band. Subsequently, these electrons have the potential to generate hydroxyl radicals, so facilitating the decomposition of organic molecules. The utilization of this technique is prevalent in the process of photocatalytic destruction of various contaminants. Titania (TiO₂) exists in three distinct crystalline structures, namely rutile, anatase, and brookite. Among these phases, anatase has superior stability and possesses significant photocatalytic properties⁵⁸.

Numerous experiments have been undertaken throughout time to provide evidence that TiO₂ facilitates the degradation of hazardous pigments discharged by textile businesses, hence mitigating water pollution. Several of these are discussed below:

Hussein et al. conducted an experiment to investigate the photocatalytic decolorization of actual textile water using TiO₂ as a photo-catalyst, under varying temperatures and UV light irradiation. The present investigation employed titanium dioxide powder in the anatase form. A suspension of 150 mg of titanium dioxide was prepared by mixing it with 30 cm³ of authentic textile dyeing effluent. This suspension was then transferred to a photoreaction cell for further experimentation. The suspended particles were removed from the wastewater by the process of filtration. To maintain homogeneity, the cell was agitated using a magnetic stirrer while simultaneously exposing it to UV rays emitted by a low-pressure mercury lamp. A volume of 2 cm³ of irradiation samples was extracted at regular time intervals using a micro syringe. The extracted samples were subsequently subjected to centrifugation in order to separate the solid catalyst. The measurement of the liquid's

absorbance was conducted utilizing a UV-Vis spectrophotometer. The measurement of absorbance at a specific time was compared to a calibration curve. The calibration plot was generated by employing a predetermined concentration of dyed aqueous solution derived from authentic textile samples⁵⁹.

According to a study conducted by Kamat et al., the total degradation of rose Bengal dye adsorbed on the surface of TiO₂ was seen under photoexcitation with visible light. The observation revealed that solely the molecules that were in direct proximity to the TiO₂ surface exhibited photo-degradation⁶⁰.

In a study conducted by Zhang et al., the degradation of eosin dye was effectively facilitated by the TiO₂-assisted technique in aqueous dispersions when exposed to visible light irradiation⁶¹.

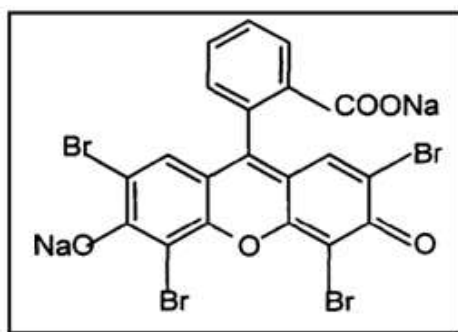


Figure 9: Chemical Structure of Eosin Dye

Isari et al. (2018) conducted an investigation on the degradability of the dye using photo-catalysis under UV radiation, utilizing TiO₂ as the photo catalyst. The researchers observed that complete removal of the dye was obtained, reaching 100%, after a duration of 150 minutes at a pH level of 7⁶².

V. FUTURE PROSPECTIVE AND CHALLENGES

1. Future Prospective: The utilization of surface-modified nanoparticles exhibits considerable potential for the advancement of wastewater treatment owing to their distinctive characteristics and adaptability. The continual progression of technology is expected to significantly enhance the potential of surface modified nanoparticles in several domains of wastewater treatment

- **Selective Elimination of Contaminants:** The alteration of nanoparticles resulting in the development of nanoparticles possessing unique affinities for particular contaminants enables the targeted removal of desired pollutants while preserving the integrity of other constituents.
- **Multi-Contaminant Removal:** In order to enhance the efficiency of the procedure, it is possible to simultaneously handle a combination of nanoparticles. These nanoparticles have the ability to selectively target a diverse array of pollutants concurrently.

- **Resource Recovery:** In addition to the elimination of impurities, nanoparticles can be customized to facilitate the retrieval of valuable resources from wastewater, such as metals or nutrients⁶³.
2. **Challenges:** While the implementation of surface modified nanoparticles for wastewater treatment offers some benefits, it is important to acknowledge the presence of associated obstacles. Several of these are discussed below
- **Stability:** The stability of nanoparticles can be influenced by surface changes. Several alterations may be susceptible to degradation under specific conditions, perhaps resulting in a decrease in treatment effectiveness.
 - **Finite Lifespan:** The aforementioned alterations may experience degradation over time, necessitating frequent replenishment or replacement of nanoparticles.
 - **Scale-Up Challenges:** One of the obstacles encountered during the scale-up process is the transition from laboratory-scale experiments to large-scale application. Maintaining uniform performance within a substantial treatment system might pose challenges.

Therefore, by adopting a long-term research approach to address existing limitations and shortcomings, the utilization of surface modified nanoparticles can prove to be a valuable solution for wastewater treatment, thereby ensuring the preservation of both environmental integrity and public health⁶⁴.

VI. SUMMARY

This chapter investigated into the potential utilization of surface modified nanoparticles in the context of wastewater treatment procedures. The chapter commenced with a concise overview of wastewater, followed by an examination of the imperative to treat it. This was accomplished by elucidating the detrimental consequences resulting from the unmitigated release of untreated wastewater into aquatic ecosystems. The conventional technique of wastewater treatment was elucidated, highlighting its drawbacks, in order to underscore the necessity of integrating surface modified nanoparticles into the treatment procedure. A comprehensive explanation was provided to elucidate the strategies employed for alteration. Additionally, the discussion revolved around the use of surface-modified nanoparticles, with a focus on the advantageous properties exhibited by TiO₂ nanoparticles. Multiple sources were included in order to acquaint the reader with the extensive range of applications of titanium dioxide in the treatment of wastewater. Finally, a comprehensive analysis of the advantages and disadvantages of surface modified nanoparticles was conducted, and potential future developments were elucidated.

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