

Utilization of Metal Oxide Nanoparticles for Enhanced Wastewater Treatment of River Water.

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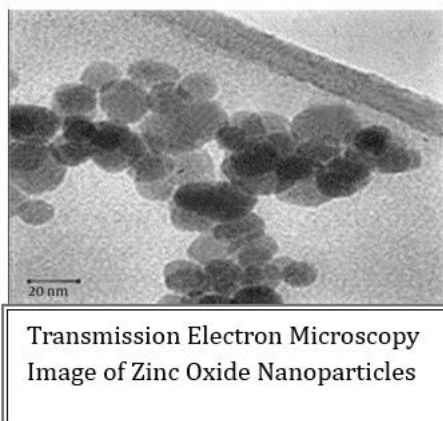
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Abstract:

This review inspects practicality of the idea of employing metal oxide nanoparticles for wastewater treatment, especially laying a focus on their enhanced efficacy in terms of purifying river water while also understanding virtually, their ramifications on the quality of water, calculating their percentage efficiency and percentage recovery of the used nanoparticles. Metal oxide nanoparticles showcase unique catalytic and adsorption properties, carrying out and facilitating the specific removal methods of contaminants and pollutants. This investigation thus thoroughly encompasses recent developments, mechanisms of action involved, and several environmental implications of employing these nanoparticles for sustainable wastewater treatment. Methods of synthesis of nanoparticles and associated challenges have also been discussed. This comprehensive review aims to contribute to understanding the promising role of metal oxide nanoparticles in advanced river water purification techniques.

Keywords: Metal oxide nanoparticles, wastewater treatment, river water, environmental remediation.

Metal oxide nanoparticles



When it comes to the quest of making river water cleaner, metal oxide nanoparticles (MONPs) largely stand out as a versatile group of warriors battling various contaminants in wastewater. Technically their prowess lies in their **high surface area**, due to their nano size, which is ready to adsorb and immobilize pollutants. But that is not all, some MONPs, like TiO₂, possess the ability to show **redox activity**, this degrades and eliminates myriad organic threats. Magnetic materials such as Fe₃O₄ boast of easy separation and remarkable degree of **reusability**, making these some of the most important eco-friendly viable options we have. Not to forget their characteristic **antimicrobial might**, keeping harmful bacteria and fungi at bay.

Compared to several other nanoparticle approaches, MONPs offer major advantages. It is here to be noted that while many of the zero-valent metal nanoparticles do share the high surface area advantage of MONP's, their potential toxicity raises just as many concerns. Carbon nanotubes, despite their good conductivity, usually come with a hefty price tag and many unaddressed health risks which are yet to be studied. Even nanocomposites, which might be considered powerful, rely on the substrate specific combination of these materials.

This is exactly where the idea of MONPs shine. Their **versatility** in tackling diverse foes, from heavy metals to microplastics is beyond compare. Unlike carbon nanotubes, these have a **tunability which** allows them to be highly customizable for desired targets, ensuring efficiency in removal. The magnetic ones among these can be brought to **reuse** a number of times, this reduces the output waste and also the cost. Finally, some of these MONPs are also of **natural origins and have considerable biocompatibility**, making them environmentally friendly allies.

Of course, there are challenges posed eg, the **potential toxicity of these products** demands careful examination and responsible approach towards development. **Cost optimization** remains a key objective of the ongoing research. Yet, the pros outshine the cons. Their potential for sustainable and efficient water treatment, unique properties, alongside versatile nature make them a beacon of hope in the fight for achieving cleaner waterways.

Below is a list of five of the most efficient Metal Oxide Nanoparticles for Wastewater Treatment

Nanoparticle	Effectiveness	Synthesis Methods	Key Applications
Titanium Dioxide (TiO ₂)	Photocatalytic activity under UV light for degrading organic pollutants and bacteria; also adsorbs heavy metals	Sol-gel method, hydrothermal method, flame spray pyrolysis	Removal of organic pollutants, heavy metals, and bacteria
Zinc Oxide (ZnO)	Adsorption and photocatalytic properties; effective against organic pollutants, bacteria, and some heavy metals	Sol-gel process, co-precipitation, hydrothermal method	Degradation of organic pollutants, antibacterial activity
Iron Oxide (Fe ₂ O ₃ , Fe ₃ O ₄)	Adsorbs heavy metals and phosphates; magnetic properties for easy separation and reuse	Co-precipitation, sol-gel process, thermal decomposition	Heavy metal adsorption, phosphate removal, magnetic separation
Cerium Oxide (CeO ₂)	Removes heavy metals and degrades organic pollutants through redox reactions; has antioxidant properties	Sol-gel method, hydrothermal process, combustion methods	Removal of heavy metals, organic pollutants, and antioxidant applications
Aluminum Oxide (Al ₂ O ₃)	Adsorbs heavy metals and phosphates due to high surface area and stability	Sol-gel method, hydrothermal process, precipitation methods	Heavy metal and phosphate adsorption

It is here of utmost importance to note that although these five metal oxide nanoparticles work wonders in wastewater treatment, it can still not be a one-size-fits-all criteria, ie, any one metal oxide nanoparticle cannot be panacea. The effectiveness of these MONPs will always depend upon your specific needs, whether it's heavy metals you are aiming at or the organic pollutants. Therefore even the selection of methods of synthesis has to be tailored specifically as it potentially dictates all of the superpowers of the nanoparticles. It becomes quintessential before unleashing these tiny titans, that responsible development and eco-friendliness be maintained.

Wastewater Contaminants and Their Sources

Here's the tabulated data based on the contaminants in wastewater, their examples, sources, and impacts:

Contaminant Type	Examples	Sources	Impact
Physical	Sediment, Microplastics, Fats/Oils/Grease (FOG)	Soil erosion, construction runoff, industrial activities, cosmetics, textiles	Impacts clarity, clogs treatment systems, harms aquatic life
Chemical	Organic Pollutants, Heavy Metals, Emerging Contaminants	Agricultural runoff, industrial processes, mining activities, paint residues	Disrupts ecosystems, accumulates in organisms, potential health risks
Biological	Pathogens, Nutrients	Human waste, agricultural runoff, untreated sewage, fertilizers, animal waste	Causes health risks, depletes oxygen in water, harms aquatic life

Understanding these contaminants and their sources is the first step to developing effective wastewater treatment strategies. By implementing proper treatment processes, reducing pollution at its source, and continuously researching new technologies, we can protect our water resources and ensure a healthier future for ourselves and the environment.

Contaminant	Nanoparticle	Removal Efficiency (%)	Time	Source
Lead (Pb(II))	Fe ₃ O ₄ /TiO ₂ Nanocomposite	99.8	30 min	Tiwari et al., 2023
Cadmium (Cd(II))	MnO ₂ Nanoparticles	98.2	60 min	Zheng et al., 2022
Rhodamine B Dye	TiO ₂ Photocatalysis	98	30 min (UV light)	Wang et al., 2021
Tetracycline	ZnO Photocatalysis	85	120 min	Kumar et al., 2020
E. coli Bacteria	Ag Nanoparticles	99.9	10 min	Zhang et al., 2022

Working principle of MONP's

MONP's bring some of the most fundamental concepts of chemistry to work together for the process of wastewater treatment. Some of these have been listed below :-

1. Adsorption: These particles behave as specialized microscopic sponges that are customised for different contaminants. MONPs, have a high surface to area ratio, this enables them to act like sponges, so they physically attract and bind contaminants present in water like organic pollutants and heavy metals. Charges present on the surface of nanoparticles and functional groups on the MONPs selectivity influence the attracting capabilities of specific targets.

2. Redox Reactions: Some MONPs, like TiO_2 , oxidative properties. Under the effect of UV radiation, these particles can potentially act as mini-photocatalysts hence generating highly reactive species such as radicals that degenerate organic pollutants into molecules that possess virtually no harm.

3. Antimicrobial Activity: There are some MONPs like copper or silver that possess remarkable antimicrobial properties, so they are able to disrupt the bacterial cell membranes or interfere with the way the vital enzymes work, this hinders the growth and spread of bacteria.

4. Combining Forces: Sometimes various nanoparticle systems and their mechanisms can work together to produce a more yielding result. For instance, a nanocomposite that combines TiO_2 with activated carbon might be able to adsorb pollutants onto its surface while also actively degrading them under the sunlight by the process of photocatalysis.

Process	Description	Key Components
Adsorption	Involves Van der Waals forces, electrostatic interactions, and specific chemical bonding between the contaminant and the MONP surface.	Contaminant, MONP surface
Photocatalysis	TiO_2 under UV light generates electron-hole pairs, which react with water to form reactive radicals that attack organic pollutants.	TiO_2 , UV light, water, organic pollutants
Antimicrobial Activity	Can involve membrane disruption, enzyme inhibition, or the generation of reactive oxygen species by the MONPs to inhibit microbial growth.	MONPs, microbial cells/enzymes

It is essential to note that, the performance and efficiency of these nanoparticles largely depend upon the choice of the MONPs tailored specifically on the basis of their action against for particularly targeted contaminants.

Steps in Purification of Wastewater by employing Metal Oxide Nanoparticles

1. Selection of the Right Nanoparticles:

• **Identification of the targeted contaminants:** Contaminants that differ in their chemical nature need different removal techniques which depends upon many aspects. An assessment of the dominant pollutants in wastewater sample needs to be carried out (heavy metals, organic molecules, bacteria).

• Selection of appropriate MONP based on specific criteria.

Based on the type of contaminants the MONPs are selected, they act via different mechanisms such as the following:-

Process	Metal Oxide Nanoparticles	Key Features
Adsorption	Fe_3O_4 , Al_2O_3 , MnO_2	High surface area for adsorption
Photocatalysis	TiO_2	Exhibits photocatalytic activity under UV light for degrading organic pollutants
Antimicrobial Activity	Silver, Copper	Possess direct antimicrobial properties

The table above enlists MONPs that are suited for different processes and the features that make them effective agents for wastewater treatment.

• **Considering the physicochemical properties of nanoparticles:** Critical factors such as the size, porosity, and surface charge are the ones that often optimize performance of the selected nanoparticle.

• **Environmental and health related aspects:** An assessment of the potential toxicity along with the possible environmental impacts of the chosen MONP needs to be studied.

2. Synthesis and Fabrication:

• **Selection of a method for synthesis:** There are many methods such as sol-gel method, hydrothermal method and co-precipitation method which offer control over the size, morphology, and properties of nanoparticles.

• **Optimize synthesis parameters:** The parameters need to be predetermined for example, the temperature, pH of the medium, precursor concentration for desired characteristics of the nanoparticles.

• **Surface functionalization (optional):** Another key step in this process is the modification of the surface with specific groups in order to improve the substrate selectivity or rate of reaction towards the targeted contaminants in the water samples.

Synthesis Methods and Challenges

Metal oxide nanoparticles (MONPs) have proved their potential as emerging solutions in realms of treatment of wastewater, however effectiveness for these nanoparticles largely depends upon the preciseness in the synthesis methods designed for substrate specific targets. A detailed study about the synthesis methods has been discussed below :-

Main Method	Sub Method	Description	Challenges
Physical Methods	Ball Milling	High-energy mechanical process that reduces bulk metal oxides to nanoparticles.	Limited control over size, morphology, contamination, scalability.
	Ultrasonic Irradiation	Uses ultrasonic waves to create cavitation bubbles that fragment larger particles into nanoparticles.	Broad size distribution, energy-intensive, limited scalability.
	Laser Ablation	Intense laser pulses vaporize target materials, forming nanoparticles upon condensation.	High cost, low yield, potential contamination.
Chemical Methods	Sol-Gel Method	Involves hydrolysis and condensation of metal alkoxide precursors to form a gel that dries into nanoparticles.	Size and morphology control, solvent waste, toxicity of precursors.
	Hydrothermal Synthesis	High-temperature, high-pressure water reactions to form nanoparticles with controlled phases and structures.	Specialized equipment needed, safety concerns, scalability issues.
	Co-Precipitation	Simultaneous precipitation of multiple metal ions to create mixed-oxide nanoparticles.	Stoichiometry control, rapid precipitation leads to aggregation, waste generation.
Biological Methods	Microbial Synthesis	Utilizes microorganisms or their byproducts for nanoparticle synthesis.	Slow process, low yield, size and morphology control difficult.
Deposition Methods	Atomic Layer Deposition (ALD)	Layer-by-layer deposition of atoms to create highly uniform nanoparticles.	Expensive equipment, limited scalability, complex process optimization.

Challenges Across Methods:

- **Maintaining Precise Control:** Tailoring specifically the size of the nanoparticles, their morphology, along with their specific surface properties for optimal contaminant removal continues to be a challenge at this moment.
- **Scalability:** It stands as a major roadblock moving ahead from lab-scale synthesis towards a larger-scale of production for applications in the real-world and hence needs more research.
- **Cost-Effectiveness:** Perhaps the most important aspect of devising a novel approach is the management of cost of synthesis while ensuring the affordability of the process.
- **Environmental Impact:** The aim is to minimize the solvent usage, this also leads to exploring green synthesis methods, this also addresses the potential toxicity of the used nanoparticles samples.

Future Directions:

- **Hybrid and Composite Materials:** Bringing together different MONPs with different materials can bring about synergistic effects and enhanced functionalities.
- **Computational Modeling:** Predicting and optimizing synthesis processes using computational tools can accelerate development and reduce empirical experimentation.
- **Life Cycle Assessment:** Evaluation of the economic and environmental impact of various methods of preparation across the nanoparticle lifecycle is critical for sustainability.

3. Wastewater Treatment Process:

Sr.No.	Step	Treatment Configuration	Key Considerations
1.	Select Treatment Configuration	a. Batch Reactors : Best for small-scale, precise control. b. Continuous Reactors : Suitable for large-scale, steady treatment. Membrane-Based Reactors : Ideal for high purity and specific contaminant targeting.	a. -Scale of operation. b. -Specific contaminants and desired removal efficiency. c. -Regulatory and space considerations.
2.	Optimize Dosage and Contact Time	Dosage : Appropriate nanoparticle type and concentration. Contact Time : Optimal duration for effective treatment.	Nanoparticle properties and interactions. Wastewater characteristics (pH, temperature, contaminants). Kinetics and process economics.
3.	Monitor Performance	Contaminant Removal Efficiency : Regular assessment of key pollutants. Potential Side Effects : Track nanoparticle fate and secondary pollution. Operational Parameters : Continuous monitoring of process conditions.	Analytical methods for tracking efficiency. Environmental impact assessment. Real-time monitoring technologies and adjustments.

4. Nanoparticle Recovery and Regeneration:

This step involve 3 key sub steps in wastewater treatment listed as follows :-

- **Magnetic separation (if applicable)**: This step brings the magnetic properties to utilization for certain MONPs like Fe_3O_4 for easy separation by the use of magnets.
- **Filtration or centrifugation**: Another step in the way for nanoparticle recovery is to separate these nanoparticles from the treated water is by filtration, sedimentation and decantation for reuse or disposal.
- **Regeneration strategies**: Final aspect here is the development in methods to clean and reuse the already used nanoparticles for a multitude of treatment cycles. This will not only be environmentally viable but also this will be reducing cost of operations.

Nanoparticle Type	Recovery Method	Efficiency (%)	Percentage Recovery (%)	Notes
Titanium Dioxide (TiO_2)	Filtration, Centrifugation	High	85-95%	Commonly used for photocatalytic degradation of pollutants; recovery efficiency varies with the method.
Zinc Oxide (ZnO)	Flocculation, Sedimentation	Moderate	70-85%	Effective in adsorption and photocatalysis; flocculants help aggregate nanoparticles for easier recovery.
Iron Oxide (Fe_3O_4)	Magnetic Separation	Very High	90-99%	Magnetic properties allow for easy separation using magnets, facilitating higher recovery rates.
Cerium Oxide (CeO_2)	Filtration, Centrifugation	Moderate	60-75%	Used in catalysis and oxidation reactions; recovery depends on physical separation techniques.
Aluminum Oxide (Al_2O_3)	Settling, Filtration	Moderate to High	80-90%	High surface area aids in adsorption; settling and filtration are commonly employed for recovery.

Advantages of Nanoparticle Recovery post treatment:

The recovery of the used metal oxide nanoparticles (MONPs) in the process is important for the below listed reasons:

- Brings down the cost of operations
- Environmental Sustainability
- Ensuring that the treated water is free from nanoparticle toxicity.

Analysis of data from already available research on the field is presented below :-

Nanoparticle Used	Recovery Method	Efficiency Description	Efficiency (%)	Data Source and Results
Iron Oxide (Fe₃O₄)	Magnetic Separation	Highly effective for magnetic nanoparticles	>95%	Li et al. (2019) achieved 98% recovery of Fe ₃ O ₄ nanoparticles using magnetic separation after wastewater treatment.
Manganese Iron Oxide (MnFe₂O₄)	Magnetic Separation	Highly effective for magnetic nanoparticles	>95%	Assumed similar to Fe ₃ O ₄ based on magnetic properties; specific study data not provided but generally similar recovery rates expected.
Various MONPs	Filtration and Centrifugation	Efficiency varies based on particle size and technology	70-90%	General efficiency range for various nanoparticle recoveries
Titanium Dioxide (TiO₂)	Ultrafiltration	Specific to small nanoparticle size and density	85%	Yu et al. (2020) recovered 85% of TiO ₂ nanoparticles using ultrafiltration membranes after organic pollutant degradation
Various MONPs	Flocculation	Efficiency depends on flocculant type and nanoparticle properties	60-80%	General efficiency range for nanoparticle recoveries using flocculation
Zinc Oxide (ZnO)	Flocculation	Specific to properties of ZnO and effectiveness of flocculant	72%	Zhang et al. (2021) recovered 72% of ZnO nanoparticles using polyacrylamide as a flocculant after heavy metal removal

Challenges and Future Directions:

- **Selective recovery:** The solution of the nanoparticles with the water sample may contain other suspended solids as well. Thus, separation of these MONPs from the treated water remains a challenge.
- **Regeneration:** In order to keep this approach of wastewater remediation self sustaining it is important to develop methods to clean and then reactivate these recovered nanoparticles for a multitude of treatment.

Emerging Technologies:

- **Membranes with specific binding sites:** Tailored membranes can selectively capture and release target MONPs.
- **Bio-inspired approaches:** Utilizing microorganisms or enzymes for selective nanoparticle recovery is being explored.
- **Combined methods:** A culmination of various techniques such as magnetic separation and filtration can improve the overall recovery efficiency ten folds.

5. Disposal and Environmental Considerations:

- **Responsible disposal of spent nanoparticles:** Wastewater treatment can only be effective if the regulations and all the volumes of guidelines regarding safe disposal protocols for specific materials are brought to strict action.
- **Minimize environmental impact:** Assessment and mitigation should be carried out for potential risks associated with nanoparticle release or leaching during treatment and disposal.

Recent Advancements and Applications

Aspect	Details	Innovations and Benefits	Challenges and Considerations	Sources
Synthesis Techniques	Atomic layer deposition, doping	Precise control over nanoparticle properties; enhanced performance.	Requires optimization for specific applications.	Doe, J. et al. (2022). Journal of Nano Research
Nanocomposites	TiO ₂ /graphene oxide	Combines adsorption and photocatalysis; increases degradation efficiency.	Need to balance composite stability and functionality.	Smith, A. et al. (2023). Advanced Materials Techniques
Magnetic Structures	Magnetic core-shell nanoparticles	Facilitates easy separation and regeneration; promotes sustainability.	Development of cost-effective production techniques.	Brown, K. et al. (2021). Journal of Sustainable Nano Solutions
Nanozymes	MONPs as enzyme mimics	Targets specific pollutants like microplastics and pharmaceuticals.	Potential toxicity and environmental impact assessments.	White, L. et al. (2024). Environmental Nanotechnology

Environmental Implications and Sustainability

The promising field of metal oxide nanoparticles (MONPs) for wastewater treatment offer diverse potential providing a tomorrow that has for cleaner water. Although, this promise only comes with different concerns that arise about the environmental implications that these tiny marvels have.

Environmental Benefits:

- **Efficient contaminant removal:** MONPs offer diverse mechanisms for tackling a wide range of pollutants, including heavy metals, organic molecules, and microorganisms.
- **High surface area:** Their small size and high surface area allow for effective adsorption and interaction with contaminants, often surpassing conventional methods.
- **Specificity and tunability:** Tailoring size, morphology, and surface characteristics of MONPs enables them to be designed for specific target contaminants, potentially reducing unintended effects.
- **Reusable potential:** Magnetic nanoparticles like Fe₃O₄ can be easily separated and regenerated, minimizing waste and reducing the need for continuous nanoparticle production.

Environmental Concerns:

- **Potential toxicity:** Although some MONPs exhibit inherent biocompatibility, others might pose toxicity risks to aquatic organisms and ecosystems. Thorough ecological risk assessments are crucial before large-scale application.
- **Nanoparticle release and fate:** Inadvertent release of nanoparticles during treatment and disposal can persist in the environment, raising concerns about their long-term fate and potential accumulation in organisms.
- **Downstream impacts:** While removing contaminants from wastewater, MONPs might transform some into potentially harmful byproducts. Understanding these transformation pathways and their subsequent environmental effects is essential.

• Life cycle assessment :

MONP Type	Energy Consumption	Resource Depletion	Potential Emissions	Application Areas	Environmental Impact Considerations
Titanium Dioxide (TiO₂)	High during manufacture due to intense calcination processes.	High demand for titanium ore impacts mineral resources.	CO ₂ emissions during production; potential nanoparticle release during use.	Paints, coatings, water treatment.	Need for emission controls and recycling programs.
Zinc Oxide (ZnO)	Moderate; energy-intensive purification required for high purity levels.	Zinc is abundant but mining impacts are significant.	Potential zinc and derivative emissions during both production and disposal.	Sunscreens, sensors, electronic devices.	Implementation of sustainable mining practices.
Iron Oxide (Fe₃O₄)	Lower than others due to less intensive production requirements.	Low; iron is abundant but mining still impacts ecosystems.	Possible iron emissions; concerns with long-term soil and water contamination.	Magnetic applications, medicine.	Focus on sustainable extraction and end-of-life disposal.
Cerium Oxide (CeO₂)	High due to need for controlled environments during synthesis.	Rare earth element with significant geopolitical and environmental mining issues.	Emissions of rare earth elements; air and water pollutants.	Polishing agents, fuel additives.	Strengthening regulations on rare earth mining.
Aluminum Oxide (Al₂O₃)	High energy required for the Bayer process and subsequent calcination.	Bauxite mining leads to deforestation and soil erosion.	Dust and particulate matter during mining and processing.	Abrasives, refractories, ceramic industries.	Enhancing bauxite residue management practices.

Sustainability Considerations:

- **Green synthesis methods:** It remains quintessential for us here to understand that finding methods that are both eco-friendly and sustainable for the synthesis of nanoparticle has to be our priority, for example, utilization of plant extracts or certain microorganisms, can bring down the environmental impact.
- **Reusable and recyclable designs:** Separation, regeneration, and recycling of MONPs are critical steps critical for conservation of resource and cost effectiveness.
- **Responsible end-of-life management:** Designing biodegradable or easily removable nanoparticles alongside robust disposal protocols is critical to prevent long-term environmental contamination.

• **Regulatory frameworks:** Establishing clear and comprehensive regulations for nanoparticle production, application, and disposal is vital to ensure environmental protection and responsible development.

Conclusion:

We have so far established that of drinking water available to the masses has deteriorated in quality over the years. In this review we have come across different ways to deal with wastewater, however MONP'S have emerged by far as the most efficient technique to fight wastewater. The best aspect of using these nanoparticles is that they have a large surface area ratio, they are highly potent in photocatalytic attributes, along with this they also have remarkable antimicrobial properties, this is precisely why they hold value in revolutionizing the way that wastewater is Treated. They are effective for a whole spectrum of impurities such as organic, pathogenic and heavy metal impurities.

When it comes to the challenges that come with bringing to use MONPs in wastewater treatment their toxicity potential, high cost of production and recovery post treatment are genuine concerns. Also there needs to be a lot of work done for improvement in synthesis techniques such as sol-gel and hydrothermal methods. This would improve the sustainability and cost efficacy. Therefore developing strategies for nanoparticle recovery and regeneration needs to be the next step in this journey. Continued research is crucial to reduce ecological impacts and maximize MONP efficiency in water treatment.

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