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Recent Advances on Iron Oxide Magnetic Nanoparticles as Sorbents of Organic Pollutants in Water and Wastewater Treatment

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Abstract: The constant growth in population worldwide over the past decades continues to put forward the need to provide access to safe, clean water to meet human needs. There is a need for cost-effective technologies for water and wastewater treatment that can meet the global demands and the rigorous water quality standards and at the same maximizing pollutant efficiency removal. Current remediation technologies have failed in keeping up with these factors without becoming cost-prohibitive. Most recently, nanotechnology has been sought as the best alternative to increase access to water supplies by remediating those already contaminated and offering ways to access unconventional sources. The use of iron oxide magnetic nanoparticles as nanoadsorbents has led way to a new class of magnetic separation strategies for water treatment. This review focuses on highlighting some of the most recent advances in core-shell iron oxide magnetic nanoparticles and nanocomposites containing iron oxide nanoparticles currently being developed for water and wastewater treatment of organic pollutants. We discuss the novelty of these novel materials and the insight gained from their advances that can help develop cost-effective reusable technologies for scale-up and commercial use.

Keywords: adsorption; environmental remediation; magnetic nanoparticles; nanoadsorbent; water treatment.
Contamination due to organic pollutants continues to pose a health risk to aquatic environments and humans. Persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, various industrial additives and pharmaceutical and personal care products (PPCPs), are ubiquitous in nature (11, 12). POPs have consistently been found in groundwater, drinking water, sewage effluents and sludge, and they can enter the food chain and bioaccumulate to detrimental levels for human health (13, 14). Despite their widespread distribution, most POPs are found at very low concentrations and in complex environmental matrices making their enrichment, capture and degradation a strenuous task. Traditional treatment techniques are limited to site excavation (15), bacterial remediation in situ (16) and degradation with highly reactive techniques are limited to site excavation (15), bacterial remediation in situ (16) and degradation with highly reactive nanoparticles (zero valent iron, bimetallic Fe0/Pd or Au/Pd) to less harmful species (10, 17, 18).

In this review, we focus on highlighting some of the most recent developments in the application of core-shell IONPs as nanoadsorbents of organic contaminants for water and wastewater treatment. The design of these materials and their current applications are discussed, placing special emphasis on core-shell structures or nano-composite materials. The environmental behavior, stability and other implications of IONPs use for environmental remediation fall out of the scope of this review and therefore will not be addressed here.

**Core-shell IONPs**

Adsorption is the most commonly used technique to remove most organic and inorganic contaminants from water and wastewater treatment (19–22). Conventional adsorbents like activated carbon (AC) are used to trap the contaminant within its pores. Nonetheless, despite the inexpensiveness of the raw materials needed, the energy requirements to obtain high quality AC and regenerate it after use has proven to have detrimental environmental effects on its own (23). Moreover, the efficacy of such adsorbents is often limited by available surface area or active sites, lack of selectivity and their adsorption kinetics. IONPs, due to their very small size, offer significant improvements in terms of higher surface area and sorption sites and the ability to tune their surface chemistry for enhanced selectivity. Core-shell IONPs consist on an iron magnetic core and a shell materials that comprises the core (outer layer). The shell of these nanoparticles can be organic, inorganic or a combination of both, and its material selections strongly depends upon the end applications and use. The shell tailoring allows for the development of nanocomposite materials that have high affinity for specific contaminants and can be readily used in the environment.

Surfactants are commonly used surface modifiers to help control bare IONP aggregation and interactions (24, 25). Surfactants can be nonionic, amphoteric, cationic or anionic depending on the end application. Recently, magnetic permanently confined micelle arrays (Mag-PCMAs) have been synthesized and have proven to be effective in removing organic contaminants from aqueous solutions (26, 27). A silica porous layer is used to confine the cationic surfactant micelles into the mesopores preventing loss during subsequent use. Huang et al. (28) demonstrated high adsorption rate and capacity for three different industrial effluents and PPCPs (methyl orange, sulfamethoxazole and gemfibrozil) as well as two different PAHs (acenaphthene and phenantrrene). By adding a micelle swelling agent during synthesis and then removing it Huang et al. (28), were able to increase the pore volume and surface area of the Mag-PCMA, thus increasing their sorption capacity and diffusion rate. The methyl orange removal efficiency and the visual color change due to fast sorption kinetics of three different Mag-PCMAs synthesized with different amount of swelling agent is shown in Figure 1A,B. Here, it can be seen the rapid adsorption in the first 30 min, achieving a 98% removal efficiency. Further studies showed that pollutant sorption formed a monolayer dominated by hydrophobic interactions between the surfactants and the molecule in question. Overall, Mag-PCMAs show promise as high efficiency sorbents for organic pollutant with large pore sizes and more porous channels than those synthesized in other ways, hence providing a sustainable fast and reusable water treatment technique that can be extended and scaled-up to continuous batch reactors.

β-Cyclodextrin (β-CD) is a seven glucose cyclic oligosaccharide that is well known for its capacity to form host-guest complexes with a variety of molecules due to the formation of cavities with an external hydrophilic surface, an internal hydrophobic pocket and a specific diameter (29, 30). Thanks to these specific host-guest interactions, β-CD has been widely used as a surface modifier of IONPs specifically for the capture of some hydrophobic organic contaminants, such as PCBs, and has gained interests in environmental remediation (31–33). In the past year, Wang et al. (34) developed a core-shell magnetic nanoparticle consisting of a magnetite core and a silica bonded β-cyclodextrin layer (Fe3O4@β-CD) capable of adsorbing PCB-28 and PCB-52 in aqueous solutions, as shown in Figure 1C. The adsorption capacities of Fe3O4@β-CD for
the PCB congeners were studied in water and incubated for 24 h, after which the nanoparticles were isolated with a magnet and UV absorbance measurements were used to determine the concentration of the residual solution. It was demonstrated that the \( \beta \)-CD can increase the binding capacity almost three-fold when compared to the magnetite core. The PCB inclusion within the \( \text{Fe}_3\text{O}_4 @ \beta \)-CD cavity was 1:1, and due to the specific diameter of the cavity, the specific adsorption for PCB-28 was a little higher than that for PCB-52. The Langmuir isotherms for PCB-28 and PCB-52 are shown in Figure 1D, where the absorptive capacities of 40.01 and 30.32 mmol/kg, respectively, can be seen. The functionalized core-shell nanoparticle developed by Wang et al. (27) can effectively be used to concentrate organic contaminants from water, easily separated from the contamination source and readily extended and applied for environmental remediation.

Recently, our group has described a novel and versatile one step coprecipitation synthesis methodology of curcumin stabilized iron oxide magnetic nanoparticles (C-IO MNPs), shown in Figure 2A, that can potentially be used in environmental remediation, biomedical and catalysis applications (35). Curcumin is a naturally occurring antioxidant and polyphenol found in the Indian spice turmeric, with a high content of aromatic groups in its molecular structure (36, 37). The presence of these groups offers the possibility of interaction through pi-pi sticking with similar molecules, such as PCBs, in a variety of environments. Bhandari et al. (35) demonstrated successful incorporation of the curcumin onto the surface of the IONPs, representing around 10–12% in mass of the nanoparticle’s weight. The C-IO MNPs showed a 10-fold increase in safe administration limits compared to uncoated IONPs when incubated for 24 h with human umbilical vein endothelial cells (HUVECs), thanks to the antioxidant response of curcumin. Additionally, when these cells were exposed to PCB 126 in the presence of C-IO MNPs, a protective effect against this inflammatory agent was seen. Figure 2B shows...
the % viability of HUVECs preincubated with 10 μg/mL of curcumin iron oxide nanoparticles for 0, 12 and 24 h followed by a 24-h exposure to 50 μM PCB 126. It can be seen that the antioxidant effect of curcumin protects the cells against PCB 126 showing a greater cell viability between treated and nontreated cells. This protection can be attributed to the interactions between PCB 126 and curcumin, most likely through pi-pi stacking, which reduced the bioavailability of this stressor and the cell burden in general. The results from this study can be further extended to environmental burden and reduced bioavailability of organic contaminants such as PCBs in contaminated water sources due to the aforementioned pi-pi stacking interactions that can be employed to capture/adsorb and sense these pollutants.

**IONP nanocomposites**

Another approach to developing high efficiency nanomaterials for treatment of POPs in water consists on using IONPs in a confined micro- or macroscale support, which allows for the nanoparticles to still exhibit their reactivity while being complemented by the adsorbent properties of the accompanying materials. One such material is chitosan (CS). CS is a natural material that is hydrophilic and contains active sites along its polymeric chain due to the presence of -NH₂ groups. Because of these properties, CS has recently been regarded as one of the most promising biosorbents for water and wastewater treatment for negatively charged contaminants (38, 39). A very successful nanocomposite fabricated using CS, lignocellulose fibers (LCF) and IONPs has been developed by Zhou et al. (40) for biosorptive removal of acidic azo dyes. First, the CS decorated LCF was prepared via surface deposition crosslinking and then magnetized through blending in an aqueous solution containing IONPs allowing for spontaneous adherence, as seen in Figure 3A. The magnetic CS/LCF (mCS/LCF) was used to adsorb acid red 18 (AR 18) as model azo dye from water at different pH, ionic strength and temperature. As expected, the adsorption of azo dyes onto mCS/LCF is highly pH dependent due to the protonation of the amino groups (−NH₃⁺) in CS at lower pH, which increases electrostatic interactions between the negatively charged AR 18 anions and the positively charged adsorption sites. Additionally, the adsorption isotherms of mCS/LCF indicate a homogeneous surface where the adsorption process is govern by intraparticle diffusion. As the AR 18 molecule is adsorbed onto the exterior surface of mCS/LCF, the available sites diminish until saturation is reached. From this point on, the AR 18 molecules need to overcome the diffusion resistance of the saturated surface to diffuse into the pores, resulting on a longer time needed to reach equilibrium. Hence, the two distinct slopes observed for the Weber-Morris diffusion model plot (Figure 3B) of AR 18 adsorption on mCS/LCF. Furthermore, Zhou et al. (40) demonstrated that the removal of AR 18 remained at around 99.68% throughout 10 consecutive cycles. Overall, the newly developed mCS/LCF nanocomposite offers a facile and reusable biosorbent that can be easily separated from the adsorption medium by means of applying a magnetic field, all while obtaining remarkably high adsorption capacities, 1181 mg/g compared to 828.1 mg/g for pure nanochitosan.

Similarly, Arya and Phillip (41) have recently designed a nanocomposite containing clay, activated carbon, chitosan and IONPs for the adsorption of pharmaceuticals in water. Although activated carbon itself has long been considered one of the best available control technologies for a wide range of pollutants, the removal efficiencies reported for hydrophilic pollutants tend to be smaller (42). Therefore, with this new magnetic clay composite, the ability to remove cationic or anionic, and hydrophilic or hydrophobic contaminants was achieved. The selected pharmaceuticals
for the adsorption studies utilized by Arya and Phillip were atenolol (beta blocker), ciprofloxacin (antibiotic) and gemfibrozil (lipid regulator), of which the first two are hydrophilic. A high removal for atenolol and ciprofloxacin was observed, 85% and 95%, respectively. This was attributed to the hydrophilic nature of these compounds and of the CS-clay composite, as well as to cation exchange between the cationic form of the pharmaceuticals and the magnetic composite. Correspondingly, a high removal of gemfibrozil, 90%, was seen and attributed to the hydrophobic nature of the pharmaceutical and the activated carbon, as well as surface interactions with CS. Figure 3C shows the equilibrium sorption of the pharmaceuticals to the nanocomposite at different initial concentrations. It can be observed that the maximum adsorption capacity was higher for ciprofloxacin (39.1 mg/g) than for gemfibrozil (24.8 mg/g) and atenolol (15.7 mg/g). Additionally, the equilibrium data shed insight into the highly heterogeneous nature of the nanocomposite, which favored the adsorption of the pharmaceuticals used. The adsorption process was discovered to be occurring through ion exchange rather than physisorption. This discovery was corroborated by Figure 3D, where it was seen that adsorption of these pollutants was also highly pH dependent, similar to the findings from Zhou et al. (40), and the pH determines the ionization of the pharmaceuticals. At lower pH, the adsorption of anionic pollutants, like gemfibrozil, will be favored because of the presence of protonated amine groups on the surface of the clay and CS, as well as the presence of the IONPs, which contribute to an overall positive charge on the nanocomposite. Finally, the nanocomposite developed by Arya and Phillip proves to be a promising adsorbent for pharmaceuticals in water and wastewater treatment that is reusable and easy to use.
Conclusion

The present review has examined the most recent developments of iron-based nanoparticle technologies used for water and wastewater treatment. The unique properties of iron nanoparticles, specifically its magnetic characteristics, have proven to be advantageous for a variety of adsorbents and present great opportunities to keep revolutionizing the available techniques for organic pollutant remediation. Although many of the technologies being developed are still in the laboratory research stage, they have shown success in adsorbing pollutants from water under different pH, temperature, ionic strength and organic matter conditions with high adsorption capacities and good reusability, showing progress towards pilot testing, upscaling and even commercialization.

The challenges faced by water and wastewater treatment IONP technologies rely mainly on the potential for human and environmental risk associated with their use, life cycle and disposal. The implications of these nanomaterials, however, can prove to be only temporary as more research is conducted in the area. Another important factor is the cost of making an applying these technologies, which has recently seen a decrease due to the use of readily available and low cost precursor materials such as iron, clay, silica and CS, to name a few. In addition, there is a need for comparative testing to be adopted by the research community that allows comparison between different adsorbent materials and performance so that developments in the area can move forward at a faster pace.

The key towards a successful iron oxide nanoadsorbents that meet the stringent environmental regulations lies in developing a high surface area nanocomposite with increased reactivity that does not sacrifice the magnetic properties of its components, all while minimizing the costs of the entire production process. The future for nanoadsorbents based on iron oxide nanoparticles looks very promising not only for removal of organic pollutants from water and wastewater but for other contaminants and from other contaminated media.

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