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A Review Based on the Bioremediation of Industrial Wastewater and Effluents

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Abstract: *Industries face a formidable challenge in dealing with pollutant removal from their effluents, given the severe environmental risks posed by these contaminants. Nanotechnology emerges as a promising approach, as it allows the creation of eco-friendly nanomaterials, thereby reducing the financial burden associated with pollutant mitigation. The use of nanomaterials gains considerable attention owing to their enhanced physical, chemical, and mechanical properties. Integrating microorganisms in nanoparticle production further bolsters green biotechnology as a nascent field within nanotechnology, offering sustainable production and cost reduction prospects. This mini review delves into the various facets of industrial effluent bioremediation through the incorporation of microbial nanotechnology. By harnessing nanotechnology alongside enzymes, we can achieve heightened enzyme activity and reusability. Additionally, this review underscores the advantages of nanotechnology over conventional practices in these crucial domains.*

Keywords: industrial effluents, pollutant removal, nanotechnology, eco-friendly nanomaterials, microorganisms, green biotechnology, cost reduction, microbial nanotechnology, enzyme activity

I. INTRODUCTION

Water, being crucial for life on Earth, faces significant pollution challenges that demand urgent attention. The rise of industrialization has escalated water consumption, resulting in vast quantities of industrial effluents. To achieve sustainable development for both industries and the environment, efficient and cost-effective treatment of these effluents is essential. While several techniques such as electrochemical processes, advanced oxidation, and valorization methods have been employed to reduce wastewater toxicity and promote sustainability [1], their widespread implementation remains limited due to cost constraints. However, the advent of nanotechnology and nanoscience has unlocked promising avenues for water pollutant remediation. Nanotechnological approaches exhibit enhanced efficiency compared to conventional methods, attributed to their small size, high surface area to volume ratio, and exceptional chemical properties. A notable development in this area is the synthesis of green nanomaterials derived from microorganisms and extracts of other organisms, offering eco-friendly solutions for pollution remediation. Notably, iron nanoparticles have emerged as green nanoparticles effectively utilized in remediation due to their redox potential when interacting with water, magnetic susceptibility, and non-toxic nature [2].

Effluent removal can be effectively achieved through the utilization of membrane-associated nanomaterials. These nanomaterials offer several advantages, including improved membrane permeability, resistance to fouling, enhanced mechanical and temperature strength, and the introduction of innovative functionalities for pollutant degradation. Nano-catalysts also play a significant role in boosting degradation reactions. Aside from membranes and nano-catalysts, metal-organic frameworks (MOFs) are gaining prominence in the removal of heavy metals from wastewater. These MOFs are synthesized by coordinating organic ligands with metal ion precursors. To enhance their effectiveness, MOFs can be modified by coordinating functional groups with metals instead of the organic ligands, reducing steric hindrance [3]. In this concise review, we delve into the application of nanoparticles in pollutant removal within industrial settings. Moreover, we explore the potential of microorganisms and enzyme-assisted green nanotechnology for the removal and valorization of waste materials.

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Nanotechnology For Sustainable Wastewater Treatment

Nanomaterials offer immense potential in wastewater treatment due to their small size, which enhances their effectiveness in various applications. These materials possess specific chemical, physical, and biological properties that make them highly suitable for wastewater treatment. Carbon-based nanomaterials, such as Nanocomposites or Nanotubes, along with metals and their oxide-based counterparts, have been extensively utilized for efficient effluent removal from wastewater. Wastewater management practices encompass a range of techniques, including photocatalytic degradation, adsorption, filtration through nanoparticles, and the monitoring of different contaminants and pollutants [4]. Figure 1 illustrates the application of various nano-techniques in the bioremediation of industrial effluents, showcasing their potential to address pollution challenges effectively.

Nano-Adsorbents And Nanofiltration Membranes

Nanoparticles have garnered widespread attention as effective adsorbents for the removal of harmful contaminants from industrial wastewater. These nanoadsorbents demonstrate the capability to eliminate both organic and inorganic pollutants. Classified into categories like carbon-based, metal, and metal oxide-based nanoparticles, they offer a diverse range of applications. Carbon-based nanoparticles, including carbon nanotubes (CNTs), activated carbon, graphene, and fullerene, have been extensively studied for their adsorption properties [5]. CNTs, in particular, act as potent adsorbents for toxic chemicals commonly found in manufacturing industries or pharmaceutical wastewater. [6] conducted research on multi-walled carbon nanotubes (MWCNTs) prepared through Fe-Ni supported on activated carbon using the chemical vapor deposition (CVD) technique. The adsorption characteristics of metronidazole and levofloxacin were measured at 2.5961 and 2.1363, respectively, falling within the range of good adsorption (2-10). Furthermore, the enthalpy change indicated chemisorption for metronidazole and physisorption for levofloxacin. Additionally, MWCNTs have demonstrated their capability to adsorb metals from wastewater. Carboxylated MWCNTs exhibited enhanced adsorption, achieving 250 mg/g for As(V) and 298 mg/g for Mn(VII). Thermodynamic analysis suggested chemisorption as the mechanism of metal removal [7].

Innovative approaches for wastewater treatment include the utilization of activated carbon modified nano-magnets for fluoride ion removal. demonstrated the efficiency of a nanocomposite in removing 97.4% of fluoride ions from synthetic wastewater, exhibiting an impressive uptake capacity of 454.54 mg/g.Moreover, the combination of microbial fuel cells with nanocatalysts has led to the generation of bioelectricity. Electrodes coated with Iron(II)molybdate nanocomposites proved highly effective in enhancing the efficiency of microbial fuel cells. Remarkably, this method achieved a maximum columbic efficiency of 21.3 ± 0.5%, a power density of 106 ± 3 mW/m^2, and a COD removal competence of 79.8 ± 1.5% [8]. In the realm of heavy metal removal, a superparamagnetic composite comprising iron oxide nanoparticles and activated carbon demonstrated its suitability in eliminating Cr(III) from wastewater. The treated wastewater met the discharge criteria set by the environmental protection agency (EPA), underscoring the effectiveness of magnetic separation and sorption for heavy metal removal [9].

Furthermore, advancements in nano-adsorbents have demonstrated their vital role in efficiently removing pollutants from wastewater. Magnetic nanoparticles coated with other materials have shown enhanced adsorption efficiency. For instance,magnetic nanoparticles coated with silver achieved a notable 36.56% chemical oxygen demand (COD) removal from wastewater, surpassing the performance of uncoated magnetic nanoparticles by 6.16% [10].

Similarly, the integration of magnetic polymer, Co_3O_4@SiO_2 magnetic nanoparticles coated with nylon 6, exhibited remarkable potential in adsorbing 666.67 mg/g of Pb(II) from wastewater at 298K. The polymer displayed excellent reusability for up to six cycles, with minimal loss in adsorption capacity (< 30%) [11]. This highlights the cost-effectiveness and environmental friendliness of such nanomaterials for wastewater treatment. Metal oxide-based nanomaterials have also proven to be efficient in treating effluents. Nano-porous magnesium oxide derived from solid waste from the ductile iron industry demonstrated the capability to adsorb 1,000 $mg.g^{-1}$ of toxic dye from wastewater. To enhance the adsorbent properties, a 1:1 mixture of sodium dodecyl sulfate (SDS) and polyoxyethyleneoctyl phenyl ether (TX100) was used, resulting in a suitable pore size of 16 nm . Furthermore, [12] employed magnetic nanoparticles made from iron oxide to remove heavy metals from wastewater. These iron oxide nanoparticles, grafted on hyperbranched polyglycerol, exhibited rapid removal of nickel, copper, and aluminum from wastewater within just

35 seconds. Interestingly, the adsorption efficiency of nanoparticles remained unaffected by organic content and phosphorous, while nitrogen slightly reduced the removal of heavy metals. These findings reinforce the significant potential of metal and metal oxide-based nanomaterials in industrial effluent treatment.

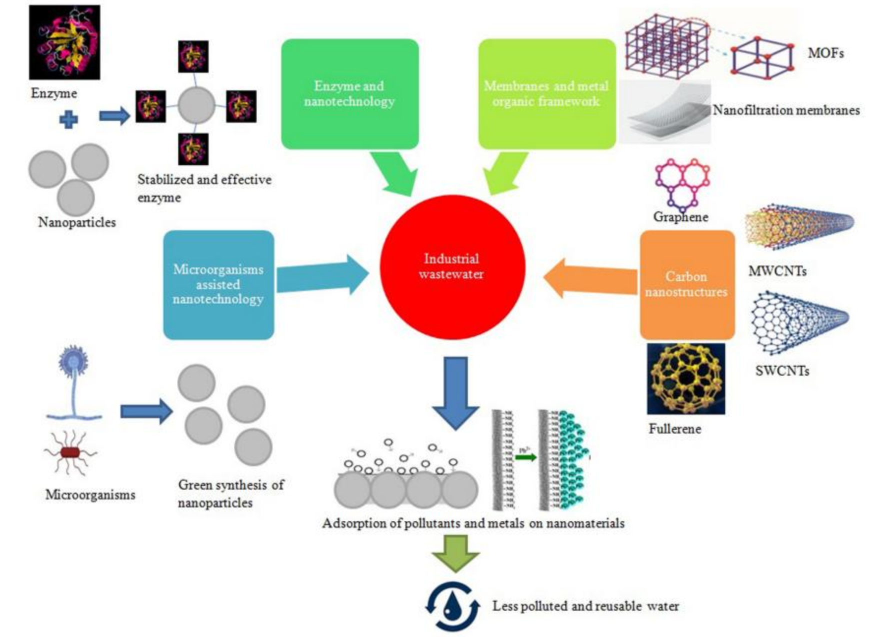

Fig 1. | Utilization of various nanotechnology approaches in combination with microbial assistance for wastewater bioremediation. MOFs: Metal organic frameworks; MWCNTs: multi-walled carbon nanotubes; SWCNTs: Single-walled carbon nanotubes

Nanofiltration (NF) membranes have emerged as a crucial player in the recovery of nutrients from industrial effluents. For instance, NF90 membrane demonstrated the highest rejection rate (70%) for phosphorous removal from pulp and paper industry effluent [13]. However, membrane fouling remains a challenge due to the high phosphorous content. To address this, [3] ingeniously integrated gold nanoparticles with a polymer blend in the NF membrane, achieving a significantly higher recovery of phosphorous from wastewater. This innovative approach led to an impressive 96.1% rejection rate of trivalent phosphate, along with enhanced fouling resistance and membrane hydrophobicity. Furthermore, a Ceramic supported graphene oxide (GO)/Attapulgite (ATP) composite membrane was developed for efficient removal of heavy metals. The membrane exhibited exceptional performance, rejecting nearly 100% of copper, nickel, lead, and cadmium ions. Notably, this membrane offered increased flux speed, immense water stability, and outstanding rejection ability [14]. Despite the promising applications of nanomaterials, concerns regarding their chemical nature and commercialization have arisen. To address these issues, researchers have turned to microorganisms for the generation of green nanostructures, ushering in a revolution in the field of green nanotechnology. These microorganism-supported nanotechnological applications offer a sustainable and environmentally friendly approach to nanomaterial synthesis and utilization

Microorganisms Assisted Nanotechnology

The combination of biofabrication techniques and microbial involvement in nanotechnology offers a more sustainable and eco-friendly approach. While chemically produced nanoparticles may have certain drawbacks, such as the use of chemicals and self-agglomeration in aqueous solutions, the green synthesis of nanoparticles from plant extracts, fungal, and bacterial enzymes emerges as a promising solution. These biofabricated nanoparticles serve as reductive agents for metal complex salts, leading to the generation of metallic nanoparticles. Notably, these nanoparticles exhibit enhanced stability in aqueous environments, achieved through co-precipitation or the addition of proteinaceous and bioactive elements onto their surfaces.

A study [15] exemplified the biofabrication of iron oxide nanoparticles using Aspergillus tubingensis (STSP 25) obtained from the rhizosphere of Avicennia officinalis in Sundarbans, India. The synthesized nanoparticles demonstrated remarkable efficiency in removing over 90% of heavy metals, including Pb(II), Ni(II), Cu(II), and Zn(II), from wastewater, with the added advantage of being reusable for up to five cycles. The metal ions underwent chemisorption on the nanoparticle surfaces in endothermic reactions. Similarly, another study employed exopolysaccharides (EPS) obtained from Chlorella vulgaris to co-precipitate with iron oxide nanoparticles. Fourier-transform infrared spectroscopy (FTIR) analysis confirmed the successful modification of nanoparticles by functional groups of EPS. The resulting nanocomposite showcased a high removal capacity of 91% for PO_4^{3-} and 85% forNH_4^+ in wastewater [16]. These findings highlight the potential of biofabricated nanomaterials for efficient pollutant removal and wastewater treatment applications.

Harnessing the power of microorganisms for the synthesis of nanoparticles presents a cost-effective and environmentally friendly strategy. In a study conducted [17], copper nanoparticles were synthesized from copper-resistant Escherichia sp. SINT7, demonstrating their potential in degrading azo dye and textile effluent. Remarkably, at a lower concentration of 25 mg/L, the reduction of reactive black-5, congo red, direct blue-1, and malachite green reached 83.61%, 97.07%, 88.42%, and 90.55%, respectively. Even at a higher concentration of 100 mg/L, significant reductions were achieved: 76.84% for reactive black-5, 83.90% for congo red, 62.32% for direct blue-1, and 31.08% for malachite green. Furthermore, the application of these biogenic nanoparticles in treating industrial effluent resulted in reduced suspended solids, chloride, and phosphate ions in the treated samples. This impressive performance highlights the potential of biogenic nanoparticles in enhancing cost-effective and sustainable production practices in industries. [18]took a unique approach in preparing iron-sulfur nanoparticles without using extra sulfur. These nanoparticles demonstrated their efficacy in degrading Napthol Green B dye through the extracellular transfer of electrons. The utilization of Pseudoalteromonas sp. CF10-13 in nanoparticle preparation provided an eco-friendly method for biodegradation. The endogenous production of nanoparticles effectively inhibited the generation of harmful gases and metal complexes, making them a superior technology for industrial effluent remediation. Besides directly producing nanoparticles, microorganisms can significantly contribute to nanotechnology in various other ways. For example, microorganisms can provide catalytic enzymes that, when combined with nanoparticles, enhance the remediation of effluents. Table 1 offers a concise overview of nanotechnology's application in wastewater bioremediation, highlighting its promising potential. Moreover, microorganisms play a crucial role in transforming industrial waste into valuable products, a topic that will be further explored in subsequent discussions. The integration of microorganisms and nanotechnology holds immense promise in advancing sustainable and efficient solutions for environmental remediation and resource recovery.

Nanotechnology And Enzyme Technology

The integration of enzymes with nanotechnology holds significant promise in reducing the environmental impact of nanomaterials. When enzyme molecules are combined with nanomaterials, they create steric hindrances and reduce surface energy, minimizing their interaction with cells [19]. Enzymes, being eco-friendly and providing unique catalytic properties, enhance the adaptability and efficiency of nanomaterials in bioremediation and green energy production.Moreover, immobilized enzymes on nanomaterials exhibit exceptional stability, resisting unfolding and being less susceptible to diffusional constraints. They can be utilized in multiple cycles and showcase improved kinetic characteristics. The substantial surface area of nanomaterials facilitates efficient enzyme immobilization, resulting in elevated enzyme loading. Separating immobilized enzymes from the reaction mixture becomes easier, especially when magnetic nanomaterials are employed as the immobilizing matrix. Additionally, multimeric enzymes, like oxidoreductases, can be effectively stabilized through immobilization on nanomaterials. Notably, enzyme immobilization on solid substrates can induce structural changes, particularly an increase in β-sheet structure and a decrease in α-helical structure. In contrast, when nanomaterials are used for enzyme immobilization, such modifications are not observed [20].The synergy between enzymes and nanotechnology offers exciting prospects in advancing eco-friendly and efficient solutions for various applications, particularly in environmental remediation and sustainable energy production.

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Recent studies have highlighted the remarkable potential of combining enzyme technology with nanotechnology for effective wastewater bioremediation. For instance, [21] demonstrated the efficiency of immobilized peroxidase enzyme on glutaraldehyde-modified iron oxide magnetic nanoparticles. The immobilized enzyme successfully removed individual green and red azo dyes within 4 hours and both dyes simultaneously in 6 hours during lab-scale experiments. Laccase, widely used for industrial effluent treatment, has been immobilized using various magnetic nanoparticle composites. Researchers utilized an Fe_3O_4 and chitosan composite as a magnetic carrier for laccase immobilization, leading to stable covalently bound laccase capable of effectively removing 2,4-Dichloro-Phenol (2,4-DCP) and 4-Choloro-Phenol (4-CP) even after 10 cycles. [22]employed Fe_3O_4 core and chelated Cu^{2+} of carbon shell to immobilize laccase, resulting in $Fe_3O_4@C\text{-}Cu^{2+}$ nanoparticles with high enzyme activities, loading capacity, and reusability. This immobilized laccase effectively degraded various synthetic dyes with impressive removal rates even after 10 continuous reuses. Likewise, immobilized lignin peroxidase on $Fe_3O_4@SiO_2$@polydopamine nanoparticles displayed superior performance in reducing organic pollutants compared to free enzyme. Researchers observed 100% dissipation of dibutyl phthalate, phenol, tetracycline, and 5-chlorophenol, and significant removal of benzo(a)pyrene, phenanthrene, and fluoranthene. Moreover, the immobilization of recombinant cyanate hydratase on iron-oxide-filled magnetic MWCNTs exhibited promising results in removing Cu, Fe, Cr, Pb, and cyanate from synthetic wastewater samples [23]. Collectively, these studies highlight the stable and efficient environment created by the combination of enzyme technology and nanotechnology, making it a compelling approach for the degradation of industrial effluents. The synergistic effects of enzymes and nanomaterials offer exciting prospects for advancing sustainable and effective solutions in wastewater treatment.

Valorization Of Waste Using Microorganisms And Nanotechnology

The utilization of technology to convert waste materials into valuable products has become a prominent focus for researchers worldwide. This innovative approach not only helps in waste reduction but also enables the generation of useful resources simultaneously. Industries have widely adopted this practice for producing diverse products, such as adsorbents, clinker, biogas, biohydrogen, biomolecules, and more [24].

Nanotechnology has played a significant role in enhancing the production rate and efficiency of converting waste into valuable resources. Researchers explored the use of nanoparticles to improve dark fermentation reactions, leading to increased biohydrogen production. By supplementing fermentative bacteria with nanoparticles, new possibilities have emerged for generating biohydrogen from wastewater. In a study mixed culture bacteria combined with single, dual, and multiple nanoparticles were employed to produce biohydrogen. The use of multiple nanoparticles resulted in the highest biohydrogen production, surpassing that of single nanoparticle use by 14%. The various nanoparticles enhanced the activity of hydrogenase and dehydrogenase enzymes, consequently increasing biohydrogen production. Similarly, the combination of nickel oxide and hematite nanoparticles yielded 1.2–4.5-fold increased biohydrogen production compared to the use of individual nanoparticles. The highest hydrogen yield of 8.83 mmol/g COD was achieved through the synergistic effect of these nanoparticles, elevating the activity of hydrogenase and ferredoxin oxidoreductase enzymes [25]. Indeed, nanotechnology offers exciting prospects for generating green energy and promoting sustainable industrial growth through eco-friendly production methods. The application of nanotechnology in waste conversion opens up new possibilities for resource recovery and environmental conservation.

Table 1: Bioremediation of different industrial effluents using advanced nanotechnology processes.

Sr. No.	Nanotechnology applied	Modification	Associated Microorganisms	Removal or adsorption capacity	Advantage/ Mechnism	Specific features	References
1	NiO and MgO nanoparticles	Silica-embedded	-	Maximum uptake of 41.36, 13.76, 7.23 (ions per nm^2) foe Cr^{3+} and Zn^{2+}	Spontaneous, endothermic, and physical adsorption of Cu^{2+} and Cr^{3+} and	Regeneration and reusability proved sustainability	[26]

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					exothermic and chemical of Zn^{2+}		
2	Electrospunn anofibrous webs	Bacterial encapsulation	Pseudomonas aeruginosa	55–70% removal of methylene blueat different concentrations	Biological removal of dye	Genetic engineering or more potent bacterial cell could prove more promising	[27]
3	Mesoporous organosilica nanoparticles (MONs)	Incorporation of ferrocene	-	High removal rate of dyes by MONs-50% and metals by MONs-25%	More surface area and πnjugation derived from non-covalent interaction facilitated by ferrocene	Novel organic-inorganic hybrid nanomaterial	[28]
4	Cobalt and cobalt oxided nanoparticle	Microwave and reductive chemical heating	-	43.6 and 39.4% degradation of murexide dye by Cobalt and cobalt oxide nanoparticles, respectively	Irradiation and large surface area	Greener, easy, and faster to make, cost-effective and photocatalytic degradation efficiency	[29]
5	Electrospuncyclodextrinfibers	Bacterial encapsulation	Lysinibacillus sp. NOSK	Removal efficiency of Ni(II) = 70 ± 0.2%, Cr(VI) = 58 ± 1.4% and Reactive black 5 = 82 ± 0.8	Bacterial bioremediation	Cyclodextrin provides extra carbon source for growth of bacteria	[30]
6	Zirconia nanoparticles	Syntheis from microbial cell free culture supernantant	Pseudomonas aeruginosa	Tetracycline adsorption of 526.32 mg/g	Chemisorptions and strong electrostatic interaction among zwitter ions	Green synthesis of nanoparticles and sustainable bioremediation	[24]
7	Enzyme immobilized nanoparticle	Laccase immobilization	P. ostreatus	Degradation bisphenol-A=90% and	Oxidation by immobilized laccase	Reusable enzyme and cost	[31]

	s			carbamazepine =10%		effective	
8	Graphene oxide and carbon nanotubes	Nano-sized nickel metal organic framework	-	Methylene blue adsorption of 222 mg/g	Hydrophobic and/or π-π interactions, high surface area, occurrence of the pores among the MOFs and the platforms and diverse morphological features of mixed nanocomposites	Superior interation of nanocomposite	[32]
9	Silica nanopartilces	Synthesized from actinomycetes	Actinomycetes	80% decolorization of industrial effluent	Photocatalytic degradation	Cost-effective and Sustainable	[33]

II. FUTURE PERSPECTIVE AND CHALLENGES

The intriguing benefits of nanotechnology have captured the attention of researchers, owing to its expansive surface area, versatility for multiple uses, stability in harsh conditions, ease of material manipulation, enhanced interaction capabilities, and more. Integrating microorganisms and enzymes with nanotechnology has paved the way for a greener approach to industrial effluent management. By leveraging microorganisms, the risks associated with chemically synthesized nanoparticles can be mitigated, as the residues left behind are either biocompatible or easily separated using simple filtration/precipitation techniques. However, the challenge lies in commercializing these nanotechnological advancements. So far, only 1% of such aspects have been commercialized. Expanding the application of these efficient microorganism-assisted nanotechnology techniques on a larger scale will be a significant milestone for industries. This necessitates continuous support and validation from researchers and government funding to harness the full potential of nanotechnology for sustainable and cost-effective production in various industries. The collaboration between nanotechnology and microorganisms opens up promising avenues for addressing environmental challenges and optimizing industrial processes. By fostering the development and implementation of these innovative technologies, we can pave the way towards a greener and more efficient industrial landscape.

III. CONCLUSION

The integration of nanotechnology with microorganisms has ushered in a green approach to efficiently remediate industrial effluents. The synthesis of nanomaterials through microorganisms presents promising opportunities for cost-effective and sustainable effluent treatment. Enzyme nanotechnology has also demonstrated its value by providing stable, highly active, and long-lasting enzymes with multiple applications. It is essential to further explore and scale up this technique to fully harness its potential. Additionally, there is great potential in advancing waste valorization, specifically in generating biohydrogen and bioelectricity from industrial waste. This initiative holds the key to boosting the industrial economy through the production of green energy. By focusing on these endeavors, we can make significant strides towards a more sustainable and environmentally friendly industrial landscape

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