TiO2-NPs: Wastewater Treatment and Ago-Environment

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The tremendous increase in the production and consumption of titanium dioxide (TiO_2) nanoparticles (NPs) in numerous industrial products and applications has augmented the need to understand their role in wastewater treatment technologies. The use of TiO_2 NPs as the representative of photocatalytic technology for industrial wastewater treatment is coming to the horizon. As the use of industrial wastewater to feed agriculture land has been a common practice across the globe and the sewage sludge generated from wastewater treatment plants is also used as fertilizer in agricultural soils. Therefore, it is necessary to be aware of possible exposure pathways of these NPs, especially in the perspective of wastewater treatment and their impacts on the agro-environment.

TiO2 NPs applications wastewater treatment agro-environment

1. Introduction

TiO_2 NPs are one of the most extensively used NPs in different sectors [1]. For example, TiO_2 NPs are widely used in the agriculture sector for different purposes such as nano-pesticides and nano-fertilizers to introduce sustainable agricultural practices [2]. The availability of these nano-based agrochemicals in the market is expected to rise in near future [3]. Similarly, the use of TiO_2 NPs has also gained the utmost importance in other fields, and eventually from different sources, the inevitable release of these NPs into the environment is obvious either through a direct or indirect route. For example, in 2008, the first evidence of TiO_2 NPs leaching (3.5×10^7 NPs per L) into the aquatic environment from facade paints was reported [4]. In 2011, TiO_2 NPs were first detected in effluents of wastewater treatment plants, which were discharged into freshwater bodies where these NPs can cause unknown ecological risks [5]. TiO_2 NPs have also been observed to detach from some textiles and paints due to washing or weathering and to run into wastewater treatment plants [6][7] and especially in sewage sludge reaching the approximate concentration of 2 $g{\cdot}kg^{-1}$ [8]. Sewage sludge is commonly employed as soil fertilizer in agriculture at the rate of approximately 3 tons per hectare (on a dry weight basis) annually [9][10][11] and become an ultimate source of TiO_2 NPs dissemination in agricultural soils. However, the overall concentration of these NPs in the environment through direct exposure route will be much higher than the indirect release. Interestingly, in both soil and water medium, TiO_2 NPs can be used for purification purposes due to their unique characteristics of photocatalysis in the presence of ultraviolet (UV) light [12][13]. Figure 1 below illustrates the brief overview of TiO_2 NPs applications, their role in wastewater treatment and their impacts on agro-environment.

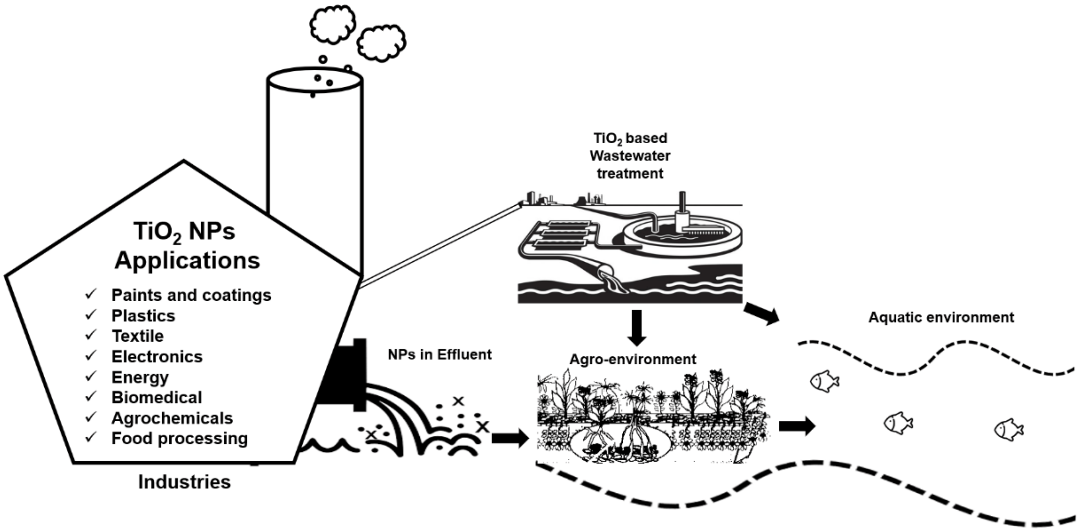

Figure 1. Illustration of the wide range of TiO_2 NPs applications from industries, their release into the wastewater, and their possible exposure routes towards the agro-environment.

2. Wastewater Treatments

With the onset of industrialization, there has been a steady increase in the types and amount of pollutants released in the environment. These environmental problems have garnered much attention on the global scale, especially water scarcity. Global water scarcity is a temporal and graphical mismatch between freshwater resources and the world's water demand. The increasing world population and urban industrialization have made water scarcity more alarming as shown in Figure 2, predicting the gap between supply (4200 billion m^3) and demand (6900 billion m^3) of freshwater in 2030. A major proportion of this water is used for the agriculture sector and then for the industrial sector.

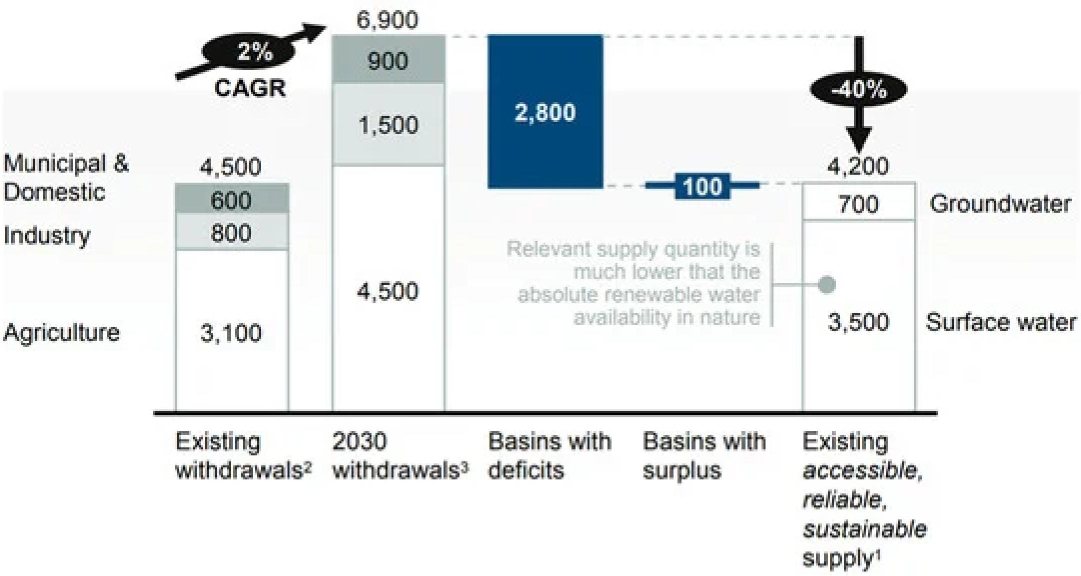

Figure 2. Comparison of current and future water demand, Reproduced with permission from [14], published by McKinsey & Company, New York, NY, USA, 2009.

With a growing world population, an ever-increasing demand for food production and potable water is questionable. The agriculture sector requires a surplus amount of water for irrigation. To avoid water scarcity issues, the reuse of wastewater is tremendously increasing across the planet. Reusing wastewater is a sustainable strategy to manage natural water resources [15] . However, the use of untreated wastewater for irrigation is a usual practice in developing countries causing serious threats to the ecosystem as well as human health. Specifically, carcinogenic pollutants pose a solemn threat to agricultural land, irrigated with industrial effluent without any treatment [16].

The whole world stands as a witness to unintended repercussions caused by rapid industrialization. The wastewater generated from industrial sectors has pronounced effects on humans as well as landmass fertility. Some industrial estates have operational wastewater treatment plants but unfortunately, they cannot handle a large proportion of industrial effluent. To meet the international standards of wastewater discharge, suitable technologies are required for wastewater treatment before discharging to streams. It could help to reduce the burden on freshwater resources by reusing treated water in various industrial processes. Due to the widely used application of nanotechnology, challenges, and opportunities of using engineered nanomaterials (ENMs) in wastewater treatment is a matter of endless concern. Based on the wastewater standards, a technique using TiO_2 NPs for resilient pollutants in the context of wastewater treatment has become popular in recent years. Up to date, TiO_2 NPs have drawn attention over other photocatalysts in every field of life. Over the last few decades, TiO_2 NPs with high photocatalytic efficacy has been tested to reduce the pollution load from various industrial units. The conventional wastewater treatment methods mostly come up with high costs as well as lower efficiencies. However, the advantages of the use of TiO_2 NPs (non-toxic, inexpensive, stable, and reusable NPs) appeared as a promising strategy to save the environment from pollution.

3. Impacts of TiO_2 NPs in the Agro-Environment

In agro-environment, soil is the main and complex matrix in which analyzing the fate of TiO_2 NPs is a challenging task. Furthermore, the impacts of TiO_2 NPs are difficult to measure in the soil due to the high geogenic background of Ti (≈0.6% of the terrestrial crust). Up until now, modeling studies had helped to estimate the approximate amount of TiO_2 NPs that is accumulating in the environment. According to recent forecasts, TiO_2 NPs sludge treated soils (with 45,000 tons) were observed to be the largest sink for NPs release among different environmental compartments [4]. The crop plants served as an entry route for NPs' uptake into the food chain. Presently, there are limited data available about these NPs interactions within the soil matrix. As nanotechnology is emerging in the field of agriculture sector in terms of growing global food production, nutritional contents, quality, food safety, and security [17]. Besides all these aspects, there are several other applications of NPs in agro-environments such as food processing and production, nano-fertilizer, nano-pesticides, etc. but the important concern arises here is the fate of these NPs.

Scientists have investigated the effects of TiO_2 NPs on the soil–plant continuum and have observed diverse impacts based on different characteristics of NPs, plant species, experimental conditions, and exposure period. For example, Figure 3, shows the TiO_2 NPs effects on plants with respect to different stages, concentration range, and exposure time. In a recent study, experiments were conducted on growth-promoting rhizobacteria (PGPR) inoculation with and without TiO_2 NPs in peat soil under the three stress situations. TiO_2 NPs were reported to enhance the performance of growth-promoting rhizobacteria which further promotes the solubilization of insoluble phosphates [18]. A grassland soil was treated with TiO_2 NPs at the rate of 0, 500, 1000, and 2000 mg kg^{-1} of soil. These NPs were observed to negatively affect the soil bacterial communities after 60 days of exposure [19]. TiO_2 NPs effects on several bacterial taxa were also studied using incubated soil microcosms having concentrations range of TiO_2 NPs 0, 0.5, 1.0, and 2.0 mg g^{-1} soil. Of the identified taxa that exist in all samples, 9 taxa were found to be positively correlated with TiO_2 NPs, 25 taxa were negatively correlated whereas 135 taxa were not affected by TiO_2 NPs [20]. In another study, TiO_2 NPs effects were investigated at concentrations ranging from 0.05 to 500 mg kg^{-1} dry soil on different bacterial communities. The abundance of ammonia-oxidizing archaea was reported to decrease by 40% in response to TiO_2 NPs whereas *Nitrospira* was not affected at all. Furthermore, the abundance of ammonia-oxidizing bacteria and *Nitrobacter* were also reported to reduce due to TiO_2 NPs treatments [21].

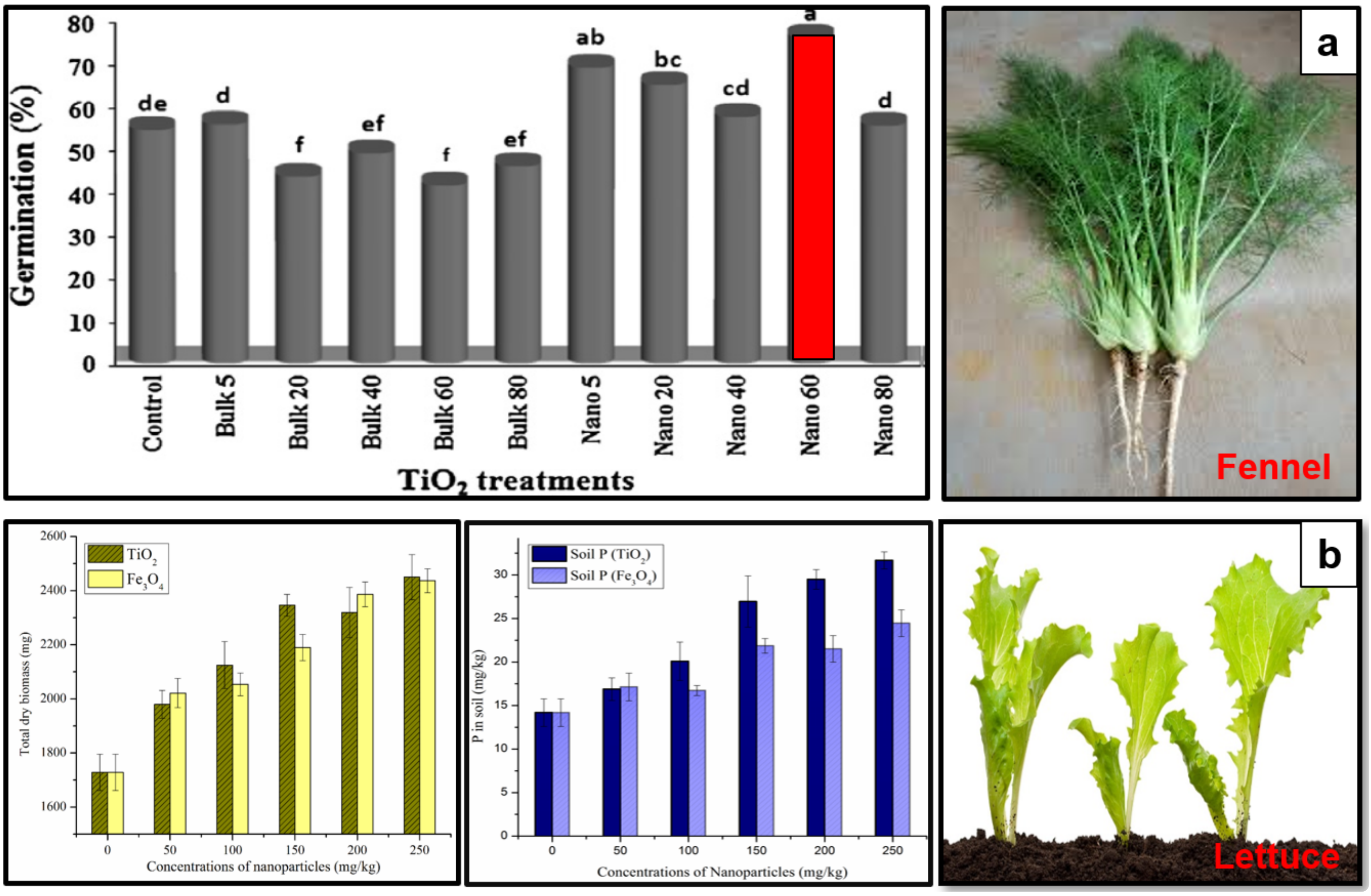

Figure 3. Effects of TiO_2 NPs on plants with respect to different stages, concentration range, and exposure time. (**a**) represents the effects of TiO_2 NPs on germination % of fennel seeds after short term exposure in a petri dish, the lowercase letters show the level of significance such as 'a' represent significant increase in germination

percentage at Nano 60 treatment compared to control group. Adapted with permission from [22], published by ELSEVIER, 2013, (**b**) shows the effects of these NPs on lettuce plants after long term exposure of 90 days in soil, Adapted with permission from [24], published by American Chemical Society, 2015.

TiO_2 NPs (0, 5, 20, 40, 60, and 80 mg/kg) were used to study phytotoxicity and stimulatory impacts on fennel after 14 days of exposure. The mean germination percentage was increased by 76% at 60 mg L^{-1}, while the mean germination time was decreased by 31% at 40 mg L^{-1} [22]. Similarly, in another study, plant shoot-root length was increased by 49% and 62%, respectively at 100 mg kg^{-1} of NPs treatment in lettuce after 14 days exposure in soil medium [23]. Another study was performed using TiO_2 NPs treatments (0, 50–250 mg kg^{-1}) in soil medium for a period of 90 days. The total dry biomass was observed to increase 1.4-fold and phyto-available phosphorus (P) in soil by 2.2-fold, respectively [24]. Table 1 enlists the recent studies conducted for the investigation of TiO_2 NPs effects on different plants.

Table 1. TiO_2 NPs applications since 2010 on different plants and their impacts.

Experimental Conditions	Plants	Impacts of TiO_2	Ref.
TiO_2 NPs Size: 20–30 nm Treatments: 0, 50, 100 and 200 mg L^{-1}) in the growth medium of cocopite and perlite. Period: 60 days	Moldavian balm	Plants cultivated in salt stress conditions were observed to have improved physical traits and increased antioxidant enzyme activity in response to TiO_2 NPs treatment compared to control.	[25]
TiO_2 NPs Size: 50 and 68 nm Treatments: 100 mg *n*TiO_2/kg on 10 mg kg^{-1} of Cd-spiked soils Period: 14 days	Cowpea	No change in chlorophylls occurred. In leaves and roots, both ascorbate peroxidase and catalase activities were improved by NPs. TiO_2 NPs have the potential for soil nano-remediation and could be an environmentally friendly option to tolerate soil Cd toxicity in cowpea plants.	[26]
TiO_2 NPs Size: 30 nm Treatments: 0, 30, 50 and 100 mg kg^{-1} Period: 60 days	Wheat	TiO_2 NPs without P fertilizer increased Ca (316%), Cu (296%), Al (171%), and Mg (187%) contents in shoots at 50 mg kg^{-1} TiO_2 NPs treatment which shows improved grain quality and crop growth.	[27]
TiO_2 NPs Treatments: 0, 5, 10, 15, and 20 mg L^{-1} (foliar spray) Medium: Soil Period: 55 days	Rice *(Oryza sativa)*	The foliar spray of TiO_2 NPs reduced the soil bioavailable Cd by 10, 14, 28, and 32% in response to 5, 10, 20, and 30 mg/L NPs treatments compared to their control values. These NPs also significantly decreased the Cd concentration in the shoot as well.	[28]

Experimental Conditions	Plants	Impacts of TiO_2	Ref.
TiO_2 NPs Size: <40 nm Treatments: 0, 50, and 100/mg kg^{-1} Medium: Soil Period: 40 days	Wheat *(Triticum aestivum)*	Shoots and root lengths of wheat plants increased by16% and 4%, respectively. Phosphorus in shoots and roots was increased by 23.4% and 17.9% at 50/mg kg^{-1} of soil compare to control.	[29]
TiO_2 NPs Size: <40 nm Treatments: 0, 25, 50, 150, 250, 500, 750 and 1000 mg L^{-1} Medium: Soil	Wheat *(Triticum aestivum)*	TiO_2 NPs at the highest treatment level of 1000 mg kg^{-1}, plant growth, biomass. Phosphorus content along with other tested parameters did not shown any improvement in the testing soils.	[30]
TiO_2 NPs Treatments: 0, 100 and 500 mg kg^{-1} Medium: soil Period: 60 days	Wheat *(Triticum aestivum)*	No effect of phytotoxicity was observed in plant growth, chlorophyll content, and biomass.	[31]
TiO_2 NPs Treatments: 0–750 mg kg^{-1} Medium: Soil Period: 90 days	Rice *(Oryza sativa)*	Phosphorus concentration was increased in roots by 2.6-fold, shoots 2.4-fold, and grains 1.3-fold upon 750 mg kg^{-1} of NPs treatment. Metabolomics study revealed that levels of amino acids, glycerol content, and palmitic acid were also improved in grains.	[32]
TiO_2 NPs Treatments: 0, 100, 150, 200, 400, 600, and 1000 mg L^{-1} Medium: Hydroponics Period: 7 days	Barley (*Hordeum vulgare* L.)	No adverse effect on shoot growth. Root growth inhibited as the concentration of TiO_2 NPs increases. No effect on chlorophyll *a* and *b*. No significant effect on biomass.	[33]
TiO_2 NPs Treatments: 0–100 mg kg^{-1} Medium: Soil Period: 60 days	Wheat *(Triticum aestivum)*	NPs treatment at the rate of 20, 40, and 60 mg kg^{-1} increased plant growth and phosphorus uptake. 32.3% of chlorophyll content increased at 60 mg kg^{-1} while 11.1% decrease at 100 mg kg^{-1}.	[34]
TiO_2 NPs Size: >20 nm Treatments: 0, 100, 250, 500 and 1000 mg L^{-1} Medium: Soil Period: 5 weeks	*Arabidopsis thaliana* (L.)	Plant biomass and chlorophyll content decreased as the NPs treatment increase. Higher concentrations of NPs improved root growth. NPs treatments from 100 to 1000 µg mL^{-1} affect vitamin E content in plants. Decrease in plant biomass by 3-fold in response to 500 and 1000 mg/ml NPs treatment, whereas, at	[35]

Experimental Conditions	Plants	Impacts of TiO_2	Ref.
		100 mg/mL, the biomass decreases to half relative to control.	
TiO_2 NPs Treatments: 250 and 500 µg/mL	Cabbage, Cucumber, Onion	The germination of cabbage significantly increased. In cucumber and onion, significant root elongation was observed.	[36]
TiO_2 NPs P25: 29 ± 9 nm, E171: 92 ± 31nm, Non-nanomaterial TiO_2: 145 ± 46 nm Treatments: 1, 10, 100, 1000 mg kg^{-1} Period: 12 weeks	Wheat, Red clover	TiO_2 NPs showed restricted mobility from soil to leachate. No significant translocation of Ti was observed in both plant species, while average Ti content increased from 4 to 8 mg kg^{-1} at the highest treatments.	[37]
TiO_2 NPs Size: 22 and 25 nm Period: 6 weeks	Soya bean	Plant growth significantly decreased which corresponds to the reduced carbon content in leaves.	[38]
TiO_2 NPs Treatments: 0, 10, 20, 40 and 80 mg L^{-1} Medium: Petri dish Period: 10 days	*Alyssum homolocarpum, Salvia mirzayanii, Carum copticum, Sinapis alba, and Nigella sativa*	TiO_2 NPs affected the germination and seedling vigor of 5 medicinal plants. Appropriate concentration levels had improved the germination as well as the vigor index of the subjected plant.	[39]
TiO_2 NPs Treatments: 0, 10, 20, 30, and 40 mg mL^{-1}	Parsley	Significant increase in seedlings germination percentage, germination rate index, shoot-root length, fresh biomass, vigor index, and chlorophyll content. 30 mg mL^{-1} was observed to be the optimum concentration of NPs. Increased germination percentage (92.46%) was observed at 40 mg mL^{-1} treatment, relative to the lowest one (44.97%) at control.	[40]
TiO_2 NPs Treatments: 0, 0.01%, 0.02%, and 0.03% Medium: Soil Period: 14 days	Wheat *(Triticum aestivum)*	Under the water-stressed conditions, the plant's length, biomass, and seed number along with the other tested traits like gluten and starch content were increased at 0.02% of NPs treatment.	[41]
TiO_2 NPs Size: 14–655 nm	Wheat *(Triticum aestivum)*	NPs treatment improved root length. NPs above 140 nm diameter are not accumulated in wheat roots. NPs above 36 nm threshold diameter, can be accumulated (at concentration 109 mg Ti/kg dry weight) in wheat root parenchyma cells but are	[42]

Experimental Conditions	Plants	Impacts of TiO_2	Ref.
		unable to translocate to the shoot. Enhanced wheat root elongation was observed when exposed to 14 and 22 nm TiO_2 NPs.	
TiO_2 NPs Size: 5 nm Treatments: 0.25% NPs Medium: Hoagland nutritive fluid Period: 35 days	*Arabidopsis thaliana*	Improved photosynthesis and growth in plants were reported. Generally, the absorption of light in chloroplast and light-harvesting complex II was supposed to be stimulated by TiO_2 NPs; thus, enhancing the transformation of light energy to electronic energy, the evolution of oxygen, and water photolysis.	[43]
TiO_2 NPs (43%) with sucrose coating Size: >5 nm	*Arabidopsis thaliana*	Results revealed that small NPs entered plant cells and got accumulated in distinct subcellular locations.	[44]
TiO_2 NPs Size: <100 nm Treatments: 0, 5, 10 and 20 mg L^{-1} Period: 20 days	*Zea mays* L.	TiO_2 NPs treatment significantly reduced the shoot, root biomass, and chlorophyll contents of leaves in a dose-dependent manner. Whereas positive effects were reported on the N, P, K, Zn Mn, and Cu contents except for Fe.	[45]
TiO_2 NPs Size: <100 nm Treatments: 15, 30, 60, 120 and 240 mg L^{-1} Period: at different time intervals up to a maximum of 82 days	*Vicia faba*	TiO_2 NPs were reported to induce variations in a meiotic activity which results in an increased number of chromosomal abnormalities in the plant's reproductive parts.	[46]
TiO_2 NPs Size: <100 nm (tetragonal crystals), <10 nm (spherical shape) Treatments: 50 mg L^{-1} Period: 3 days	*Vicia faba*	Based on the characteristics of size and shape, TiO_2 NPs can induce different levels of toxicity in terms of seed vigor index, aberration index and oxidative stress in plants.	[47]

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4. Conclusions and Future Perspectives

Based on the recent developmental facts related to TiO_2 NPs in wastewater treatment technologies and the agro-environment, the use of TiO_2 NPs will further increase for promising applications in the near future. In wastewater treatment technologies, downstream separation of these NPs after photocatalytic degradation is still a matter of concern which can be minimized by using TiO_2 in photocatalytic reactors either in slurry form or immobilized on a solid substrate. Immobilization might result in loss of potential active sites which could be minimized by adding NMs into the polymeric substrate. The polymer can provide firm anchoring to TiO_2 NPs, however, there is still a chance of NPs leaching into the treated water and reaching the agricultural soils via irrigation. Since the agriculture sector is the backbone of the economy in most countries, studies based on crop improvement using TiO_2 NPs could help to overcome the burden of nutrient deficit in soils providing better crop yield. Apart from the potential benefits of TiO_2 NPs there are also some limitations that we could not ignore. At this stage, we could not claim with surety that the use of NPs is fully safe for human health and the environment or if it is harmful. Risks associated with chronic exposure of these NPs, interaction with flora and fauna, and their possible bioaccumulation effects have not been fully considered yet. The other limitations include the lack of information about a safe range of NPs' concentration, scalability of research and development for prototypes, industrial production, and public concern about health and safety issues. Detailed investigations are necessarily required to resolve these concerns and provide conclusive statements. We need to optimize the useful concentration levels of TiO_2 NPs for various applications and limit their usage for environmental safety.

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