

REVIEW ARTICLE

Titanium: Metal of the future or an emerging environmental contaminant?

Supplementary File

Table S1. Largest titanium (Ti) reserves and an overview of the global supply chain

Country	Ti reserve ^a		Supply chain ^b			
	Ilmenite (thousand metric tons)	Rutile (thousand metric tons)	Ti mineral production (metric tons of TiO ₂)	Percentage of total (%)	Ti sponge production (metric tons of TiO ₂)	Percentage of total (%)
China	200,000	-	3,400,000	36	120,000	57
Australia	160,000	24,000	790,000	8	-	-
India	85,000	7,400	-	-	250	0.1
South Africa	63,000	8,300	995,000	10	-	-
Brazil	43,000	1,200	-	-	-	-
Madagascar	40,000	-	414,000	4	-	-
Norway	37,000	-	468,000	5	-	-
Canada	31,000	-	430,000	5	-	-
Mozambique	14,000	-	1,108,000	12	-	-
Ukraine	5,900	2,500	411,000	4	-	-
Senegal	-	-	491,000	5	-	-
Kenya	-	-	253,000	3	-	-
Japan	-	-	-	-	35,000	17
Russia	-	-	-	-	27,000	13
Kazakhstan	-	-	-	-	16,000	8
Saudi Arabia	-	-	-	-	3,700	2
United States	-	-	-	-	500	0.2
Other countries	26,000	400	740,000	8	-	-
World total	700,000	48,000	9,500,000	100	210,000	100

Notes: ^aSource from the United States Geological Survey.¹ ^bSource from Bhutada.²

Table S2. Distribution of different forms of titanium in soil and aquatic environments

Forms of titanium	Distribution in soil and aquatic environments	References
Ilmenite (FeTiO ₃)	In igneous rocks, sediments, and beach sands	3
Rutile (TiO ₂)	In metamorphic rocks and igneous rocks	4
Anatase (TiO ₂)	In some igneous and metamorphic rocks	5
Particulate titanium (forms of TiO ₂ particles)	As solid particles suspended in water	6
Titanium dioxide (TiO ₂)	In the form of fine particles	7
Complexes with organic matter	Complex with organic matter in water, forming colloidal complexes	8

Table S3. Plant–titanium (Ti) interactions: Studies investigating the direct addition of titanium dioxide (TiO₂) for plant benefit

Plant Species	Concentration	Treatment technologies	Effects	References
<i>Vigna unguiculata</i>	62 – 125 mL/ha	Field trials conducted to investigate foliar TiO ₂ as a growth promoter	Yield increased by 8 – 50%; foliar and pod disease severity reduced	9
<i>Salvia officinalis</i>	0 – 80 mg/L	Three-week trial with impacts on germination and plant growth	Germination increased, but there was no effect on shoot, root, and seedling elongation and biomass	10
<i>Allium cepa</i>	0 – 50 mg/L	Impact on germination, seedling growth, and hydrolytic and antioxidant enzymes	Enhanced germination, growth, and enzyme activity at low doses; inhibition at higher doses	11
<i>Solanum lycopersicum</i>	0 – 1,000 mg/kg	Field study to conduct trials on Ti translocation	Foliar application of lower doses increased growth; no effect at higher doses	12
<i>Fragaria ananassa</i>	0 – 150 mg/kg	Growth and yield under low light conditions	Yield, hardness, and pigments increased with foliar application; decreased phenolics	13
<i>Vicia faba</i>	0 – 0.03%	Impact on growth and tolerance to saline stress	Dose-dependent positive impacts on growth under control and saline stress conditions	14
<i>Triticum aestivum</i>	-	Fertigation impacts on drought tolerance of four cultivars evaluated	Fertigation under stress enhanced leaf thickness and longevity, and increased pigment content and photosynthesis	15
<i>Coriandrum sativum</i>	0 – 400 mg/L	Impacts on growth and nutritional content under hydroponic conditions	Lower doses increased growth and nutrient uptake; higher doses triggered oxidative stress	16
<i>Dracocephalum moldavica</i>	0 – 250 mg/L	Impact on growth and tolerance to saline stress	Dose-dependent alleviation of saline stress	17
<i>C. sativum</i>	0 – 160 mg/L	Effect of seed priming on biochemistry, morphology, and growth under cadmium stress	TiO ₂ decreased in planta cadmium content, improved biochemistry, and increased growth	18
<i>Vicia faba</i>	10 – 20 mg/L	Impact on growth and tolerance to saline stress	Reduced osmotic and salinity-induced stress	19
<i>Melissa officinalis</i>	0 – 100 mg/L	Impact on tolerance to drought stress	Increased resistance to drought stress by increased photosynthesis, photosynthetic pigments, antioxidant activity, nutrient absorption, and decreased reactive oxygen species	20
<i>Sesamum indicum</i>	0 – 15%	Impact on growth and biochemistry under heat stress	Dose-dependent increased growth and positively impacted biochemistry under heat stress	21

Table S4. Plant–titanium interactions: Studies involving the use of plant extracts to synthesize nanoscale titanium dioxide

Plant species	Concentration	Preparation methods	Effects	References
<i>Eclipta prostrata</i>	-	Leaf extract used for nanoparticle (NP) synthesis	Particles characterized by FTIR, XRD, AFM, and FESEM	22
Plant extracts	-	Using plant and other biological extracts for NP synthesis	Review article	23
<i>Moringa oleifera</i> , <i>Triticum aestivum</i>	0 – 80 mg/L	<i>Moringa oleifera</i> -derived NPs were synthesized, characterized, and applied to <i>T. aestivum</i> infected with leaf blotch	Dose-dependent suppression of disease damage and an increase in plant growth	24
<i>Buddleja asiatica</i> , <i>T. aestivum</i>	0 – 80 mg/L	<i>Buddleja asiatica</i> -derived NPs were synthesized, characterized, and applied to <i>T. aestivum</i> under saline stress	Dose-dependent increase in growth and improvement in biochemistry	25
<i>Puccinia striiformis</i> , <i>T. aestivum</i>	0 – 80 mg/L	<i>Puccinia striiformis</i> -derived NPs were synthesized, characterized, and applied to <i>T. aestivum</i> under pathogen stress	Dose-dependent modulation of biochemistry that alleviates pathogen damage	26
<i>Glycine max</i>	0 – 50 mg/L	Biosynthesized nanoscale TiO ₂ (aloe vera extract) added to soybean	Dose-dependent alleviation of salinity stress observed	27

Abbreviations: AFM: Atomic force microscopy; FESEM: Field emission scanning electron microscopy; FTIR: Fourier transform infrared spectroscopy; XRD: X-ray diffraction.

Table S5. Selected references on the potential remediation methods of titanium (Ti) contamination in soil and aquatic environments

Environmental matrix	Initial concentration	Test plant and/or amendment	Detailed description	References
Soil environment				
Soil	-	Pedunculate oak (<i>Quercus robur</i> L.)	<ul style="list-style-type: none"> The concentration of Ti content in wood accumulated up to 1,900 mg/kg 	28
Ilmenite soil	2.3 – 31.3%	Beach morning glory (<i>Ipomoea biloba</i>)	<ul style="list-style-type: none"> The concentration of Ti content in leaves accumulated 135 – 1,521 mg/kg 	29
Mineralized area soil	-	Horsetail (<i>Equisetum</i> spp.)	<ul style="list-style-type: none"> The average Ti content in the above-ground parts of the plants reached 460 mg/kg, and the maximum concentration reached 1,200 mg/kg 	30
V-Ti magnetite mine tailings soil	104.5±8.31 mg/kg	<i>Pongamia pinnata</i> (inoculated with <i>Bradyrhizobium Liaoning ense</i> PZHK1)	<ul style="list-style-type: none"> Inoculation of PZHK1 increased plant <i>P. pinnata</i> biomass by an additional 44.76% Inoculation also increased the metal accumulation capacity and superoxide dismutase activity of <i>P. pinnata</i> The bioconcentration factor of <i>P. pinnata</i> after inoculation increased from 0.05 to 0.13 	31
	-	<i>Pongamia pinnata</i>	<ul style="list-style-type: none"> Soil rapidly available nutrients, enzyme activity, and microbial carbon and nitrogen contents increased <i>Rhizobium</i> and <i>Nordella</i> were identified as the keystone taxa 	32
	-	<i>Pongamia pinnata</i>	<ul style="list-style-type: none"> Soil microbial communities were reshaped by <i>P. pinnata</i> 	33
Red gypsum, produced by the neutralization of wastewaters with limestone from a TiO ₂ plant	6,245±90 mg/kg	Poplar cuttings, cucumber, pepper, cabbage, and lettuce	<ul style="list-style-type: none"> Although the total Ti of gypsum was high, the Ti contents after CaCl₂ extraction were below the limit of quantification The highest Ti content was found in lettuce leaves, and the lowest in poplar leaves There is a potential risk of Cr content in cucumber fruits 	34
TiO ₂ NPs contaminated soil	100 and 1,000 mg/kg	<i>Suaeda glauca</i> and <i>Brassica campestris</i>	<ul style="list-style-type: none"> <i>Suaeda glauca</i> has stronger resistance to TiO₂ NPs compared to <i>B. campestris</i> Phytoremediation removes approximately 60% of TiO₂ NPs from the soil 	35
Aquatic environments				
Natural water	5 mg/L	FeCl ₃ or poly-aluminum chloride	<ul style="list-style-type: none"> The removal rate of TiO₂ NPs reached beyond 90% The average particle size of the suspended TiO₂ NPs after treatment decreased from 145 nm to 43 nm Increasing the ionic strength in the media sink enhanced the removal rate of TiO₂ NPs 	36
Four synthetic waters of different concentrations and organic properties (hydrophilic/hydrophobic)	10 mg/L	Commercial poly-aluminum chloride	<ul style="list-style-type: none"> The removal of TiO₂ NPs in all types of water samples was >90% Hydrophobic water requires a higher dose of coagulant than hydrophilic water to obtain the same removal of TiO₂ NPs The main mechanism for TiO₂-NP removal is charge neutralization 	37
Artificial groundwater and artificial surface water	10 – 100 mg/L	Iron chloride, iron sulfate, and alum	<ul style="list-style-type: none"> The removal rates of TiO₂ NPs in groundwater were >90% for all coagulants In surface water, the removal rates of FeSO₄ and Al₂(SO₄)₃ were >90%, whereas for FeCl₃, the removal rate was less than 60% The removal of TiO₂ NPs was not effective at high zeta potential (>35 mV) 	38

(Cont'd...)

Table S5. (Continued)

Environmental matrix	Initial concentration	Test plant and/or amendment	Detailed description	References
Natural surface water	1 mg/L	Commercial poly-aluminum chloride coagulant/flocculant	<ul style="list-style-type: none"> The removal rate of TiO₂ NPs reached over 99% by coagulation, flocculation, and sedimentation The Ti removal rate was 98% in low turbidity water (1.91±0.36 NTU) and 99% in medium turbidity water (63.33±5.37 NTU) 	39
Distilled water	0 – 10 mg/L	Fe ₃ O ₄ -SiO ₂ and Fe-C-SO ₃ H composites	<ul style="list-style-type: none"> Under ideal conditions, 99.7% TiO₂-NP removal can be achieved in 30 min 	40
Natural water	5 – 125 mg/L	Poly-L-lysine glasses covered with lecithin	<ul style="list-style-type: none"> The average removal rate is 58% No coagulation, flocculation, or precipitation required 	41
Dye water	2 mg/L	Modified cellulose nanofiber-based polyvinylidene fluoride microfiltration membrane	<ul style="list-style-type: none"> The retention rate of Fe₂O₃ NPs exceeds 99% It can effectively adsorb positively charged crystalline violet dyes 	42
Natural water	5 mg/L	0.10 µm and 0.45 µm microfiltration membranes	<ul style="list-style-type: none"> The removal rate of TiO₂ NPs reached more than 90% Addition of 1.0 mM phosphate enhances the removal rate of TiO₂ NPs in 0.10 µm microfiltration membranes 	36

Supplementary information

1. Toxicity of TiO₂ to animals and human health

Several medical studies showed that a 2-year exposure of rats to high levels of fine TiO₂ caused the formation of lung tumors.^{43,44} A growing body of evidence suggests the potentially toxic effects of TiO₂ nanoparticles (NPs) in biota through inhalation, ingestion, and injection.⁴⁵ Although the tumorigenic effect of fine TiO₂ has been questioned,⁴⁶ collective reports suggest that TiO₂, particularly those in nanoscale form, are more toxic than fine particles. TiO₂ NPs were found to be 40-fold more potent in the induction of lung inflammation and damage than fine TiO₂.⁴⁷ The European Food Safety Authority⁴⁸ declared that TiO₂ could no longer be deemed safe when used as a food additive. For example, studies have shown that TiO₂ NPs can lead to sublethal effects on earthworm survival and reproduction.⁴⁹⁻⁵¹

Animals, including humans, are exposed to Ti through ingestion, respiration, or direct contact, with most studies focused on TiO₂ NPs. Dietary routes include the ingestion of animals of a lower trophic level,⁵² plants containing TiO₂,⁵³ and in humans, food additives with TiO₂ NPs in their formulation.^{54,55} Studies focused on exposure by respiration or direct contact have a broad range of experimental designs. In aquatic environments, the particles are suspended in water where organisms might ingest or inhale TiO₂ NPs.⁵² Terrestrial animals inhale airborne particles,⁵⁶ while in humans, dermal exposure occurs through contact with particles embedded

within formulations of personal care products, such as sunscreen.⁵⁷ Numerous toxicological studies have been conducted to assess the effects of TiO₂ NPs exposure on biota.⁵⁸⁻⁶⁰ Despite the vast number of studies, the toxicity of TiO₂ NPs on animals and humans, as well as the underlying mechanisms of action, remain topics of debate and continue to be investigated.⁴⁵

1.1. Aquatic species

Different models demonstrated that TiO₂ NPs exist in water with concentrations ranging from 0.7 to 100 µg/L in coastal zones.^{61,62} Importantly, Mueller and Nowack⁶² calculated that doses <1 µg/L are not expected to cause adverse effects (predicted no effect concentration). Toxicity studies have focused on fish, crustaceans, mollusks, nematodes, frog embryos, and coral, with most doses being sublethal but at high concentrations in the parts per million (mg/L) range.^{59,63} A small number of representative studies for each group are noted in the following sections.

1.2. Fish

In *Scophthalmus maximus* (flatfish turbot), citrate-coated TiO₂ NPs impaired lipid metabolism at sublethal concentrations with a daily intake of 1.5 mg/kg fish weight administered through pellets. Higher numbers of lipid droplets (lipid storage organelles) in the liver were associated with smaller citrate-coated TiO₂ (anatase, 5 nm), and decreased lipid droplets were linked to larger particles (anatase/rutile, 25 nm).⁶⁴ Different exposure routes (TiO₂ at 30, 50 or 100 mg/L in water where fish were submerged or through the intake of clamworms treated with TiO₂ NPs) led to similar accumulation and distribution

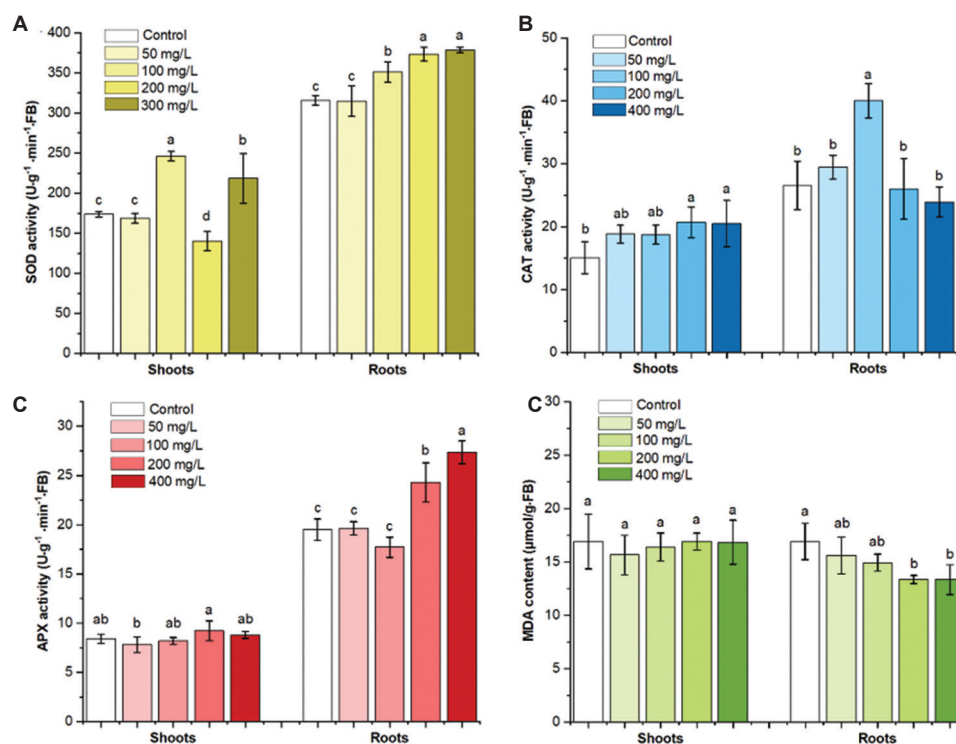


Figure S2. The effects of TiO₂ at different concentrations on the activities of various antioxidant enzymes and lipid peroxidation in coriander shoots and roots: (A) Superoxide dismutase (SOD) activity; (B) Catalase (CAT) activity; (C) Ascorbate peroxidase (APX) activity; and (D) Malondialdehyde (MDA) content. Modified from Hu *et al.*¹⁶ Copyright 2020 Elsevier.

at 0.1, 0.5, and 1 mg/L, altered liver and intestine cells were evident under continuous exposure.⁶⁸ Hou *et al.*⁵⁹ compiled a list of studies on different fishes, such as *Cyprinus carpio* (common carp), *Carassius auratus* (goldfish), *Oryzias latipes* (Japanese rice fish), and *Pimephales promelas* (fathead fish), mostly in freshwater-like media, showing that high Ti concentrations induced toxic effects, including variations in body weight, alterations to enzymatic activity, and oxidative stress (lipid peroxidation).

1.3. Crustaceans, mollusks, and other benthic zone species

Daphnia magna has been a model organism to assess both the toxic effects of TiO₂ NPs as well as the protective capabilities of TiO₂ NPs against ultraviolet (UV) radiation. Anatase TiO₂ NPs' toxicity to *D. magna* was shown to be dependent on the radiation intensity. After 8 h of sunlight exposure, the concentration causing 50% mortality (LC₅₀) was 139 μg/L under 100% exposure to natural sunlight, 778 μg/L at 50% intensity, and more than 500 mg/L at 10% sunlight exposure.⁶⁹ Conversely, 80:20 anatase/rutile TiO₂ NPs from 0.1 to 10 mg/L protected *D. magna* from UV-B light (200 μW/cm²) by absorbing and blocking the radiation.⁷⁰ As a popular test model for ecotoxicological tests, there are many studies available on *D. magna* and a

more limited number for other crustaceans. Several studies have shown species-dependent effects and variable indices of toxicity from TiO₂NP exposure.^{44,59,63,71}

Mussels feed in the bottom layer of water bodies (benthic zone) and are capable of filtering large volumes of water. Their behavior is crucial for maintaining water quality; they are vulnerable to pollutants present in the benthic zone and are valuable bioindicators of environmental health. In *Mytilus galloprovincialis* (Mediterranean mussel), TiO₂ NPs (0.05 – 5 mg/L) destabilized the lysosomal membrane in the immune cells (hemocytes) and digestive glands. These NPs induced the accumulation of neutral lipids and increased the enzymatic activity of catalase (CAT) and glutathione in the digestive gland without affecting the CAT or glutathione S-transferase activities in the gills.⁷² Leite *et al.*⁷³ reported that after 28 d of exposure to rutile TiO₂ (0, 5, 50, or 100 μg/L), *M. galloprovincialis* exhibited histopathological effects at both low (18°C) and high (22°C) temperatures, while biochemical impacts were observed only at the higher temperature. Exposure to a concentration of TiO₂ at 100 μg/L for 14 d in a medium simulating ocean warming (28°C) down regulated the messenger RNA expression related to the byssus production and impaired the byssal threads' mechanical strength of *Mytilus coruscus*.^{74,75} Wang *et al.*⁷⁶ found that the effects

of TiO₂ (0.1, 1.0, and 10 mg/L) were size (25 and 100 nm) and concentration dependent. They observed that the highest concentration (10 mg/L) and the smaller particle size (25 nm) of TiO₂ NPs were more toxic to *M. coruscus* hemocytes. Likewise, Huang *et al.*⁷⁷ observed that TiO₂ NPs induced oxidative stress in *M. coruscus*, with similar effects under seawater acidification.

1.4. Rodents and humans

Pure Ti, a biocompatible material widely used in orthopedical implants, is inert. Hip and knee replacements are often made with pure Ti or alloyed with other elements (e.g., Al, V, and Nb).⁷⁸ Unlike the highly stable Ti and Ti-alloys used in medical implants, Ti-based nanomaterials are more reactive. Characteristics such as size, shape, and crystalline structure of TiO₂ NPs influence the bioavailability and severity of TiO₂ NP's toxicity.⁵⁷ *In vitro* studies with human cell lines showed that the anatase structure exhibited higher cytotoxicity than a mixture of anatase/rutile or rutile alone.^{79,80} Moreover, a study that assessed the toxicity of different TiO₂ shapes (bipyramids, rods, and platelets) reported that toxicity was influenced by shape and light exposure, with rods after light exposure being the most harmful to cells.⁸¹ Li and Tang⁸² discussed the toxicity of TiO₂ NPs to mammalian organs, noting that TiO₂ NPs damage tissues and disrupt organ function. They also identified common mechanisms of toxicity, such as TiO₂ inducing oxidative stress, damaging organelles, and activating inflammatory responses. However, similar to aquatic species, the impacts of Ti NPs on rodents and humans vary significantly with dose and exposure scenario.

Supplementary information

2. Removal of titanium from aquatic environments

Phytoremediation, a sustainable and environmentally friendly technology, is widely recognized for its effectiveness in eliminating diverse pollutants from soil and aquatic environments.⁸³⁻⁸⁵ Among the various phytoremediation techniques, phytoextraction is the most employed approach.⁸⁶⁻⁸⁸ This technique primarily involves the extraction of environmental pollutants by accumulating plants and their subsequent translocation to the above-ground tissues, effectively eliminating contaminants from the specific environment after plant harvesting.⁸⁹⁻⁹¹ In the case of Ti removal, certain plant species, namely pedunculate oak (*Quercus robur* L.), horsetail (*Equisetum* spp.), and beach morning glory (*Ipomoea biloba*), exhibit substantial potential for phytoremediation owing to their exceptional ability to accumulate Ti.^{92,93} While the implementation of phytoremediation for Ti removal lacks

extensive engineering cases, some high-biomass tree species, such as poplar and willow trees, are extensively utilized for phytoremediation of metal elements.^{34,94,95}

The application of TiO₂ NPs for the remediation of soil heavy-metal contamination has gained attention due to their unique properties, such as high redox potential, presence of interconnected pores, eco-friendly nature, and polymorph crystalline size/shapes, as discussed earlier.⁹⁶ Notably, plants possess the ability to simultaneously absorb TiO₂ NPs and the pollutants adsorbed onto them.⁹⁷ However, earlier studies predominantly focused on investigating the phytotoxicity of TiO₂ NPs, primarily through hydroponic experiments, neglecting the potential of plants to remove TiO₂ NPs.⁹⁸⁻¹⁰⁰ More recently, several studies were carried out to explore the efficiency of phytoremediation using TiO₂ NPs as contaminants. For example, Song *et al.*³⁵ discovered that the halophyte plant species *Suaeda glauca* exhibited an ability to eliminate 60% of TiO₂ NPs from the soil with a TiO₂-NP concentration of 1,000 mg/kg.

The accumulation and removal of TiO₂ NPs in the aquatic environment (as pollution) has garnered significant attention (Figure S1B).^{38,101,102} Similar to other NPs, Ti NPs can be remediated through various technologies, such as coagulation, flocculation, sedimentation, adsorption, and membrane filtration.^{36,41,103} Conversely, addressing water pollution using the photocatalytic or absorption properties of TiO₂ has also been discussed by researchers in a number of recent publications.¹⁰⁴⁻¹⁰⁶

2.1. Coagulation, flocculation, and sediment

Coagulation, flocculation, and sedimentation are vital processes employed in conventional drinking-water treatment, offering efficient and cost-effective removal of various types of particulate matter and soluble inorganic compounds.¹⁰⁷ The neutralization of positive and negative charges on NPs is the key mechanism in coagulation for TiO₂-NP removal, achieving a removal efficiency of 90% or higher.³⁷ The overall efficiency of TiO₂-NP removal is influenced by factors such as the coagulant type and dosage, water quality, and other parameters. Studies have investigated coagulants, such as alum and those based on iron and aluminum, for TiO₂-NP removal.^{37,38,102} Notably, previous researchers have achieved high removal rates of NPs using significant amounts of coagulants, such as alum at concentrations up to 50 mg/L.³⁸ For low (1.91 ± 0.36 NTU) and medium (63.33 ± 5.37 NTU) turbidity natural waters, Ti removal rates of 98% and 99%, respectively, were obtained.³⁹ Interestingly, hydrophobic constituents in water necessitate a higher coagulant concentration compared to hydrophilic constituents to achieve the same TiO₂-NP removal rate.³⁷ According

to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the interparticle repulsive forces diminish as the media ionic strength increases due to the compression of the bilayer.¹⁰⁸⁻¹¹⁰ Consequently, the addition of NaCl or CaCl₂ enhances the removal of TiO₂ NPs.³⁶ Furthermore, the removal effectiveness is closely related to the zeta potential. Zhang *et al.*³⁶ found that TiO₂-NP removal was highest (>90%) when the zeta potential value was <10 mV, while removal was poor (<60%) when the zeta potential exceeded 35 mV.

2.2. Adsorption

The process of adsorption and adhesion is determined by various forces, such as van der Waals forces, double-layer forces as described by the DLVO theory, and non-DLVO interactions, including hydraulic forces, spatial forces, steric hindrance, and magnetic interactions.^{111,112} Inexpensive materials, including activated carbon, halloysite, and iron oxide magnetic particles, are currently utilized for NP removal.¹¹³⁻¹¹⁵ Adsorption materials possessing magnetic properties, particularly magnetic halloysite and iron oxide magnetic particles,¹¹⁵ offer the advantages of easy separation and reusability after recovery. Furthermore, TiO₂ NPs can be encapsulated by polydopamine and liposomes and subsequently removed through adsorption onto poly-L-lysine glasses coated with lecithin.⁴¹ This method does not require coagulation, flocculation, and sedimentation, and shows an average removal rate of 58%.¹¹⁶ Magnetic NPs hold great potential for TiO₂-NP removal due to their larger specific surface area. For example, Fe₃O₄-SiO₂ and Fe-C-SO₃H composites can achieve 99.7% TiO₂ removal within 30 min.⁴⁰ The authors observed that among all the mentioned techniques, the composite/magnetic NP-induced remediation was the most efficient for the removal of TiO₂ in practice.

2.3. Membrane filtration

Membrane filtration, particularly nanofiltration, is widely recognized as one of the most effective technologies for contaminant removal.¹¹⁷ Nanofiltration technology can filter out 99.9% of NPs in a solution.¹¹⁸ However, nanofiltration membranes possess small pore sizes and exhibit lower efficiency in water treatment.¹¹⁹ Conversely, microfiltration technology offers higher water treatment efficiency and can potentially achieve 99% removal of NPs.⁴² Nevertheless, the high concentration of NP agglomeration may result in a reduction of membrane pore size and pore blockage, thereby diminishing the efficiency of water treatment.¹²⁰ For example, Zhang *et al.*³⁶ discovered that microfiltration (0.45 μm) alone for TiO₂-NP removal could yield higher removal rates compared to the combined coagulation-flocculation-precipitation-microfiltration process, but with

lower water treatment efficiency. They also observed that the addition of 1.0 mM phosphate enhanced the removal of TiO₂ NPs using 0.10 μm microfiltration membranes.

2.4. Other technologies

Other techniques, including biofilm, activated sludge, and artificial wetlands, have demonstrated effectiveness in removing NPs from aqueous environments.¹²¹⁻¹²³ However, there is still relatively little information on Ti removal with these techniques. Notably, when employing bio-related water treatment methods, it is crucial to closely monitor the removal efficiency of other indicators, considering the biological toxicity and antibacterial properties associated with high concentrations of TiO₂ NPs.¹²³ For example, the presence of 50 mg/L TiO₂ NPs significantly diminished microbial diversity within activated sludge, resulting in a decrease in total nitrogen removal efficiency from 80.3% to 24.4%.¹²⁴

References

1. U.S. Geological Survey (USGS). *Mineral Commodity Summaries 2014*; 2014. Available from: <https://apps.usgs.gov/minerals-information-archives/mcs/mcs2014.pdf> [Last accessed on 2025 Jun 08].
2. Bhutada G. *This Chart Shows which Countries Produce the Most Lithium*; 2023. Available from: <https://www.weforum.org/agenda/2023/01/chart-countries-produce-lithium-world> [Last accessed on 2025 Jun 08].
3. Cornelis G, Hund-Rinke K, Kuhlbusch T, Van den Brink N, Nickel C. Fate and bioavailability of engineered nanoparticles in soils: A review. *Crit Rev Environ Sci Technol*. 2014;44(24):2720-2764.
4. Triebold S, Luvizotto GL, Tolosana-Delgado R, Zack T, von Eynatten H. Discrimination of TiO₂ polymorphs in sedimentary and metamorphic rocks. *Contrib Mineral Petrol*. 2011;161:581-596.
5. Asahi R, Taga Y, Mannstadt W, Freeman AJ. Electronic and optical properties of anatase TiO₂. *Phys Rev B*. 2000;61(11):7459-7465.
doi: 10.1103/PhysRevB.61.7459
6. Adam V, Loyaux-Lawniczak S, Labille J, *et al.* Aggregation behaviour of TiO₂ nanoparticles in natural river water. *J Nanoparticle Res*. 2016;18(1):13.
doi: 10.1007/s11051-015-3319-4
7. Li L, Yan J, Wang T, *et al.* Sub-10 nm rutile titanium dioxide nanoparticles for efficient visible-light-driven photocatalytic hydrogen production. *Nat Commun*. 2015;6(1):1-10.
8. Fan X, Wang C, Wang P, Hu B, Wang X. TiO₂ nanoparticles in sediments: Effect on the bioavailability of heavy metals in the freshwater bivalve *Corbicula fluminea*. *J Hazard Mater*. 2018;342:41-50.

- doi: 10.1016/j.jhazmat.2017.07.041
9. Owolade O, Ogunleti D. Effects of titanium dioxide on the diseases, development and yield of edible cowpea. *J Plant Prot Res.* 2008;48:329-335.
10. Feizi H, Kamali M, Jafari L, Rezvani Moghaddam P. Phytotoxicity and stimulatory impacts of nanosized and bulk titanium dioxide on fennel (*Foeniculum vulgare* Mill). *Chemosphere.* 2013;91(4):506-511.
doi: 10.1016/j.chemosphere.2012.12.012
11. Laware SL, Raskar S. Effect of titanium dioxide nanoparticles on hydrolytic and antioxidant enzymes during seed germination in onion. *Int J Curr Microbiol App Sci.* 2014;3(7):749-760.
12. Raliya R, Nair R, Chavalmane S, Wang WN, Biswas P. Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (*Solanum lycopersicum* L.) plant. *Metallomics.* 2015;7(12):1584-1594.
13. Choi HG, Moon BY, Bekhzod K, et al. Effects of foliar fertilization containing titanium dioxide on growth, yield and quality of strawberries during cultivation. *Hortic Environ Biotechnol.* 2015;56:575-581.
14. Abdel Latef AAH, Srivastava AK, El-Sadek MSA, Kordrostami M, Tran LP. Titanium dioxide nanoparticles improve growth and enhance tolerance of broad bean plants under saline soil conditions. *L Degrad Dev.* 2018;29(4):1065-1073.
15. Dawood MFA, Abeed AHA, Aldaby EES. Titanium dioxide nanoparticles model growth kinetic traits of some wheat cultivars under different water regimes. *Plant Physiol Rep.* 2019;24:129-140.
16. Hu J, Wu X, Wu F, et al. Potential application of titanium dioxide nanoparticles to improve the nutritional quality of coriander (*Coriandrum sativum* L.). *J Hazard Mater.* 2020;389:121837.
doi: 10.1016/j.jhazmat.2019.121837
17. Gohari G, Mohammadi A, Akbari A, et al. Titanium dioxide nanoparticles (TiO₂ NPs) promote growth and ameliorate salinity stress effects on essential oil profile and biochemical attributes of *Dracocephalum moldavica*. *Sci Rep.* 2020;10(1):912.
18. Sardar R, Ahmed S, Yasin NA. Titanium dioxide nanoparticles mitigate cadmium toxicity in *Coriandrum sativum* L. through modulating antioxidant system, stress markers and reducing cadmium uptake. *Environ Pollut.* 2022;292:118373.
doi: 10.1016/j.envpol.2021.118373
19. Omar SA, Elsheery NI, Pashkovskiy P, Kuznetsov V, Allakhverdiev SI, Zedan AM. Impact of titanium oxide nanoparticles on growth, pigment content, membrane stability, DNA damage, and stress-related gene expression in *Vicia faba* under saline conditions. *Horticulturae.* 2023;9(9):1030.
20. Razavizadeh R, Adabavazeh F, Mosayebi Z. Titanium dioxide nanoparticles improve element uptake, antioxidant properties, and essential oil productivity of *Melissa officinalis* L. seedlings under *in vitro* drought stress. *Environ Sci Pollut Res.* 2023;30(43):98020-98033.
21. Mahmoud NE, Abdelhameed RM. Use of titanium dioxide doped multi-wall carbon nanotubes as promoter for the growth, biochemical indices of *Sesamum indicum* L. under heat stress conditions. *Plant Physiol Biochem.* 2023;201:107844.
22. Rajakumar G, Rahuman AA, Priyamvada B, Khanna VG, Kumar DK, Sujin PJ. *Eclipta prostrata* leaf aqueous extract mediated synthesis of titanium dioxide nanoparticles. *Mater Lett.* 2012;68:115-117.
23. Ilyas M, Waris A, Khan AU, et al. Biological synthesis of titanium dioxide nanoparticles from plants and microorganisms and their potential biomedical applications. *Inorg Chem Commun.* 2021;133:108968.
24. Satti SH, Raja NI, Javed B, et al. Titanium dioxide nanoparticles elicited agro-morphological and physicochemical modifications in wheat plants to control *Bipolaris sorokiniana*. *PLoS One.* 2021;16(2):e0246880.
25. Mustafa N, Raja NI, Ilyas N, Ikram M, Mashwani ZR, Ehsan M. Foliar applications of plant-based titanium dioxide nanoparticles to improve agronomic and physiological attributes of wheat (*Triticum aestivum* L.) plants under salinity stress. *Green Process Synth.* 2021;10(1):246-257.
26. Satti SH, Raja NI, Ikram M, et al. Plant-based titanium dioxide nanoparticles trigger biochemical and proteome modifications in *Triticum aestivum* L. under biotic stress of *Puccinia striiformis*. *Molecules.* 2022;27(13):4274.
doi: 10.3390/molecules27134274
27. Abdalla H, Adarosy MH, Hegazy HS, Abdelhameed RE. Potential of green synthesized titanium dioxide nanoparticles for enhancing seedling emergence, vigor and tolerance indices and DPPH free radical scavenging in two varieties of soybean under salinity stress. *BMC Plant Biol.* 2022;22(1):560.
doi: 10.1186/s12870-022-03945-7
28. Czapek F. *Biochemie der Pflanzen*. Vol. 2. London: Forgotten Books; 1920.
29. Ramakrishna RS, Paul AA, Fonseka JPR. Uptake of titanium and iron by *Ipomoea biloba* from titaniferrous sands. *Environ Exp Bot.* 1989;29(3):293-300.
30. Cannon HL, Shacklette HT, Bastron H. *Metal Absorption by Equisetum (Horsetail)*. United States: US Geological Survey; 1968.
doi: 10.3133/b1278a
31. Yu X, Li Y, Li Y, et al. *Pongamia pinnata* inoculated with

- Bradyrhizobium liaoningense* PZHK1 shows potential for phytoremediation of mine tailings. *Appl Microbiol Biotechnol.* 2017;101:1739-1751.
32. Yu X, Kang X, Li Y, *et al.* Rhizobia population was favoured during in situ phytoremediation of vanadium-titanium magnetite mine tailings dam using *Pongamia pinnata*. *Environ Pollut.* 2019;255:113167.
doi: 10.1007/s11356-016-8242-4
33. Yu X, Shen T, Kang X, *et al.* Long-term phytoremediation using the symbiotic *Pongamia pinnata* reshaped soil micro-ecological environment. *Sci Total Environ.* 2021;774:145112.
34. Assad M, Tatin-Froux F, Blaudez D, Chalot M, Parelle J. Accumulation of trace elements in edible crops and poplar grown on a titanium ore landfill. *Environ Sci Pollut Res.* 2017;24(5):5019-5031.
doi: 10.1007/s11356-016-8242-4
35. Song U, Kim BW, Rim H, Bang JH. Phytoremediation of nanoparticle-contaminated soil using the halophyte plant species *Suaeda glauca*. *Environ Technol Innov.* 2022;28:102626.
doi: 10.1016/j.eti.2022.102626
36. Zhang C, Lohwacharin J, Takizawa S. Effect of ions on removal of TiO₂ Nanoparticles by coagulation and microfiltration. *Environ Eng Sci.* 2017;35(5):420-429.
doi: 10.1089/ees.2017.0057
37. Serrão Sousa V, Corniciuc C, Ribau Teixeira M. The effect of TiO₂ nanoparticles removal on drinking water quality produced by conventional treatment C/F/S. *Water Res.* 2017;109:1-12.
doi: 10.1016/j.watres.2016.11.030
38. Honda RJ, Keene V, Daniels L, Walker SL. Removal of TiO₂ Nanoparticles during primary water treatment: Role of coagulant type, dose, and nanoparticle concentration. *Environ Eng Sci.* 2014;31(3):127-134.
doi: 10.1089/ees.2013.0269
39. Sousa VS, Ribau Teixeira M. Removal of a mixture of metal nanoparticles from natural surface waters using traditional coagulation process. *J Water Process Eng.* 2020;36:101285.
doi: 10.1016/j.jwpe.2020.101285
40. Bakhteeva IA, Medvedeva IV, Filinkova MS, *et al.* Magnetic sedimentation of nonmagnetic TiO₂ nanoparticles in water by heteroaggregation with Fe-based nanoparticles. *Sep Purif Technol.* 2019;218:156-163.
doi: 10.1016/j.seppur.2019.02.043
41. Taylor AT Iraganje E, Lai EPC. A method for the separation of TiO₂ nanoparticles from Water through encapsulation with lecithin liposomes followed by adsorption onto poly(L-lysine) coated glass surfaces. *Colloids Surf B Biointerfaces.* 2020;187:110732.
doi: 10.1016/j.colsurfb.2019.110732
42. Gopakumar DA, Pasquini D, Henrique MA, de Moraes LC, Grohens Y, Thomas S. Meldrum's acid modified cellulose nanofiber-based polyvinylidene fluoride microfiltration membrane for dye water treatment and nanoparticle removal. *ACS Sustain Chem Eng.* 2017;5(2):2026-2033.
doi: 10.1021/acssuschemeng.6b02952
43. Lee KP, Trochimowicz HJ, Reinhardt CF. Pulmonary response of rats exposed to titanium dioxide (TiO₂) by inhalation for two years. *Toxicol Appl Pharmacol.* 1985;79(2):179-192.
doi: 10.1016/0041-008x(85)90339-4
44. Menard A, Drobne D, Jemec A. Ecotoxicity of nanosized TiO₂. Review of *in vivo* data. *Environ Pollut.* 2011;159(3):677-684.
doi: 10.1016/j.envpol.2010.11.027
45. Luo Z, Li Z, Xie Z, *et al.* Rethinking nano-TiO₂ safety: Overview of toxic effects in humans and aquatic animals. *Small.* 2020;16(36):e2002019.
doi: 10.1002/smll.202002019
46. Olin SS. The relevance of the rat lung response to particle overload for human risk assessment: A workshop consensus report. *Inhal Toxicol.* 2000;12(1-2):1-17.
doi: 10.1080/08958370050029725
47. Sager TM, Kommineni C, Castranova V. Pulmonary response to intratracheal instillation of ultrafine versus fine titanium dioxide: Role of particle surface area. *Part Fibre Toxicol.* 2008;5:17.
doi: 10.1186/1743-8977-5-17
48. EFSA Panel on Food Additives and Flavourings (FAF), Younes M, Aquilina G, *et al.* Safety assessment of titanium dioxide (E171) as a food additive. *Efsa J.* 2021;19(5):e06585.
49. Chouhan N, Tripathi G. Biological effects of nanoparticles (NPS) with special reference to ZnO NPs and earthworm. *Biochem Cell Arch.* 2020;20(2):4389-4410.
50. García-Gómez C, Babín M, García S, Almendros P, Pérez RA, Fernández MD. Joint effects of zinc oxide nanoparticles and chlorpyrifos on the reproduction and cellular stress responses of the earthworm *Eisenia andrei*. *Sci Total Environ.* 2019;688:199-207.
doi: 10.1016/j.scitotenv.2019.06.083
51. Samarasinghe SVAC, Krishnan K, Aitken RJ, Naidu R, Megharaj M. Multigenerational effects of TiO₂ rutile nanoparticles on earthworms. *Environ Pollut.* 2023;336:122376.
52. Wang Z, Yin L, Zhao J, Xing B. Trophic transfer and accumulation of TiO₂ nanoparticles from clamworm (*Perinereis aibuhitensis*) to juvenile turbot (*Scophthalmus maximus*) along a marine benthic food chain. *Water Res.* 2016;95:250-259.
doi: 10.1016/j.watres.2016.03.027

53. Wu J, Bosker T, Vijver MG, Peijnenburg WJGM. Trophic transfer and toxicity of (Mixtures of) Ag and TiO₂ Nanoparticles in the lettuce-terrestrial snail food chain. *Environ Sci Technol.* 2021;55(24):16563-16572.
doi: 10.1021/acs.est.1c05006
54. Boutillier S, Fourmentin S, Laperche B. History of titanium dioxide regulation as a food additive: A review. *Environ Chem Lett.* 2022;20(2):1017-1033.
doi: 10.1007/s10311-021-01360-2
55. Han H, Yang M, Yoon C, *et al.* Toxicity of orally administered food-grade titanium dioxide nanoparticles. *J Appl Toxicol.* 2021;41(7):1127-1147.
doi: 10.1002/jat.4099
56. Pujalté I, Dieme D, Haddad S, Serventi AM, Bouchard M. Toxicokinetics of titanium dioxide (TiO₂) nanoparticles after inhalation in rats. *Toxicol Lett.* 2017;265:77-85.
doi: 10.1016/j.toxlet.2016.11.014
57. Pelclova D, Navratil T, Kacerova T, *et al.* NanoTiO₂ sunscreen does not prevent systemic oxidative stress caused by UV radiation and a minor amount of NanoTiO₂ is absorbed in humans. *Nanomaterials (Basel).* 2019;9(6):888.
doi: 10.3390/nano9060888
58. Ayorinde T, Sayes CM. An updated review of industrially relevant titanium dioxide and its environmental health effects. *J Hazard Mater Lett.* 2023;4:100085.
doi: 10.1016/j.hazl.2023.100085
59. Hou J, Wang L, Wang C, *et al.* Toxicity and mechanisms of action of titanium dioxide nanoparticles in living organisms. *J Environ Sci.* 2019;75:40-53.
doi: 10.1016/j.jes.2018.06.010
60. Shi H, Magaye R, Castranova V, Zhao J. Titanium dioxide nanoparticles: A review of current toxicological data. *Part Fibre Toxicol.* 2013;10:15.
doi: 10.1186/1743-8977-10-15
61. Garner KL, Suh S, Keller AA. Assessing the risk of engineered nanomaterials in the environment: Development and application of the nanoFate Model. *Environ Sci Technol.* 2017;51(10):5541-5551.
doi: 10.1021/acs.est.6b05279
62. Mueller NC, Nowack B. Exposure modeling of engineered nanoparticles in the environment. *Environ Sci Technol.* 2008;42(12):4447-4453.
doi: 10.1021/es7029637
63. Sharma S, Sharma RK, Gaur K, *et al.* Fueling a hot debate on the application of TiO₂ nanoparticles in sunscreen. *Mater (Basel).* 2019;12(14):2317.
doi: 10.3390/ma12142317
64. Fonseca E, Vázquez M, Rodríguez-Lorenzo L, *et al.* Getting fat and stressed: Effects of dietary intake of titanium dioxide nanoparticles in the liver of turbot *Scophthalmus maximus*. *J Hazard Mater.* 2023;458:131915.
doi: 10.1016/j.jhazmat.2023.131915
65. Lei L, Qiao K, Guo Y, Han J, Zhou B. Titanium dioxide nanoparticles enhanced thyroid endocrine disruption of pentachlorophenol rather than neurobehavioral defects in zebrafish larvae. *Chemosphere.* 2020;249:126536.
doi: 10.1016/j.chemosphere.2020.126536
66. Prakash J, Venkatesan M, Sebastian Prakash JJ, *et al.* Investigations on the *in-vivo* toxicity analysis of reduced graphene oxide/TiO₂ nanocomposite in zebrafish embryo and larvae (*Danio rerio*). *Appl Surf Sci.* 2019;481:1360-1369.
doi: 10.1016/j.apsusc.2019.03.287
67. Abegoda-Liyanage CS, Pathiratne A. Comparison of toxicity of nano and bulk titanium dioxide on Nile tilapia (*Oreochromis niloticus*): Acetylcholinesterase activity modulation and DNA damage. *Bull Environ Contam Toxicol.* 2023;110(6):101.
doi: 10.1007/s00128-023-03746-0
68. De Silva WAPM, Pathiratne A. Nano-titanium dioxide induced genotoxicity and histological lesions in a tropical fish model, Nile tilapia (*Oreochromis niloticus*). *Environ Toxicol Pharmacol.* 2023;98:104043.
doi: 10.1016/j.etap.2022.104043
69. Mansfield CM, Alloy MM, Hamilton J, *et al.* Photo-induced toxicity of titanium dioxide nanoparticles to *Daphnia magna* under natural sunlight. *Chemosphere.* 2015;120:206-210.
doi: 10.1016/j.chemosphere.2014.06.075
70. Liu J, Wang WX. The protective roles of TiO₂ nanoparticles against UV-B toxicity in *Daphnia magna*. *Sci Total Environ.* 2017;593-594:47-53.
doi: 10.1016/j.scitotenv.2017.03.155
71. Cattaneo A, Gornati R, Chiriva Internati M, Bernardini GB. Ecotoxicology of nanomaterials: The role of invertebrate testing. *Invertebr Surviv J.* 2009;6:78-97.
72. Canesi L, Fabbri R, Gallo G, Vallotto D, Marcomini A, Pojana G. Biomarkers in *Mytilus galloprovincialis* exposed to suspensions of selected nanoparticles (Nano carbon black, C60 fullerene, Nano-TiO₂, Nano-SiO₂). *Aquat Toxicol.* 2010;100(2):168-177.
doi: 10.1016/j.aquatox.2010.04.009
73. Leite C, Coppola F, Monteiro R, *et al.* Toxic impacts of rutile titanium dioxide in *Mytilus galloprovincialis* exposed to warming conditions. *Chemosphere.* 2020;252:126563.
doi: 10.1016/j.chemosphere.2020.126563
74. Li S, Chen H, Liu C, *et al.* Dietary exposure to nTiO₂ reduces

- byssus performance of mussels under ocean warming. *Sci Total Environ.* 2023;881:163499.
doi: 10.1016/j.scitotenv.2023.163499
75. Wang T, Huang X, Jiang X, Hu M, Huang W, Wang Y. Differential *in vivo* hemocyte responses to nano titanium dioxide in mussels: Effects of particle size. *Aquat Toxicol.* 2019;212:28-36.
doi: 10.1016/j.aquatox.2019.04.012
76. Wang S, Cai LM, Wen HH, Luo J, Wang QS, Liu X. Spatial distribution and source apportionment of heavy metals in soil from a typical county-level city of Guangdong Province, China. *Sci Total Environ.* 2019;655:92-101.
doi: 10.1016/j.scitotenv.2018.11.244
77. Huang X, Liu Z, Xie Z, *et al.* Oxidative stress induced by titanium dioxide nanoparticles increases under seawater acidification in the thick shell mussel *Mytilus coruscus*. *Mar Environ Res.* 2018;137:49-59.
doi: 10.1016/j.marenvres.2018.02.029
78. Hanawa T. Titanium-tissue interface reaction and its control with surface treatment. *Front Bioeng Biotechnol.* 2019;7:170.
doi: 10.3389/fbioe.2019.00170
79. Sayes CM, Wahi R, Kurian PA, *et al.* Correlating nanoscale titania structure with toxicity: A cytotoxicity and inflammatory response study with human dermal fibroblasts and human lung epithelial cells. *Toxicol Sci.* 2006;92(1):174-185.
doi: 10.1093/toxsci/kfj197
80. Xue C, Wu J, Lan F, *et al.* Nano titanium dioxide induces the generation of ros and potential damage in HaCaT Cells Under UVA irradiation. *J Nanosci Nanotechnol.* 2010;10(12):8500-8507.
doi: 10.1166/jnn.2010.2682
81. Gea M, Bonetta S, Iannarelli L, *et al.* Shape-engineered titanium dioxide nanoparticles (TiO₂-NPs): Cytotoxicity and genotoxicity in bronchial epithelial cells. *Food Chem Toxicol.* 2019;127:89-100.
doi: 10.1016/j.fct.2019.02.043
82. Li C, Tang M. The toxicological effects of nano titanium dioxide on target organs and mechanisms of toxicity. *J Appl Toxicol.* 2023;44(2):152-164.
doi: 10.1002/jat.4534
83. Hou D, Al-Tabbaa A, O'Connor D, *et al.* Sustainable remediation and redevelopment of brownfield sites. *Nat Rev Earth Environ.* 2023;4(4):271-286.
doi: 10.1038/s43017-023-00404-1
84. Wang L, Hou D, Shen Z, *et al.* Field trials of phytomining and phytoremediation: A critical review of influencing factors and effects of additives. *Crit Rev Environ Sci Technol.* 2020;50(24):2724-2774.
85. Zhao S, Qin L, Wang L, *et al.* Soil bacterial community responses to cadmium and lead stabilization during ecological restoration of an abandoned mine. *Soil Use Manag.* 2022;38(3):1459-1469.
doi: 10.1111/sum.12797
86. Bian X, Cui J, Tang B, Yang L. Chelant-induced phytoextraction of heavy metals from contaminated soils: A review. *Polish J Environ Stud.* 2018;27(6):2417-2424.
doi: 10.15244/pjoes/81207
87. Jin Y, Wang L, Song Y, *et al.* Integrated life cycle assessment for sustainable remediation of contaminated agricultural soil in China. *Environ Sci Technol.* 2021;55(17):12032-12042.
doi: 10.1021/acs.est.1c02535
88. Xiao J, Li X, Cao Y, Chen G. Does micro/nano biochar always good to phytoremediation? A case study from multiple metals contaminated acidic soil using *Salix jiangsuensis* "172." *Carbon Res.* 2023;2(1):21.
doi: 10.1007/s44246-023-00053-5
89. Evangelou MWH, Ebel M, Schaeffer A. Chelate assisted phytoextraction of heavy metals from soil. Effect, mechanism, toxicity, and fate of chelating agents. *Chemosphere.* 2007;68(6):989-1003.
doi: 10.1016/j.chemosphere.2007.01.062
90. Hou D. Sustainable soil management for food security. *Soil Use Manag.* 2023;39(1):1.
doi: 10.1111/SUM.12883
91. Shi L, Li J, Palansooriya KN, *et al.* Modeling phytoremediation of heavy metal contaminated soils through machine learning. *J Hazard Mater.* 2023;441:129904.
doi: 10.1016/j.jhazmat.2022.129904
92. Dumon JC, Ernst WHO. Titanium in plants. *J Plant Physiol.* 1988;133(2):203-209.
doi: 10.1016/s0176-1617(88)80138-x
93. Lyu S, Wei X, Chen J, Wang C, Wang X, Pan D. Titanium as a beneficial element for crop production. *Front Plant Sci.* 2017;8:597.
doi: 10.3389/fpls.2017.00597
94. Pulford I. Phytoremediation of heavy metal-contaminated land by trees-a review. *Environ Int.* 2003;29(4):529-540.
doi: 10.1016/s0160-4120(02)00152-6
95. Wang L, Hou D. Plant-based strategies for the sustainable management of soil contamination. In: *Soil Constraints Product.* United States: CRC Press; 2023. p. 25-44.
doi: 10.1201/9781003093565-2
96. Zhou P, Adeel M, Shakoob N, *et al.* Application of nanoparticles alleviates heavy metals stress and promotes

- plant growth: An overview. *Nanomaterials (Basel)*. 2020;11(1):26.
doi: 10.3390/nano11010026
97. Hussain A, Ali S, Rizwan M, *et al.* Responses of wheat (*Triticum aestivum*) plants grown in a Cd contaminated soil to the application of iron oxide nanoparticles. *Ecotoxicol Environ Saf*. 2019;173:156-164.
doi: 10.1016/j.ecoenv.2019.01.118
98. Deng Y, Petersen EJ, Challis KE, *et al.* Multiple method analysis of TiO₂ nanoparticle uptake in Rice (*Oryza sativa* L.) Plants. *Environ Sci Technol*. 2017;51(18):10615-10623.
doi: 10.1021/acs.est.7b01364
99. Ji Y, Zhou Y, Ma C, *et al.* Jointed toxicity of TiO₂ NPs and Cd to rice seedlings: NPs alleviated Cd toxicity and Cd promoted NPs uptake. *Plant Physiol Biochem*. 2017;110:82-93.
doi: 10.1016/j.plaphy.2016.05.010
100. Mohammadi H, Esmailpour M, Gheranpaye A. Effects of TiO₂ nanoparticles and water-deficit stress on morpho-physiological characteristics of dragonhead (*Dracocephalum moldavica* L.) plants. *Acta Agric Slov*. 2016;107(2):385-396.
doi: 10.14720/aas.2016.107.2.11
101. Loeb SK, Alvarez PJJ, Brame JA, *et al.* The technology horizon for photocatalytic water treatment: Sunrise or sunset? *Environ Sci Technol*. 2019;53(6):2937-2947.
doi: 10.1021/acs.est.8b05041
102. Sun Y, Yu Y, Li D, Zhai J, Zheng H. Enhanced coagulation for TiO₂-NPs removal by using a hybrid flocculant. *Sep Purif Technol*. 2021;277:119480.
doi: 10.1016/j.seppur.2021.119480
103. Zhang J, Jia W, Yan Y, Zhao S. Coagulation removal and recycling strategy of TiO₂ nanoparticles based on *Enteromorpha prolifera* polysaccharide application. *J Water Process Eng*. 2022;49:103083.
doi: 10.1016/j.jwpe.2022.103083
104. Gopinath KP, Madhav NV, Krishnan A, Malolan R, Rangarajan G. Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review. *J Environ Manage*. 2020;270:110906.
doi: 10.1016/j.jenvman.2020.110906
105. Etafo NO, Bamidele MO, Bamisaye A, Alli YA. Revolutionizing photocatalysis: Unveiling efficient alternatives to titanium (IV) oxide and zinc oxide for comprehensive environmental remediation. *J Water Process Eng*. 2024;62:105369.
106. Rosa D, Abbasova N, Di Palma L. Titanium dioxide nanoparticles doped with iron for water treatment via photocatalysis: A review. *Nanomaterials (Basel)*. 2024;14(3):293.
doi: 10.3390/nano14030293
107. Xu F. Review of analytical studies on TiO₂ nanoparticles and particle aggregation, coagulation, flocculation, sedimentation, stabilization. *Chemosphere*. 2018;212:662-677.
doi: 10.1016/j.chemosphere.2018.08.108
108. Gao J, Wang L, Ok YS, *et al.* Nanoplastic stimulates metalloid leaching from historically contaminated soil via indirect displacement. *Water Res*. 2022;218:118468.
doi: 10.1016/j.watres.2022.118468
109. Ninham BW. On progress in forces since the DLVO theory. *Adv Colloid Interface Sci*. 1999;83(1-3):1-17.
doi: 10.1016/s0001-8686(99)00008-1
110. Wang JL, Alasonati E, Fisticaro P, Benedetti MF. Titanium nanoparticles fate in small-sized watersheds under different land-uses. *J Hazard Mater*. 2022;422:126695.
doi: 10.1016/j.jhazmat.2021.126695
111. Wang L, Guo J, Wang H, Luo J, Hou D. Stimulated leaching of metalloids along 3D-printed fractured rock vadose zone. *Water Res*. 2022;226:119224.
doi: 10.1016/j.watres.2022.119224
112. Wang S, Gao P, Zhang Q, *et al.* Application of biochar and organic fertilizer to saline-alkali soil in the Yellow River Delta: Effects on soil water, salinity, nutrients, and maize yield. *Soil Use Manag*. 2022;38(4):1679-1692.
doi: 10.1111/sum.12829
113. Janacek D, Kvitek L, Karlikova M, Pospiskova K, Safarik I. Removal of silver nanoparticles with native and magnetically modified halloysite. *Appl Clay Sci*. 2018;162:10-14.
doi: 10.1016/j.clay.2018.05.024
114. Piplai T, Kumar A, Alappat BJ. Removal of mixture of ZnO and CuO nanoparticles (NPs) from water using activated carbon in batch kinetic studies. *Water Sci Technol*. 2017;75(4):928-943.
doi: 10.2166/wst.2016.521
115. Zhou XX, Li YJ, Liu JF. Highly efficient removal of silver-containing nanoparticles in waters by aged iron oxide magnetic particles. *ACS Sustain Chem Eng*. 2017;5(6):5468-5476.
doi: 10.1021/acssuschemeng.7b00797
116. Syafuiddin A, Fulazzaky MA, Salmiati S, Kueh ABH, Fulazzaky M, Salim MR. Silver nanoparticles adsorption by the synthetic and natural adsorbent materials: An exclusive review. *Nanotechnol Environ Eng*. 2020;5(1):1.
doi: 10.1007/s41204-019-0065-3
117. Mohammad AW, Teow YH, Ang WL, Chung YT, Oatley-Radcliffe DL, Hilal N. Nanofiltration membranes review: Recent advances and future prospects. *Desalination*. 2015;356:226-254.

- doi: 10.1016/j.desal.2014.10.043
118. Sadik OA, Du N, Yazgan I, Okello V. Nanostructured membranes for water purification. In: *Nanotechnology Applications for Clean Water*. Netherlands: Elsevier Inc.; 2014. p. 95-108.
doi: 10.1016/b978-1-4557-3116-9.00006-8
119. Wang Z, Wang Z, Lin S, *et al.* Nanoparticle-templated nanofiltration membranes for ultrahigh performance desalination. *Nat Commun*. 2018;9(1):2004.
doi: 10.1038/s41467-018-04467-3
120. Richards HL, Baker PGL, Iwuoha E. Metal nanoparticle modified polysulfone membranes for use in wastewater treatment: A critical review. *J Surf Eng Mater Adv Technol*. 2012;2(3):183-193.
doi: 10.4236/jsemat.2012.223029
121. Ebrahimbabaie P, Meeinkuirt W, Pichtel J. Phytoremediation of engineered nanoparticles using aquatic plants: Mechanisms and practical feasibility. *J Environ Sci*. 2020;93:151-163.
doi: 10.1016/j.jes.2020.03.034
122. Park HJ, Kim HY, Cha S, *et al.* Removal characteristics of engineered nanoparticles by activated sludge. *Chemosphere*. 2013;92(5):524-528.
doi: 10.1016/j.chemosphere.2013.03.020
123. Walden C, Zhang W. Biofilms versus activated sludge: Considerations in metal and metal oxide nanoparticle removal from wastewater. *Environ Sci Technol*. 2016;50(16):8417-8431.
doi: 10.1021/acs.est.6b01282
124. Zheng X, Chen Y, Wu R. Long-term effects of titanium dioxide nanoparticles on nitrogen and phosphorus removal from wastewater and bacterial community shift in activated sludge. *Environ Sci Technol*. 2011;45(17):7284-7290.
doi: 10.1021/es2008598