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Nanotechnology in Immobilization: Harnessing the Magnetic Nanoparticles for Medicine and Remediation Applications

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Review Article

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Abstract

Magnetite nanomaterials have garnered significant interest in the field of biomedical sciences and hold great promise for various applications. One such innovative technique is the loading of microorganisms using magnetic-based carriers, which has gained more research interest in environmental pollution control. However, despite its potential, this approach remains relatively unexplored in the existing literature. Compared to conventional methods of cell immobilization and suspended microorganism technology, magnetic nanoparticles offer several advantages, including the ease of catalyst retrieval from the liquid phase. This review highlights the applications of immobilized magnetic nanomaterials in both environmental contaminant remediation and the medical field. Immobilization techniques offer effective solutions to enhance the efficiency and stability of catalytic enzymes, enabling their separation and facilitating reusability in industrial processes. Our discussion proved that magnetic nanoparticles (MNPs) are considered a promising choice for immobilization due to their outstanding properties, including easy recovery, stabilization, and reusability. Magnetic nanomaterials hold great potential as a future direction for immobilization, offering numerous advantages in various applications.

Keywords: Magnetite Nanoparticles; Microorganism Immobilization; Removal of Toxic Pollutants; Nano-Medicine; Biocatalysis

Abbreviations: MNPs: Magnetic Nanoparticles; SLNs: Solid Lipid Nanoparticles; RSV: Loaded With Trans-Resveratrol; FER: Ferulic Acid; FA: Folic Acid; COD: Chemical Oxygen Demand; MFC: Microbial Fuel Cell; MBBR: Moving Bed Biofilm Reactor.

Introduction

Nanotechnology, the science and engineering of manipulating matter at the nanoscale, has revolutionized numerous fields, including medicine, electronics, energy, and materials science [1]. Its unique properties and capabilities have also found compelling applications in the field of immobilization. Immobilization, the confinement of biological entities such as cells, enzymes, or biomolecules within a matrix or support material, has been employed in various areas such as biocatalysis, bioremediation, biosensors, and drug delivery systems [2,3]. The integration of nanotechnology with immobilization techniques has opened up new frontiers, offering unprecedented control, efficiency, and versatility in immobilization systems [4,5]. By leveraging nanomaterials and nanoscale engineering, researchers have overcome traditional limitations associated with conventional immobilization methods, enabling precise control over the immobilized entities' behavior, stability, and functionality [6].

Nanotechnology brings forth a multitude of benefits, including improved mass transfer rates, enhanced surface area-to-volume ratio, tunable surface properties, and compatibility with diverse biological entities [7,8]. One of the key advantages of nanotechnology in immobilization is the ability to tailor the properties of the immobilization matrix at the nanoscale. Nanomaterials such as nanoparticles, nanofibers, nanocomposites, and nanogels offer a wide range of physical, chemical, and mechanical properties that can be harnessed to optimize the immobilization process [9,10]. Nanotechnology in immobilization has witnessed remarkable progress in recent years, owing to advancements in nanomaterial synthesis, characterization techniques, and surface functionalization strategies [11]. Researchers have exploited a wide range of nanomaterials, including metal and metal oxide nanoparticles, carbon-based nanomaterials, polymeric nanoparticles, and hybrid nanocomposites, to achieve tailored immobilization platforms with enhanced performance [12]. Novel fabrication techniques such as electrospinning, self-assembly, layer-by-layer deposition, and 3D printing have enabled the creation of complex nanoscale architectures for immobilization applications [13]. New nanomaterials with high sorption capacities have revolutionized the capture of heavy metal ions by rapidly reaching equilibrium. These nanoparticles are a promising generation of environmental remediation technologies, particularly for removing toxic pollutants like heavy metals and metalloids. Additionally, nanoparticles offer flexible and versatile support for microbial cells, providing large specific surfaces in relation to their volume [14].

Compared to metallic nanoparticles, magnetic nanoparticles can achieve greater adsorption capacity. Magnetic immobilization involves trapping microbial cells within magnetic nanoparticles, enabling manipulation through external magnetic fields. This innovative approach, specifically in the magnetic separation of biosorbents from streams of the wastewaters and groundwater, has led to the development of microbial nanoparticles with promising applications [15]. The immobilization process can be achieved through various techniques such as physical adsorption, covalent binding, or encapsulation [16].

This review focuses on exploring the key properties and advantages of magnetic nanoparticles. Additionally, it discusses their application in the fields of medicine and environmental pollutant removal, highlighting their significance and potential benefits.

Magnetic Nanoparticles Properties

Magnetic nanoparticles (NPs) are nanoscale particles composed of magnetic elements, such as iron, chromium, manganese, nickel, gadolinium, and cobalt. They exhibit super paramagnetic properties, making them highly versatile in various applications. Ferrite nanoparticles are the most commonly studied MNPs [17]. Magnetic nanoparticles exhibited robust selectivity to contact functional molecules and directed to specific locations using an external magnetic field. To prevent aggregation and interaction with the environment, surface coating is necessary, often achieved through modifications with silicones, surfactants, or silica [18,19]. The properties of MNPs depend on the synthesis method and their chemical composition. MNPs display zero coercivity, no hysteresis, and can be magnetized and demagnetized by an external magnetic field, making them suitable for environmental applications, targeted drug delivery, and controlled therapy [20,21]. Additionally, MNPs exhibit the magnetocaloric effect, heating up in a magnetic field and cooling down when the field is removed. Their small size and large surface area offer advantages over conventional bulk materials, enabling improved heat exchange with the surroundings. Various techniques can be employed to produce magnetic nanostructures in different morphologies, such as, nanosphere, nanocubes, nanorod, and nanowires. Iron oxide magnetic nanoparticles, for instance, can be synthesized using various strategies, like wet chemistry or "bottom-up" approaches like sol-gel, solvothermal, co-precipitation, hydrothermal, electrochemical, laser pyrolysis techniques, and flow injection syntheses [22,23].

Immobilization on Magnetic Particles

The immobilization technology encompasses various methods for attaching or entrapping particles or cells, including microbial cells, enzymes, plant cells, and animal cells, as illustrated in Figure 1. The researchers also have been reported the using of immobilized non-living microbial biomass. These immobilization techniques find applications in diverse industries such as biotechnology, environmental, pharmaceutical, and food [16]. The utilization of immobilized microorganisms offers several advantages over free cells in industrial biotransformation, bioprocesses, and biodegradation. These advantages include improved regeneration, recovery, higher stability, and recycling of the biocatalyst. Additionally, immobilized cells can serve as effective alternatives to enzyme immobilization, acting as carriers of necessary enzyme activities while being insoluble in water. "The confinement of microbial cells within a defined region, retaining their catalytic activities, allows for continuous use of the catalyst. This approach has found success in various environmental operations [24,25]. Nanomaterials, with their unique physico-chemical properties such as specific efficient diffusion loading, surface area, high mechanical strength, mass transfer resistance, and provide interesting structures for immobilizing microbes [15]. Magnetic nanoparticles have the added advantage of easy separation using an external magnetic field [26]. Therefore, immobilizing microbial cells within magnetic nanoparticles shows promise in enhancing the viability of microorganisms in industrial applications. Unfortunately, the high construction costs of MNPs for large-scale applications pose a significant challenge in microorganism immobilization. The development of low-cost and environmentally friendly methods for synthesizing nanoparticles on a large scale is an ongoing endeavor [27].

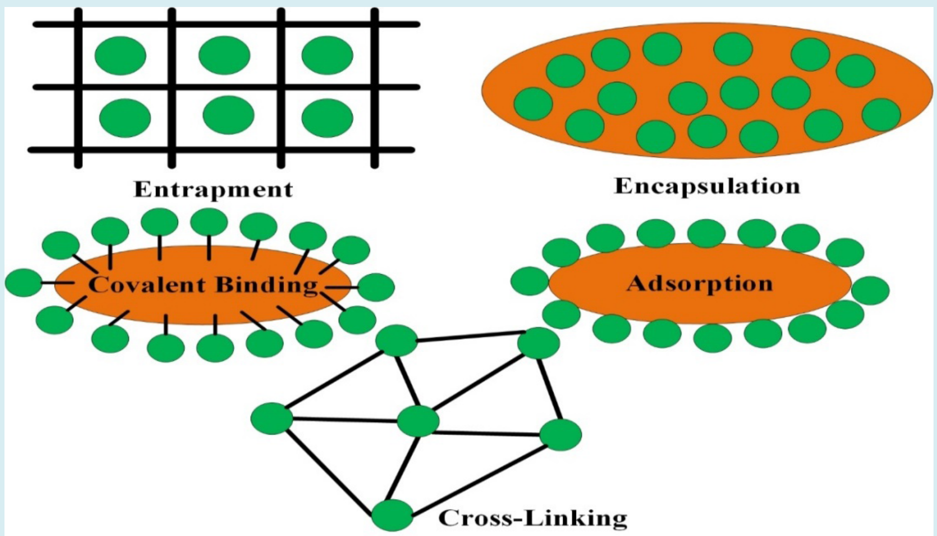

Figure 1: Immobilization types [16].

Application

Magnetic nanoparticles immobilized cell applications involve the use of magnetic nanoparticles (MNPs) that are attached or immobilized onto beads or microspheres for various purposes. This approach combines the unique properties of MNPs with the advantages of bead-based systems, creating a versatile platform for a wide range of applications [28]. The immobilization of MNPs onto cells allows for easy handling and separation of the nanoparticles from the surrounding medium using an external magnetic field. The beads serve as a support matrix, providing stability and a larger surface area for the attachment of MNPs [29]. One of the key applications of magnetic nanoparticles immobilized cell systems is in biotechnology and the field of diagnostics. These systems are commonly utilized for the separation and purification of biomolecules, including proteins, DNA, and viruses. The MNPs attached to the beads act as affinity ligands, allowing for efficient and selective capture of the target molecules from complex biological samples [30,31]. The magnetic separation capability enables rapid and easy isolation of the target molecules, making it a valuable tool in research laboratories and clinical settings.

Furthermore, magnetic nanoparticles immobilized bead systems find applications in environmental remediation, particularly in the removal of pollutants and heavy metals from water and soil. The MNPs attached to the beads can selectively bind to the contaminants, facilitating their extraction from the environment. The magnetic separation enables the effective removal of the loaded beads, allowing for repeated use and regeneration of the system [15]. In addition, magnetic nanoparticles immobilized bead systems have been explored for drug delivery applications. The MNPs can be functionalized with therapeutic agents and attached to the beads, creating a platform for targeted and controlled drug release. The magnetic field can be utilized to guide the drug-loaded beads to the desired site within the body, enhancing the specificity and efficiency of drug delivery [23,32].

Two main approaches are used for functionalizing magnetic nanoparticles. The first involves coating the nanoparticles with biofunctional molecules like antibodies, ligands, or receptors. "This enables specific interactions with biological entities, offering control over tagging and providing high selectivity and sensitivity for various biological applications. The second approach involves integrating magnetic nanoparticles with other materials, such as metallic nanoparticles, to form heterodimer structures. These structures have distinct surfaces and properties, allowing attachment of different functional molecules to specific parts. This opens up possibilities for binding to multiple receptors, serving as agents for multimodality imaging, and acting as platforms for bacteria detection and therapeutic agents" [33].

Biomedical Field: Magnetic nanoparticles have diverse applications in hyperthermia, targeted drug delivery, imaging, and biomolecule extraction. They play a crucial role in cancer treatment, particularly in hyperthermia-based therapies that can induce antitumoral immunity. Unlike nonselective cytotoxic drugs, MNPs offer a potential solution by selectively targeting cancer cells while minimizing damage to normal tissues, leveraging the inherent vulnerability of cancer cells to cytotoxic effects. MNPs hold promise for effective and precise treatment of chronic diseases like cancer [23]. Nanoparticles are engineered to have sizes comparable to biological vesicles and molecules, facilitating their transport through blood vessels to specific targets. They can then release their cargo at the disease site. The key advantage of magnetic nanoparticles is their ability to be precisely controlled in terms of location and activation using alternating magnetic fields (kHz-MHz). Importantly, these fields have minimal adverse effects on the human body [34]. Nanoparticles offer several advantages such as customizable shapes and sizes, high drug encapsulation, reduced toxicity, efficacy, stability, and the ability to incorporate hydrophilic and hydrophobic drugs. They can enter the capillary pores of cancer cells, increasing drug concentrations and targeting specific cancer cells effectively [35,36]. Also, nanoparticles can be synthesized from a wide range of precursor materials, such as inorganic materials, polymers and lipids [37]. Kumar, et al. [38] investigated the efficacy of chitosan-coated solid lipid nanoparticles (SLNs) loaded with trans-resveratrol (RSV) and ferulic acid (FER), conjugated with folic acid (FA) (C-RSV-FER-FA-SLNs), for targeting colon cancer. The SLNs demonstrated good stability, even under acidic conditions, making them suitable as a drug delivery system. These findings suggest that C-RSV-FER-FA-SLNs have potential as promising nanodrug formulations for cancer therapy.

Li, et al. [39] synthesized nanoparticles using a phospholipid complex, DSPE-PEG-FA, for delivering mitomycin C (MMC). They employed a simple one-pot self-assembly method to prepare MMC-phospholipid complex-loaded DSPE-PEG-based nanoparticles (MP-PEG-FA NPs). Cellular studies revealed MMC distribution in the nuclei following uptake, facilitating intracellular drug delivery. Notably, systemically administered MP-PEG-FA NPs exhibited improved blood persistence and enhanced tumor accumulation in nude mice bearing HeLa tumors. The findings suggest the potential of these nanoparticles for effective drug delivery in cancer therapy, as shown in Figure 2. Gawali, et al. [40] developed water-dispersible Fe_3O_4 MNPs functionalized with glutaric acid (Glu-MNPs) using a high-temperature thermal decomposition method. To enhance colloidal stability and heating efficacy, Glu-MNPs were conjugated with BSA protein through covalent bridging, resulting in protein-conjugated Glu-MNPs (Pro-Glu-MNPs). Pro-Glu-MNPs exhibited superparamagnetic behavior, biocompatibility with normal cells, and higher heating efficacy compared to Glu-MNPs under an AC magnetic field. The study highlights the potential of Pro-Glu-MNPs for hyperthermia therapy, as they are dispersible in cell culture media, phosphate buffer saline, and water, with magnetic heating efficacy dependent on the dispersing medium.

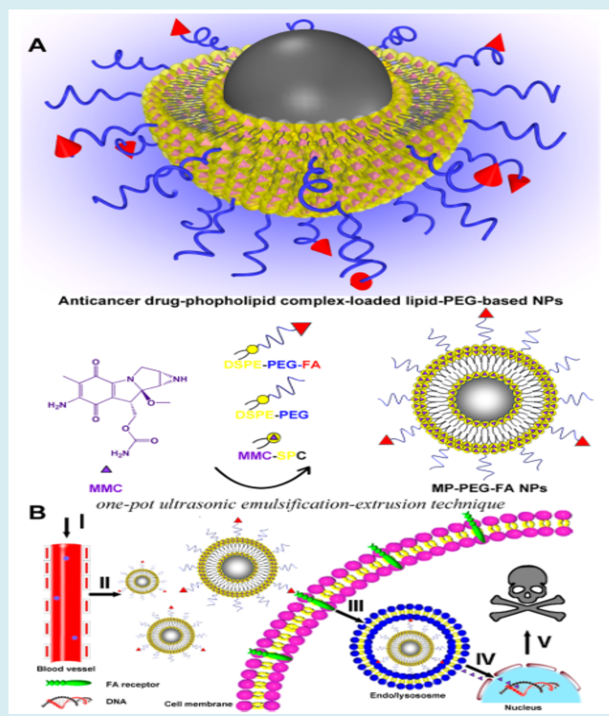

Figure 2: Schematic demonstrates the process of preparing lipid-PEG-based nanoparticles (NPs) loaded with an anticancer drug-phospholipid complex (MP-PEG FA NPs). In addition, illustrates the targeted accumulation of these NPs in tumors, the receptor-mediated endocytosis mechanism, and the intracellular dual-controlled release of the drug [39].

Contaminants Treatment

The remarkable biocompatibility, high efficiency, and natural abundance of magnetic nanoparticles have highlighted their potential for nutrient removal from wastewater. These particles are recognized for their ability to effectively and safely remove nutrients, making them a promising solution for wastewater treatment [41]. Studies have indicated that ferric oxides possess the capability to selectively eliminate phosphate from wastewater. The exceptional properties of Fe_3O_4, such as its high surface area, accessibility for pollutant interaction, favorable surface reactivity, pH stability, and eco-friendly characteristics, have captured the interest of researchers involved in the advancement of environmental remediation approaches [42]. Nonetheless, the small size of iron oxide particles presents difficulties in terms of recycling within a continuous flow system and the accumulation of substantial amounts of chemical waste, leading to heightened costs. To address this procedural limitation, numerous researchers have directed their attention towards incorporating doped ferric oxides into microbial exopolysaccharides, resulting in larger particle sizes. Darwesh, et al. [43] achieved the immobilization of peroxidase on Fe_3O_4 magnetic nanoparticles using glutaraldehyde co-precipitation. The resulting MNPs-immobilized peroxidase displayed exceptional stability against temperature and pH changes compared to the free enzyme. It retained full activity after storage at 4 and 25°C for 90 days and through 100 recycling cycles. Notably, the MNPs-immobilized peroxidase effectively decolorized dyes with diverse chemical compositions in a laboratory-scale bioreactor. Govarthanan, et al. [41] synthesized a novel magnetic nano-composite particle called Fe_3O_4@EPS by co-precipitating iron (III) chloride and iron (II) sulfate (Fe_3O_4 nanoparticles) with exopolysaccharides (EPS) derived from the microalga Chlorella vulgaris. The researchers investigated its efficacy in nutrient removal from wastewater. Under optimized conditions (3.5 g/L of Fe_3O_4@ EPS, pH 7.0, and 13 hours of incubation), the nano-composite demonstrated effective removal of 91% of PO_4^{3-} and 85% of NH^{4+} from the wastewater. Patel, et al. [44] successfully immobilized *Rhus vernicifera* laccase (RvLac) onto magnetic nanoparticles using covalent methods. Fe_2O_3 and Fe_3O_4 nanoparticles activated with 3-aminopropyltriethoxysilane and glutaraldehyde exhibited the highest immobilization yields and relative activity, reaching up to 81.4% and 84.3% respectively, at an optimum incubation time of 18 hours and pH of 5.8. Fe_2O_3 nanoparticles achieved a maximum RvLac loading of 156 mg/g of support. The immobilized enzyme displayed a higher optimum pH and temperature of 4.0 and 45 °C, compared to 3.5 and 40°C for the free form. The study demonstrated efficient immobilization of RvLac on magnetic nanoparticles, resulting in enhanced loading, improved temperature and pH profiles, thermal and solvent stability, high reusability, and enhanced degradation of bisphenol A. Ghorbani-Vaghei, et al. [45] developed a nanocomposite consisting of gold nanoparticles (Au NPs) on a sodium alginate (Alg) covered magnetite (Fe_3O_4@Alg-AuNPs). This nanocomposite exhibited excellent catalytic performance in the reduction of 4-nitrophenol to 4-aminophenol. UV-Vis spectroscopy was employed to quantitatively monitor the reduction process, demonstrating high yields (99%) achieved in a short reaction time (1.5-4 minutes) using a low catalyst load (1-3 mg) in aqueous media at room temperature. The study highlights the potential of the Fe_3O_4@Alg-AuNPs nanocomposite as an efficient catalyst for various applications. Sabit, et al. [46] developed a dual-S-scheme system by integrating 0D $CuO/ZnFe_2O_4$ nanoparticles with 2D BiOBr nanoplates. The resulting $CuO/ZnFe_2O_4$/ BiOBr (CO/ZFO/BOB) heterojunction showed exceptional photo-efficiency in levofloxacin degradation, achieving 91% efficiency in 90 minutes. This was a significant improvement compared to individual components, with enhancements of 5.61, 3.79, and 4.19 times over BOB, ZFO, and CO, respectively. The coupling of $CuO/ZnFe_2O_4$ with BiOBr facilitated efficient photon utilization and enhanced separation of photo-carriers, operating in a unique dual-S-scheme mode". In addition, many treatment techniques used the immobilization technique in their activity such as:

Photocatalysis Technology: Which is an advanced oxidation strategy that utilizes solar or simulated light irradiation to generate potent oxidants, which are then employed to degrade environmental contaminants [47]. Jabbar, et al. [48] designed and synthesized a novel magnetic nano-hybrid, BWO/FO/ GCN, through a three-step synthesis process for antibiotic mineralization using visible and sunlight irradiation. The nano-hybrid achieved strong interfacial contact by combining hierarchical Bi_2WO_6 (BWO) and Fe_3O_4 (FO) nanoparticles with g-C_3N_4 nanosheets (GCN), resulting in an S-type charge transfer system. The optimized BWO/FO/GCN heterojunction exhibited several advantageous features, including efficient solar-light utilization, exceptional photo-redox capacity, rapid charge disintegration, easy magnetic separation, cost-effectiveness, and environmental friendliness. Moreover, the S-type heterojunction demonstrated remarkable catalytic degradation efficiency, achieving degradation percentages of 84.5% and 61.4% for the levofloxacin (LEV) antibiotic under visible and sunlight irradiation, respectively.

Microbial Fuel Cell (MFC): which are defined as modern technique for treating industrial wastewater and converting the organic content to bioenergy [49]. Liu, et al., [50] investigated a new type of anode consisting of electrospun porous α-Fe_2O_3 nanofibers integrated with carbon nanotubes (CNTs) was developed for MFCs. The CNTs/α-Fe_2O_3 anode exhibited excellent electrical conductivity, ultrahigh porosity, and a three-dimensional interpenetrated network, which facilitated the colonization of active bacteria and promoted efficient EET. As a result, the MFC equipped with the CNTs/α-

Fe_2O_3 nanofiber anode achieved a remarkable power density of 1959 mW/m^2 and a high chemical oxygen demand (COD) removal efficiency of 85.04%. These performance metrics surpassed those of an MFC with an α-Fe_2O_3 anode (940 mW/m^2; 81.66%) and a bulk carbon cloth anode (432 mW/m^2; 65.83%). Significantly, the modified CNTs/α-Fe_2O_3 anode facilitated the attachment of electrogenic active bacteria, leading to improved bioelectricity production. This research demonstrates the potential of using CNTs/α-Fe_2O_3 nanofibers as anodes in MFCs for power generation and pollutant removal.

Moving Bed Biofilm Reactor (MBBR): was developed as a solution to address various limitations encountered in other wastewater treatment systems, such as hydraulic instability, inadequate working volume in trickling filters, mechanical failures in rotating biological contactors, and uneven distribution of biofilm on support in aerated submerged fluidized-bed reactors [51]. Su, et al. [52] investigated the synthesis of a new adsorbent and bacterial cells immobilized carrier called Fe_3O_4@Cu/PVA biomaterial. The structure and morphology of the biomaterial were characterized using scanning electron microscopy. The study focused on examining the effects of various factors on autotrophic denitrification based on Mn(II) in a moving bed biofilm reactor. The results revealed that the highest efficiency in nitrate removal and Mn(II) oxidation occurred when the initial Mn(II) concentration was 80 mg/L, the hydraulic retention time was 10 hours, and the pH was 7. Chromatography analysis demonstrated that N_2 gas was produced as an end-product, with variations in gas composition depending on the concentration of Mn(II) in the MBBR. The concentration of Mn(II) significantly influenced the community diversity within the MBBR, and the bacterium Pseudomonas sp. H-117 played a crucial role in the processes of Mn(II) oxidation and nitrate removal.

Adsorption: is a process in which particles adhere to the surface of a material. Various adsorbents, such as bamboo-activated carbon, chitin, carbon nanotubes, chitosan, and peanut shell, can be utilized for this purpose [53]. Ghadami, et al. [54] conducted lab-scale and batch experiments to investigate the parameters affecting the removal of tetracycline by preparing Ho_2MoO_6/Fe_2O_3 nanocomposites via a green and simple method, including temperature, adsorbent amount, initial antibiotic concentration, and contact time. Response Surface Methodology (Central Composite Design) was utilized to optimize these parameters and develop a predictive model for tetracycline removal. The obtained data from practical tests were compared with Freundlich and Langmuir isotherms. Additionally, the adsorption kinetics of the new adsorbent were studied. The results revealed that the highest removal efficiency, reaching 99.96%, was achieved at 30°C, with 1000 mg of nano adsorbent per liter, 20 mg/L of tetracycline, and 90 minutes of incubation. Based on the Response Surface Methodology, the quadratic model proved to be the most suitable equation for predicting tetracycline separation using the nano adsorbent, with an R2 value of 0.9931. Furthermore, the adsorption kinetics followed pseudo-second-order kinetics, and the Langmuir isotherm model was found to be applicable. The nanocomposite exhibited a high adsorption capacity for tetracycline and its magnetic properties facilitated easy separation, making it an ideal choice for removing tetracycline from water.

Gas Adsorption: which is a process that occurs primarily on the surface of sensitive materials, making the surface structure crucial for high-quality sensing materials. Nanomaterials, with their large surface area, exhibit superior sensing performance [55]. Yang, et al. [55] designed and investigated four types of α-Fe_2O_3 nanorods (standing, surface-threaded, sugar-gourd-shaped, nano-zigzag) for hydrogen adsorption using reactive molecular dynamics. The results showed that nano-zigzag structures had lower hydrogen adsorption efficiency compared to standing nanorods, while surface-threaded and sugar-gourd-shaped structures performed exceptionally well. The width of the thread on surface-threaded nanorods affected the adsorption rate, while the adsorption efficiency of sugar-gourd-shaped nanorods was influenced by the diameter of the spheres. Temperature increase within the range of 300-600 K negatively impacted hydrogen adsorption on α-Fe_2O_3 nanostructures. These findings provide valuable insights for the nanoscale structural design of gas sensors [56-60].

Conclusion

Conventional methods of cell immobilization and suspended microorganism technology have limitations, such as difficulty in separating the catalyst from the liquid phase and the need for continuous replenishment of microorganisms. In contrast, magnetic nanoparticles offer several advantages in the context of immobilizing microorganisms. One key advantage is the ease of catalyst retrieval from the liquid phase. The magnetic nature of the nanoparticles allows for their efficient separation using external magnetic fields, enabling easy recovery and reuse of the immobilized microorganisms. In addition to their potential in biomedical applications, this review emphasizes the application of immobilized magnetic nanoparticles in the remediation of contaminants from the environment. Environmental pollution control is a pressing global concern, and the immobilization of microorganisms using magnetic nano-based carriers can provide an effective solution. By immobilizing microorganisms on magnetic nanoparticles, their stability and efficiency can be improved, enabling them to effectively degrade pollutants and remediate contaminated environments. Furthermore, immobilization techniques offer numerous benefits in industrial processes. By immobilizing catalytic enzymes on magnetic nanoparticles, their stability and activity can be enhanced, leading to improved performance and longevity. Additionally, the magnetic nature of the nanoparticles facilitates the separation of the catalyst from the reaction mixture, simplifying downstream processing and reducing costs. The ability to reuse the immobilized catalyst in continuous industrial processes further enhances the economic and environmental sustainability of the immobilization approach. Among various supporting materials for immobilization, magnetic nanoparticles are considered a promising direction for future research and applications. Their exceptional properties, such as stabilization, easy recovery, and reusability, make them highly suitable for immobilization purposes. The ease of recovery through magnetic separation simplifies the separation process and allows for repeated use of the immobilized microorganisms or enzymes, reducing costs and waste generation.

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