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Unveiling the synergistic effect of an nZVI–SiO_2–TiO_2 nanocomposite for the remediation of dye contaminated wastewater†

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Water contamination and scarcity pose critical global challenges. Existing water remediation technologies such as membrane technologies lack hydrophilic surface properties, prompting the need for novel, highly efficient supportive materials. Photocatalysis emerges as a promising solution for degrading organic pollutants in wastewater. However, existing photocatalysts such as titanium dioxide (TiO_2) suffer from rapid recombination of photogenerated charge carriers and lower catalytic activity, hindering performance. Herein, a novel, high sorption capacity nZVI–SiO_2–TiO_2 nanocomposite material was synthesized *via* a combined chemical reduction approach. The influence of synthesis pH and the synergistic effects of nZVI, SiO_2, and TiO_2 on the physicochemical properties and overall performance of the nZVI–SiO_2–TiO_2 nanocomposite were investigated. Three sets of nZVI–SiO_2–TiO_2 nanocomposites were synthesized by varying synthesis pH from 2 to 4. MB dye degradation experiments and thermal analysis revealed that the nZVI–SiO_2–TiO_2 nanocomposite synthesized under pH 2 synthesis conditions exhibited the fastest dye degradation rate, highest removal efficiency (100%), and thermal stability. Characterization techniques, including FTIR, EDS (energy dispersive X-ray spectroscopy), SEM, BET (Brunauer–Emmett–Teller), XRD, TGA (thermogravimetric analysis), and DSC (differential scanning calorimetry), revealed that lower nZVI–SiO_2–TiO_2 synthesis pH enhanced the material's specific surface area, crystallinity, and the interfacial interactions of nZVI, SiO_2, and TiO_2 components in the nanocomposite. The reusability test showed >90% efficiency after 5 successive cycles. The sorption mechanism and methylene blue (MB) dye speciation test corroborated the synergistic adsorption and reduction potential of nZVI–SiO_2–TiO_2 functional materials with 100% mineralized methylene blue (MB^+ species) at MB dye solution pH above 6.0. After economic considerations, it is believed that the exceptional adsorption and recycling abilities of the novel nZVI–SiO_2–TiO_2 material, coupled with its thermal stability, could counterbalance its upfront expenses, potentially making it a feasible choice for wastewater treatment applications.

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1. Introduction

Globally, textile industries are projected to grow at a compound annual growth rate of 4.4% from 2020 to 2025, driven by increasing consumer demand and urbanization, particularly in developing economies.[1] This anticipated expansion will inadvertently exacerbate the environmental challenges posed by industrial wastewater discharge.[2] Synthetic dyes utilized in textile, plastic, and paper industries pose a major concern due to their widespread applications and high potential toxicity, as over 200 000 tons of dye are lost to effluents during textile product production cycles alone.[3–5] A plethora of these dyes and their accompanying toxic chemicals discharged into water bodies are carcinogenic and nonbiodegradable with significant

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detrimental impacts on humans and aquatic ecosystems.[4] In 2023, the UN water conference report revealed that over two billion people (26% of the global population) lack safe drinking water, making the removal of harmful organic and inorganic contaminants discharged in water and soil environments a critical global issue threatening both public health and environmental sustainability.[6]

To address this contemporary challenge, it is crucial to develop efficient and cost-effective remediation technologies capable of combating the diverse range of toxic wastewater effluents.[4] Conventional treatment methods such as flocculation,[7,8] combination of flocculation and coagulation,[9,10] sedimentation, membrane technologies[11,12] as well as the use of trickling filters[13,14] have been utilized for decades. However, these methods lack the ability to degrade recalcitrant dyes and generate secondary waste streams.[1] Consequently, advanced oxidation processes (AOPs) and biological wastewater treatment approaches were recently explored for improved selectivity and adsorption capacity.[15,16] Conversely, long residence time for effective treatment,[17] large sludge generation,[18] and environmental concerns are the greatest challenges in these approaches.[19,20] Thus, adsorption technologies, utilizing adsorbents for environmental remediation, were reinvigorated. Adsorption emerges as a prospective alternative to conventional wastewater treatment technologies due to its simple technological requisites,[21] cost-effectiveness, and high removal efficiency for diverse contaminants coupled with limited generation of secondary pollutants.[22] Consequently, the development of efficient, cost effective, and advanced adsorbent materials is essential for practical integration of adsorption technologies in mitigating the contemporary environmental impacts of dye-contaminated wastewater. Individual and synergistically combined nanoadsorbents such as nano-zero-valent iron (nZVI),[23] silica (SiO_2),[24] titania (TiO_2)[25–27] and other composite adsorbents[28] have shown great potential for environmental and wastewater remediation operations. Recently, Das *et al.* synthesized and evaluated the sorption capacity of polyaniline-based magnesium ferrite (Pan-MgF) nanocomposite for degradation of cationic brilliant green dye, and the results corroborated the formation of the Pan-MgF nanoadsorbent with 90.28% sorption capacity for brilliant green dye.[29]

Zero valent iron (ZVI) is a cost-effective and environmentally benign adsorbent recently employed in a plethora of environmental remediation operations due to its simultaneous and synergistic adsorption and reduction capabilities.[30–34] Nano-zero valent iron (nZVI), characterized by its excellent chemical reactivity and injectivity in aquifer systems, is considered a large surface area electron donor that chemically reduces pollutants to a less harmful precipitate.[35] Despite these outstanding properties of nZVI materials in environmental remediation applications, limiting factors such as rapid passivation and particle agglomeration hindering its dispersibility and overall performance need to be addressed. Coincidently, researchers have investigated the incorporation of nZVI with other functional materials such as chitosan (CS), silica (SiO_2), and titanium dioxide (TiO_2), utilizing their synergistic effects, to overcome the susceptibility of nZVI materials to rapid oxidation and improve overall performance. For example, Zhang *et al.* (2019) synthesized a chitosan (CS) composite loaded with well-dispersed nanoscale zero-valent iron (NZVI/CS). Characterizations showed that the NZVI/CS composite contained numerous dispersed Fe^0 nanoparticles, and the NZVI/CS composite exhibited synergistic adsorption and reduction capabilities.[36] Duan *et al.* encapsulated nZVI in a porous glutaraldehyde-crosslinked chitosan (GCS), and the nZVI/GCS material showed great reusability performance.[37] Despite these advances, the stability and synergistic performance of the nZVI supported nanocomposite depend on the nature and properties of the supporting materials, making the selection of suitable supporting materials highly crucial.

SiO_2 is known for its excellent adsorption properties and ability to stabilize nZVI,[38] while TiO_2 is a widely studied adsorbent capable of mineralizing organic pollutants.[39] Previous studies have explored the use of SiO_2-supported nZVI composite materials for wastewater treatment and their results demonstrated improved performance compared to individual components.[38,40] Hejri *et al.* reported excellent nitrate removal efficiency exhibited by the TiO_2/nZVI nanocomposite with a maximum removal capacity of 98.226% achieved under optimized reaction conditions, 150 minute contact time and 4.185 pH of the solution.[39] In another study, Zhao *et al.* embedded zero-valent iron nanoparticles (nZVI) within a TiO_2 matrix *via* a one-step electrospinning process and investigated the performance of nZVI–TiO_2 nanofibers toward uranium removal. The nZVI–TiO_2 nanofibers exhibited excellent performance with significant magnetic properties due to the synergistic effects of nZVI and TiO_2 nanomaterials. Despites this synergistic performance, existing materials and their synthesis approaches often suffer from a plethora of limitations such as rapid recombination, low reducing capacity, complex operation, and the generation of secondary pollutants.

Encapsulating zero valent iron materials in SiO_2–TiO_2 functional materials *via* a combined chemical reduction method could improve chemical reactivity and catalytic activity, and slow down rapid passivation of nZVI materials.[41–46] However, the development of this ternary nZVI–SiO_2–TiO_2 composite material and the investigation of pH influence in the synthesis of this novel material have not been reported. The incorporation of SiO_2 and TiO_2 with nano-zero-valent iron (nZVI) creates a unique hybrid system that combines the strong reducing capacity of nZVI, the adsorption properties of SiO_2, and the photocatalytic activity of TiO_2. This synergistic integration of different functionalities within a single composite material epitomises a novel approach and distinguishing advantage of nZVI–SiO_2–TiO_2 over other adsorbents toward enhancing the efficiency and versatility of dye removal technologies. However, the effective synthesis of nZVI-based nanocomposites depends on the synthesis conditions, specifically the reaction pH and drying conditions.[47–49] The pH of the chemical reaction can influence the surface properties, redox potential, and interfacial interactions between the nanocomposite materials, ultimately affecting both their catalytic activity and thermal stability.[23] Hence, discerning the pH-dependent dynamics in the synthesis of nZVI–SiO_2–TiO_2 nanocomposites is essential for the optimization of this novel material for environmental