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Review

Clay-supported nanoscale zero-valent iron composite materials for the remediation of contaminated aqueous solutions: A review

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HIGHLIGHTS

- A review of contaminants removed by clay-nZVI composite materials from aqueous solutions is made.
- Reaction mechanisms of the materials with contaminants are discussed.
- Excellent removal efficiencies of contaminants by composite materials are reported.
- The review suggests research needs for future work.

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ABSTRACT

Recent industrialization and urbanization have increased the aqueous concentrations of a wide range of contaminants, which are toxic to human health and the environment. Therefore, remediation of aqueous solutions has turned into an important environmental issue. Over the last decade, growing attention has been paid to clay-supported nanoscale zero-valent iron (nZVI) composite materials as efficient and promising remediation materials in wastewater treatment and groundwater remediation technologies. This paper gives an overview of the clay minerals, zero-valent iron materials, clay-supported nZVI composites, and progress obtained during the remediation of contaminated aqueous solutions utilizing the clay-supported nZVI composites for the removal of heavy metals, nitrate, selenate, dyes, phenolic compounds, chlorinated organic compounds, nitroaromatic compounds and polybrominated diphenyl ethers. Reaction mechanisms and removal efficiencies were studied and evaluated. It was reported that the clay-supported nZVI composites have appreciable removal efficiency for different types of contaminants. This paper also reviews the use of ZVI-clay technology for the remediation of contaminated sites. Concerning clay-supported nZVI composites for future research, some recommendations are proposed and conclusions are drawn.

Abbreviations: nZVI, nanoscale zero-valent iron; WHO, World Health Organization; COCs, chlorinated organic compounds; PCs, phenolic compounds; AOPs, advanced oxidation processes; ZVI, zero-valent iron; PRBs, permeable reactive barriers; NACs, nitroaromatic compounds; PBDEs, polybrominated diphenyl ethers; mZVI, microscale zero-valent iron; SEM, scanning electron microscopy; P-nZVI, palygorskite-supported nZVI; B-nZVI, bentonite-supported nZVI; K-nZVI, kaolinite-supported nZVI; Mt-nZVI, montmorillonite-supported nZVI; R-nZVI, rectorite-supported nZVI; TCE, trichloroethylene; EDTA, ethylenediaminetetraacetic acid; S-nZVI, sepiolite-supported nZVI; M-nZVI, organo-montmorillonite-supported nZVI; XPS, X-ray photoelectron spectroscopy; EPA, Environmental Protection Agency; GAC, granular activated carbon; HA, humic acid; MB, methylene blue; LMB, leukomethylene blue; OII, orange II; MO, methyl orange; CPs, chlorophenols; BPA, Bisphenol A; CTMA, cetyltrimethylammonium; PCP, pentachlorophenol; 2,4-DCP, 2,4-dichlorophenol; TCP, 2,4,6-trichlorophenol; PCB, polychlorinated biphenyl; PCE, tetrachloroethene; HDTMA, hexadecyltrimethylammonium; CTMAB, cetyltrimethylammonium bromide; NB, nitrobenzene; TNT, 2,4,6-trinitrotoluene; THF, tetrahydrofuran; DO, dissolved oxygen; p-CP, p-chlorophenol; MC-LR, microcystin-LR; AMX, amoxicillin; CVOCs, chlorinated volatile organic compounds; DNAPL, dense nonaqueous phase liquid; cDCE, cis-dichloroethene; VC, vinyl chloride.

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Contents

1. Introduction

Rapid growth in world population and industrial activities has significantly increased the global utilization of water [1]. Data from the World Health Organization (WHO) indicates that a lack of water resources has caused serious challenges for more than 40% of the world population, as over 2 billion people have no access to sufficient clean water [1]. To address this latter issue, a great attention has been directed towards treatment of wastewater in order for it to be recycled, thus not only decreasing the need for extraction of water from precious freshwater reserves but also protecting the surrounding environment [2–4].

Water quality is an important factor with regards to reuse of the treated wastewater. Increasing urbanization and industrialization has resulted in an increase in the presence of priority organic and inorganic contaminants, such as chlorinated organic compounds (COCs) [5], phenolic compounds (PCs) [6,7], dyes [8] and heavy metals [9]; potentially threatening the health of millions of people and living organisms. While the direct effects of these priority contaminants on human health are still disputable and require further investigations, their effects on animals are well reported [10,11]. These contaminants are known to disrupt the endocrine system by blocking and disturbing function of hormones [11]. Exposure to these compounds can cause breast cancer, reproductive multifunction, kidney damage, liver damage, and renal disorders in humans [11]. Of greatest concern is the effect of these contaminants toward fetuses and newborn babies as they are the most vulnerable. Another key issue with these priority compounds is that they are both toxic and carcinogenic at very low concentrations, persistent in the environment for years or decades and easily discharged to the environment [11].

However, the remediation of these contaminants is still a big challenge due to their bio-recalcitrance for conventional aerobic wastewater treatment. Moreover, they have complex structures comprised of different functional groups, which are important factors for their toxicity and make remediation processes more difficult. Additionally, the lack of regulation limitations, especially for PCs, as related to the treatment of industrial wastewater is another challenge for these types of contaminants [11]. Hence, innovative, effective, and robust technical solutions are required to solve these problems.

A wide range of chemical, physical and biological processes have been employed in wastewater treatment technology, such as membrane filtration [4,12], microbial degradation [13], coagulation [14,15], adsorption [16,17], ion exchange [18,19] and advanced oxidation processes (AOPs) [20]. Considerable efforts have been made to continually improve these methods, both technically and economically, albeit new and better solutions for specific contaminants continue to be the focus of attention. In recent years, reactions using catalytic materials have become a promising way which can successfully degrade hazardous contaminants to completely harmless products. Of greatest interest is the use of zero-valent iron materials for the remediation of contaminated aqueous solutions.

Over the last decade, zero-valent iron (ZVI or Fe^0) has drawn a great attention in wastewater treatment and groundwater remediation. It can effectively transform, degrade and remove priority water contaminants, such as PCs [21,22], COCs [23,24], and other hazardous contaminants [25,26]. ZVI was also proposed as a reactive material in permeable reactive barriers (PRBs) because of its high ability in removing and stabilizing different types of groundwater contaminants [27–29]. It has many advantages, such as high activity, non-toxicity, and low price. ZVI with particle size at nanoscale exhibits outstanding activity due to its larger surface area [25]. However, similar to other nano-materials, this ultra-fine powder has a strong tendency to agglomerate into larger particles, resulting in an adverse effect on both effective surface area and catalyst performance; while separation and recovery of the fine nZVI particles after utilization is another disadvantage of this material [25]. Using supporting material for nZVI is a promising way to solve these problems. Clay minerals as abundant natural resources are appropriate candidates to act as supporting materials [25,30–32]; their adsorption capacity attracts contaminants to the surface and thus enhance the efficiency of nZVI particles.

In recent years, a specific focus has been devoted to clay-supported nZVI (clay-nZVI) composite materials for the remediation of contaminated aqueous solutions due to their high removal efficiency and fast degradation rate [25,30–32]. The removal of contaminants by clay-nZVI composites is mainly attributed to the synergetic effect between adsorption by the clay mineral and removal by nZVI particles. For this reason, these composite materials have higher removal efficiency compared to nZVI particles and