

Nanotechnologies for Removal of Pharmaceuticals from Wastewater

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Water pollution is a global issue that has significant economic and social consequences for both environment and human health [1, 2]. The rising shortage of useable water resources necessitates adequate wastewater treatment. In this context, finding less expensive, safer, and more efficient wastewater treatment technology is critical. The use of nanotechnology in wastewater treatment is one potential technique that has seen success in numerous studies. Pharmaceuticals compounds (PhCs) are one of the most common types of emerging pollutants [3]. Their inadequate disintegration and the indiscriminate dumping of waste from the industries, farms and medical centers have allowed for these chemicals to become part of various water bodies of the surrounding region. The presence of PhCs in water sources has been well documented all around the world. They have a negative influence on the growth of organisms, especially aquatic one.

Treatment of wastewater that contains hazardous PhCs effluents is considered one of the world's issues. In recent decades, antibiotics, hormones, pesticides, and antiviral drugs have all been removed from wastewater using nanotechnology techniques such as adsorption, biosorption, nanofiltration and photocatalysis. Nanotechnology focuses on the development of new nanomaterials and technologies owning at least one nanoscale of 1 to 100 nm. Such nanomaterials display unique physical-chemical characteristics, including nano-size, wide surface area, large-scale reactivity, a wide range of active sites, catalytic potential, porosity and significant photo-catalytic adsorption [4, 5].

Adsorption and Biosorption

Adsorption is a surface phenomenon that includes the transfer of a phase (ions or molecules) termed adsorbate onto a solid, rarely liquid surface, called an adsorbent to create a monomolecular layer on the surface under specific conditions, either physicochemical or chemical interactions [6]. Biosorption is a type of adsorption in which biological materials, such as bacteria, algae, and fungi, act as adsorbents due to their inherent ability to bind and accumulate heavy metals, even from very dilute aqueous solutions, or through metabolically mediated (ATP) or spontaneous physicochemical uptake pathways (not at the cost of ATP) [7]. The process of biosorption principally involves microprecipitation, ion exchange and cell-surface complexation. Kariim et al. developed a multi-walled carbon nanotubes (MWCNTs) adsorbent from pure activated carbon doped with nickel-ferrites (Ni-Fe) for the removal of metronidazole and levofloxacin from pharmaceutical effluent [8]. According to surface morphology (Figure 1) and the Brunette-Emmett-Teller (BET) results, the MWCNTs produced have an improved structural composition, identified and long strand formation with the surface area of $650.45 \text{ m}^2 \text{ g}^{-1}$. In addition, the results of the adsorption process revealed that the adsorption parameters were fitted to the Pseudo-second order model. The adsorption technique indicated that the MWCNTs generated had a high capacity for metronidazole and levofloxacin adsorption.

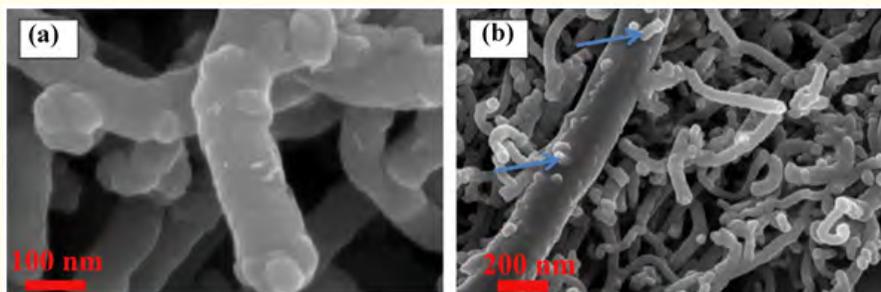


Figure 1: Field emission scanning electron microscope (FESEM) images of MWCNTs from Fe-Ni supported on activated carbon [8].

Nanofiltration Membrane

Water filtration is the process of removing or reducing the concentration of particulate matter from contaminated water, such as suspended particles, microorganisms, and other harmful biological and chemical contaminants, to produce safe and clean water. Recently, membrane technology has received much attention, and the most significant innovation in membrane technology is the nanofiltration (NF) membrane [9]. NF membranes are a mature technology that is utilized techniques for wastewater treatment. NF membranes are very flexible, low-cost, and simple to manufacture. Polak et al. designed carbon-ceramic membranes for the removal of pharmaceuticals (Tetracycline, Ibuprofen, Norfloxacin, and Sulfamethazine) from water [10]. They chemically modified the surface of the membranes using graphene oxide (GO), single-walled carbon nanotubes (SWCNTs) with -COOH groups, and MWCNTs with -COOH groups (Figure 2). The results demonstrated that carbon-ceramic membranes may be given adsorption characteristics by surface modification and then utilized as filtration membrane and adsorption process. The modified carbon-ceramic membranes exhibit the capacity to adsorb pharmaceuticals from water in contact with the membrane. MWCNT modified ceramic membrane is characterized by high tetracycline retention rates, namely, 45.4% for microfiltration membranes. Modifications to other carbon compounds such as SWCNT and GO have not resulted in good performances. In addition, the adsorption characteristics of membranes do not appreciably alter the membranes' filtering capabilities. Therefore, such membranes can be used in an integrated filtration-adsorption process.

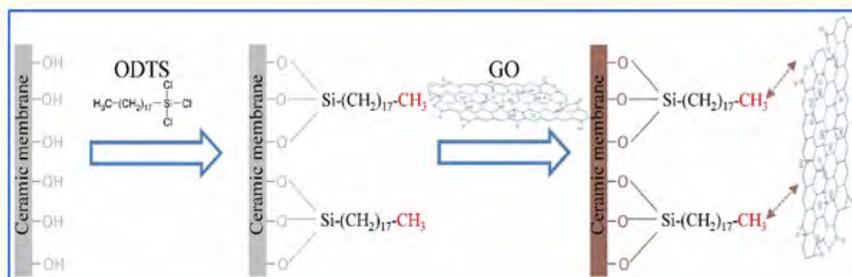
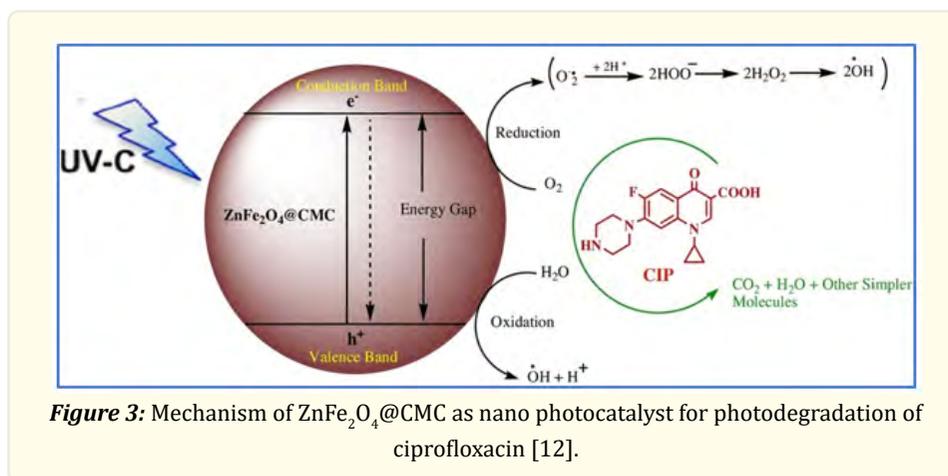


Figure 2: GO-ceramic membrane modification mechanism with Octadecyl trichlorosilane (ODTS) solution [10].

Photocatalysis

Photocatalytic degradation of PhCs by nanomaterials has caught the interest of researchers due to its high efficiency and the promise of full mineralization of target organics. As photocatalysts, titanium oxide (TiO_2), graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), zinc oxide (ZnO), iron oxide (Fe_2O_3), and tungsten oxide (WO_3) were used to degrade PhCs [11]. Despite substantial advances in the photocatalytic degradation of PhCs, two fundamental disadvantages remain: (1) the narrow spectrum for light absorption and (2) the fast rate recombination of electron-hole pairing. The wide bandgap prohibits visible light from being used, which is a bottleneck for many photo catalysts. Metal/non-metal doping, and heterojunction materials have been utilized as bandgap modification methods to improve visible light absorption. The recombination of electron-hole pairs in photo-excited material often happens on the surface or in the catalysts, squandering energy without causing a reaction. Several methods, such as noble metal doping with carbonate materials, texturally designing, and copolymerizing, have thus been used to hinder the recombination process. Malakootian et al. synthesized a heterogeneous magnetic nanophotocatalyst using carboxymethyl cellulose ($\text{ZnFe}_2\text{O}_4@\text{CMC}$) to remove Ciprofloxacin (CIP), as shown in Figure 3 [12]. The fabricated catalyst was characterized by its photocatalytic potential to remove CIP, its chemical stability and its reusability. They found superior chemical stability, reusability and excellent CIP removal potential for designed magnetic nanophotocatalyst, which would promote its industrial applications in antibiotic degradation from pharmaceutical wastewater.



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