

Magnetic Oxide Nanoparticle

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Contributor: Ebenezer Nnadozie

Magnetic oxide nanoparticles are novel building blocks and vehicle for wastewater detoxification; their stable nature makes them preferable to their metallic counterparts. The inherent properties of magnetic oxide nanoparticles such as facile preparation, ease of recovery and functionalization, reusability, promotes their biocompatibility and adaptation in wastewater treatment.

Keywords: magnetic oxide ; nanoparticles ; nanocomposites ; wastewater ; adsorption ; capping ; functionalization ; bio-compatibility ; environment

1.Introduction

Magnetic oxide nanoparticles belong to the group of nanomaterials that can be controlled with the application of a magnetic field. In wastewater treatment, spent magnetic nanocomposites can be effectively recovered from the treatment plant via magnetization by an external magnetic source for treatment and re-use. Superparamagnetic oxide nanoparticles are prepared with magnetic elements such as nickel, iron, cobalt or their oxides and alloys with ferromagnetic or ferrimagnetic characteristics ^[1].

The coating and modification of magnetic nanoparticles help to improve and protect the core against oxidation and instability while providing selectivity for the magnetic nanocomposite ^{[2][3][4]}. The shell components can be organic, inorganic or a blend of both. Silica, resin, alumina, polymers, polyelectrolytes, surfactants, carbon and hemoglobin have been utilized by various authors to modify superparamagnetic nanoparticles ^{[5][6][7][8][9][10][11]}. The preparation methods of magnetic nanomaterials are instrumental to their inherent properties. Synthetic methods and characterization procedures have been extensively covered in a similar submission and will not be emphasized in this discussion ^[2].

The morphology of magnetic nanocomposites, such as shape, surface area, pore volume, mesoporosity and point of zero charge (PZC), are important considerations for an effective and efficient adsorption process. Organically capped metal oxide nanoparticles are desirable because of their relatively large surface area and abundant functional active groups desirable for adsorption, while inorganically capped metal oxide nanoparticles have narrow band gaps, wideband edges and high electron flow and conductivity ^{[12][13]}.

2. Magnetic Oxide Nanocomposites for Wastewater Treatment

Othman et al. produced magnetic graphene oxide which had 99.6% efficiency for the remediation of methylene blue from an aqueous medium ^[14]. The regeneration study was done using 1M acetic acid. Aigbe et al. proposed a novel method for the removal of Cr(VI) using a polypyrrole-functionalized magnetic composite; the magnetic composite had low saturation magnetization and a small surface area of 28.77 m²/g, though it was 99.2% effective in the remediation of Cr(VI) from aqueous solution ^[15]. Hu et al. effectively adopted adsorption and magnetic separation using maghemite for the remediation of Cr(VI) from aqueous media; after equilibration, the spent adsorbent was regenerated using 0.01M sodium hydroxide ^[16]. The capacity of the adsorbent remained unchanged after six cycles. The regeneration of Fe₃O₄@SiO₂@NH₂ adsorbent was feasible using a 1 mol/L HCl solution and had satisfactory adsorption after four cycles ^[17]. Cationic dyes were effectively desorbed from Fe₃O₄@APS@AA-co-CA using a mixture of methanol and acetic acid solution (acetic acid 5% v/v) ^[18]. The use of 0.01M NaOH as an eluent was effective for the desorption of Cr(VI) from maghemite nanoparticles ^[16]. The use of 0.1M HCl gave maximum recovery of metal ions after the adsorption of As(III) to a magnetic cellulose adsorbent ^[19]. Recently, Wanjeri et al. produced a magnetic composite of Fe₃O₄@SiO₂@GO-PEA that effectively adsorbed within a wide pH range ^[20].

The magnetic composite was used for the adsorption of organophosphorus (OPP) pesticides. The modification of graphene oxide (GO) with 2-phenylethylamine (PEA) made the surface of the magnetic nanocomposite pH independent; the composite was reusable for a 10-cycle period. Mian and Liu synthesized a TiO₂/Fe/FeC-biochar composite from sewage sludge as a heterogeneous catalyst for the degradation of methylene blue ^[21]. Chitosan inclusion improved the

surface area and mesoporosity of the composite, enabling high catalytic activity in the dye degradation process through H_2O_2 activation. Cefotaxime, a ubiquitous antibiotic, was efficiently degraded by 82.48% after 100 min by a bimetallic nanocomposite (Co/Fe/MB) functionalized with alkali-modified biochar [22]. The researchers exploited the free electronic orbit of cobalt for the adsorption of atomic hydrogen and improved the degradation of the dye. The physiochemical and catalytic properties of N-doped metal/biochar were investigated by Mian and co-authors [23]. Composites prepared at a pyrolysis temperature of 800 °C (N-TiO₂-Fe₃O₄-biochar) performed best. The broad band at 3400 cm⁻¹ indicated the co-existence of NH and OH functional groups. The band gap of the composite at 1.94 eV would promote the effective harvest of solar energy in the visible region.

There are limited reports on the application of metal oxide composites as remediators for field wastewater. Wanjeri et al. [20] demonstrated the applicability of their composite for raw wastewater treatment by simulating the adsorption of organophosphorus pesticide using water from the Vaal dam and river. They reported 86.9% and 90.1% recovery of the pesticide from the dam and river simulated media, respectively. The removal of Cr(VI) by a polypyrrole magnetic composite was reported to be strongly dependent on the applied magnetic field strength [15]. Recently, Sun et al. [24] engineered a multifunctional iron-biochar composite for the simultaneous removal of toxic elements, inherent cations and hetero-chloride from hydraulic fracturing wastewater in an 8-h equilibration period.

The ratio of iron to biochar in the composite had effects on the sorption of the pollutants. Maximum removal for Na, Ca, K, Mg, Sr and Ba cations was less than 30%; the researchers attributed the low sorption to the increased positive charge of the composite by iron loading and the corresponding electrostatic repulsion force on the cations. In addition, 1, 1, 2-trichloroethane had a maximum sorption at 91%, while Cr(VI) and As(V) were removed to the tune of 58.4% and 65.9%, respectively. The recyclability study of the magnetic composite, however, was not reported. The pseudo-second-order rate equation described the reaction kinetics of the pollutants from the wastewater better. The report of Sun and co-workers is a milestone in the investigation of multifunctional magnetic composite viability for wastewater treatment. More studies are needed on the removal of anions, polychlorinated biphenyls (PCBs), endocrine-disrupting chemicals, dioxins, radioactive compounds and other hydrophilic and hydrophobic pollutants for the informed modeling of raw wastewater treatment.

3. Conclusions

Magnetic oxide nanoparticles are viable building block for wastewater treatment. The coating and functionalization processes reduce agglomeration and promote colloid stability. Furthermore, these nano adsorbents are applicable to range of pollutants, are easily recoverable and re-usable and are largely scalable and relatively cost effective. The synthetic route in addition to the nature of the capping and functionalizing moieties impacts the morphology and magnetic properties of the nanocomposites. Organic capping agents have a lower reducing effect than inorganics on the hysteresis loop of the magnetic oxide nanocomposite. Adsorption is a cheap, facile and robust method for the removal of pollutants from wastewater. However, the efficiency of the process is dependent on both the pH and temperature of the reaction matrix. More research is needed for the development of environmentally responsive and friendly nanocomposites with inherent capabilities to work within a wide pH and temperature range. An environment auto-moderated magnetic nanocomposite would harness natural sources of energy and significantly reduce chemical and engineering costs, while driving a green economy in tandem with the United Nations Sustainable Development Goals.

For better adaptation, more studies still need to be done on developing facile and environment-friendly methods to produce superparamagnetic nanocomposites with large saturation magnetization (Ms); high specific surface area; and anti-corrosive coating on the surface of the magnetic nanostructures, while providing abundant adsorption sites and efficient process design for the simultaneous adsorption and subsequent desorption of ubiquitous pollutants from wastewater. Studies on the optimal saturation magnetization values of magnetic oxide nanocomposites, recovery time and the adsorbate–adsorbent relationship in the presence of a magnetic field during adsorption are desirable for wastewater system engineering. Furthermore, kinetics and thermodynamic properties from pilot studies in the laboratory should be comprehensive and detailed to serve as a modeling tool for industrial scale-up and design. The applied effect(s) of a magnetic field in both biological and environmental media are also desirable for informed policy and environmental frameworks.

References

1. Zhu, J.; Wei, S.; Chen, M.; Gu, H.; Rapole, S.B.; Pallavkar, S.; Ho, T.C.; Hopper, J.; Guo, Z. Magnetic nanocomposites for environmental remediation. *Adv. Powder Technol.* 2013, 24, 459–467.
2. Kanchi, S. Nanotechnology for water treatment. *J. Environ. Anal. Chem.* 2014, 1, 1–3.

3. Badruddoza, A.Z.M.; Shawon, Z.B.Z.; Rahman, M.T.; Hao, K.W.; Hidajat, K.; Uddin, M.S. Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. *Chem. Eng. J.* 2013, 225, 607–615.
4. Dubey, S.; Banerjee, S.; Upadhyay, S.N.; Sharma, Y.C. Application of common nano-materials for removal of selected metallic species from water and wastewaters: A critical review. *J. Mol. Liq.* 2017, 240, 656–677.
5. Bitar, A.; Vega-Chacón, J.; Lgourna, Z.; Fessi, H.; Jafellicci Jr, M.; Elaissari, A. Submicron silica shell–magnetic core preparation and characterization. *Colloids Surf. A Phys. Eng. Asp.* 2018, 537, 318–324.
6. Li, K.; Cheng, D.; Yu, H.; Liu, Z. Process optimization and magnetic properties of soft magnetic composite cores based on phosphated and mixed resin coated Fe powders. *J. Magn. Magn. Mater.* 2020, 501, 166455.
7. Fu, Q.-T.; He, T.-T.; Ying, R.-J. Preparation and Properties of Magnetic Hematite Core/Alumina Shell Nanospheres. *Des tech Trans. Eng. Technol. Res.* 2017.
8. Tenório-Neto, E.T.; Baraket, A.; Kabbaj, D.; Zine, N.; Errachid, A.; Fessi, H.; Kunita, M.H.; Elaissari, A. Submicron magnetic core conducting polypyrrole polymer shell: Preparation and characterization. *Mater. Sci. Eng. C* 2016, 61, 688–694.
9. Habila, M.A.; AlOthman, Z.A.; El-Toni, A.M.; Labis, J.P.; Khan, A.; Al-Marghany, A.; Elafifi, H.E. One-Step Carbon Coating and Polyacrylamide Functionalization of Fe₃O₄ Nanoparticles for Enhancing Magnetic Adsorptive-Remediation of Heavy Metals. *Molecules* 2017, 22, 2074.
10. Essandoh, M.; Garcia, R.A. Efficient removal of dyes from aqueous solutions using a novel hemoglobin/iron oxide composite. *Chemosphere* 2018, 206, 502–512.
11. Abu-Dief, A.M.; Abdel-Fatah, S.M. Development and functionalization of magnetic nanoparticles as powerful and green catalysts for organic synthesis. *Beni-Seuf Univ. J. Appl. Sci.* 2018, 7, 55–67.
12. Kumar, A.; Sharma, G.; Naushad, M.; Ala'a, H.; García-Peñas, A.; Mola, G.T.; Si, C.; Stadler, F.J. Bio-inspired and biomaterials-based hybrid photocatalysts for environmental detoxification: A review. *Chem. Eng. J.* 2019, 122937.
13. Aguer, J.-P.; Richard, C. Influence of the excitation wavelength on the photoinductive properties of humic substances. *Chemosphere* 1999, 38, 2293–2301.
14. Othman, N.H.; Alias, N.H.; Shahruddin, M.Z.; Bakar, N.F.A.; Him, N.R.N.; Lau, W.J. Adsorption Kinetics of Methylene Blue Dyes onto Magnetic Graphene Oxide. *J. Environ. Chem. Eng.* 2018, 6, 2803–2811.
15. Aigbe, U.O.; Das, R.; Ho, W.H.; Srinivasu, V.; Maity, A. A novel method for removal of Cr (VI) using polypyrrole magnetic nanocomposite in the presence of unsteady magnetic fields. *Sep. Purif. Technol.* 2018, 194, 377–387.
16. Hu, J.; Chen, G.; Lo, I.M. Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. *Water Res.* 2005, 39, 4528–4536.
17. Wang, J.; Zheng, S.; Shao, Y.; Liu, J.; Xu, Z.; Zhu, D. Amino-functionalized Fe₃O₄@SiO₂ core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. *J. Colloid Interface Sci.* 2010, 349, 293–299.
18. Ge, F.; Ye, H.; Li, M.-M.; Zhao, B.-X. Efficient removal of cationic dyes from aqueous solution by polymer-modified magnetic nanoparticles. *Chem. Eng. J.* 2012, 198–199, 11–17.
19. Zhou, S.; Wang, D.; Sun, H.; Chen, J.; Wu, S.; Na, P. Synthesis, characterization, and adsorptive properties of magnetic cellulose nanocomposites for arsenic removal. *Water Air Soil Pollut.* 2014, 225, 1945.
20. Wanjeri, V.; Sheppard, C.; Prinsloo, A.; Ngila, J.; Ndungu, P. Isotherm and kinetic investigations on the adsorption of organophosphorus pesticides on graphene oxide based silica coated magnetic nanoparticles functionalized with 2-phenylethylamine. *J. Environ. Chem. Eng.* 2018, 6, 1333–1346.
21. Mian, M.M.; Liu, G. Sewage sludge-derived TiO₂/Fe/Fe₃C-biochar composite as an efficient heterogeneous catalyst for degradation of methylene blue. *Chemosphere* 2019, 215, 101–114.
22. Wu, H.; Feng, Q.; Lu, P.; Chen, M.; Yang, H. Degradation mechanisms of cefotaxime using biochar supported Co/Fe bimetallic nanoparticles. *Environ. Sci. Water Res. Technol.* 2018, 4, 964–975.
23. Mian, M.M.; Liu, G.; Yousaf, B.; Fu, B.; Ahmed, R.; Abbas, Q.; Munir, M.A.M.; Ruijia, L. One-step synthesis of N-doped metal/biochar composite using NH₃-ambiance pyrolysis for efficient degradation and mineralization of Methylene Blue. *J. Environ. Sci. (China)* 2019, 78, 29–41.
24. Sun, Y.; Iris, K.; Tsang, D.C.; Cao, X.; Lin, D.; Wang, L.; Graham, N.J.; Alessi, D.S.; Komárek, M.; Ok, Y.S. Multifunctional iron-biochar composites for the removal of potentially toxic elements, inherent cations, and hetero-chloride from hydraulic fracturing wastewater. *Environ. Int.* 2019, 124, 521–532.

