



Carbothermal synthesis of ordered mesoporous carbon-supported nano zero-valent iron with enhanced stability and activity for hexavalent chromium reduction



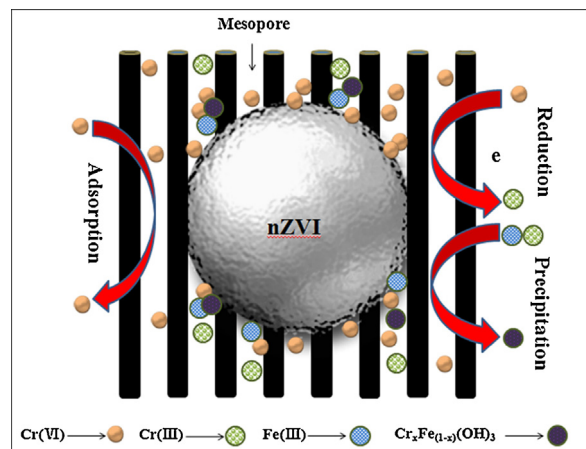
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GRAPHICAL ABSTRACT



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ABSTRACT

Composites of nano zero-valent iron (nZVI) and ordered mesoporous carbon (OMC) are prepared by using simultaneous carbothermal reduction methods. The reactivity and stability of nZVI are expected to be enhanced by embedding it in the ordered pore channels. The structure characteristics of nZVI/OMC and the removal pathway for hexavalent chromium (Cr(VI)) by nZVI/OMC are investigated. Results show that nZVI/OMC with a surface area of $715.16 \text{ m}^2 \text{ g}^{-1}$ is obtained at 900°C . nZVI with particle sizes of 20–30 nm is uniformly embedded in the OMC skeleton. The stability of nZVI is enhanced by surrounding it with a broad carbon layer and a little $\gamma\text{-Fe}$ is derived from the passivation of $\alpha\text{-Fe}$. Detection of ferric state ($\text{Fe } 2p_{3/2}$, around 711.2 eV) species confirms that part of the nZVI on the outer surface is inevitably

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oxidized by O_2 , even when unused. The removal efficiency of $Cr(VI)$ (50 mg L^{-1}) by nZVI/OMC is near 99% within 10 min through reduction (dominant mechanism) and adsorption. nZVI/OMC has the advantage in removal efficiency and reusability in comparison to nZVI/C, OMC and nZVI. This study suggests that nZVI/OMC has the potential for remediation of heavy metal pollution in water.

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1. Introduction

Nano zero-valent iron (nZVI) is an environmentally friendly and useful material that has the characteristics of small particle size, high surface area, strong reducing ability, fast reaction, etc. [1]. Therefore, in recent years, nZVI has been widely used in the field of remediation of bodies of water. nZVI has been proven to be highly effective in the removal/degradation of a wide range of pollutants, including PCBs [2], bromides [3], dyes [4], nitrates [5], and heavy metals [6]. The rank for removal of heavy metals by nZVI has been shown to be as follows: $As > Cr > Cu > Hg > Pb > Zn > Cd > Ni$ [7]. This shows that nZVI has a universal capability for reducing of heavy metals in water, and the pathway (mechanism) for the removal of the heavy metals includes reduction, adsorption, and co-precipitation [8,9]. Therefore, the use of nZVI as a reducing agent is a simple and convenient method for eliminating the heavy metal pollution from water.

However, nZVI has some shortcomings areas where it has been applied, such as poor air stability, difficulty of preservation, and easy reunion [1,6,8–10]. In recent years, many studies have been conducted to find methods for preparing stable and efficient nZVI. Initially, a small amount of surfactant, which can play a protective role for nZVI, was added during the preparation process to improve the dispersibility of nZVI [11]. However, this method does not completely solve the problem of poor stability. Subsequently, it has been found that the use of a carrier (supporter) is a very effective way to improve the stability of nZVI. The carrier materials can lessen the oxidization of nZVI (to some extent) and improve its performance, even after use or storage [12]. The dispersibility and surface area of nZVI can be improved by using the carrier materials. The carriers usually used include inorganic compounds, organic compounds, silica, polymers, clays, carbon materials, etc. Petala et al. have successfully synthesized a stable nZVI-composite by using MCM-41 as a carrier [13]. By using diatom mud as the carrier, nZVI has been successfully loaded onto its surface and pore channels [14]. This carrier can greatly improve the dispersion of nZVI and enhance its capacity of remediation of bodies of water polluted by chlorinated organics. The cation exchange resin-supported nZVI-composite has been used for the decoloration of azo dye acid blue 113, and it shows a strong decolorization capacity (100%, within 30 min) [15].

Currently, the most common method for supporting nZVI is to immerse the carrier in a solution of an iron salt and then reduce the $Fe(II)/Fe(III)$ to Fe^0 with a reducing agent, such as $NaBH_4$. The ordered mesoporous carbon (OMC) impregnated with $FeSO_4 \cdot 7H_2O$ was pyrolyzed at 300°C for 4 h and then treated with $NaBH_4$ (2.1 M) to reduce the $Fe(II)$ to metallic Fe^0 [16]. The peak at 44.6° for nZVI in the nZVI/OMC ($452\text{ m}^2\text{ g}^{-1}$) is negligible, which implies that the crystallinity and stability of nZVI are relatively poor [16]. Although, this method is fast and effective, there are also some disadvantages: $NaBH_4$ is expensive, and the conditions for reduction are rigorous. Therefore, some researchers choose the carbothermal reduction method to synthesize the nZVI/C composites [17]. By comparison with the conventional liquid-phase reduction method, it has the following advantages: the carbon is capable of supporting a large amount of nZVI and the stability of the nZVI in air is improved [18]. By pyrolyzing the mixture of carbon black and iron nitrate

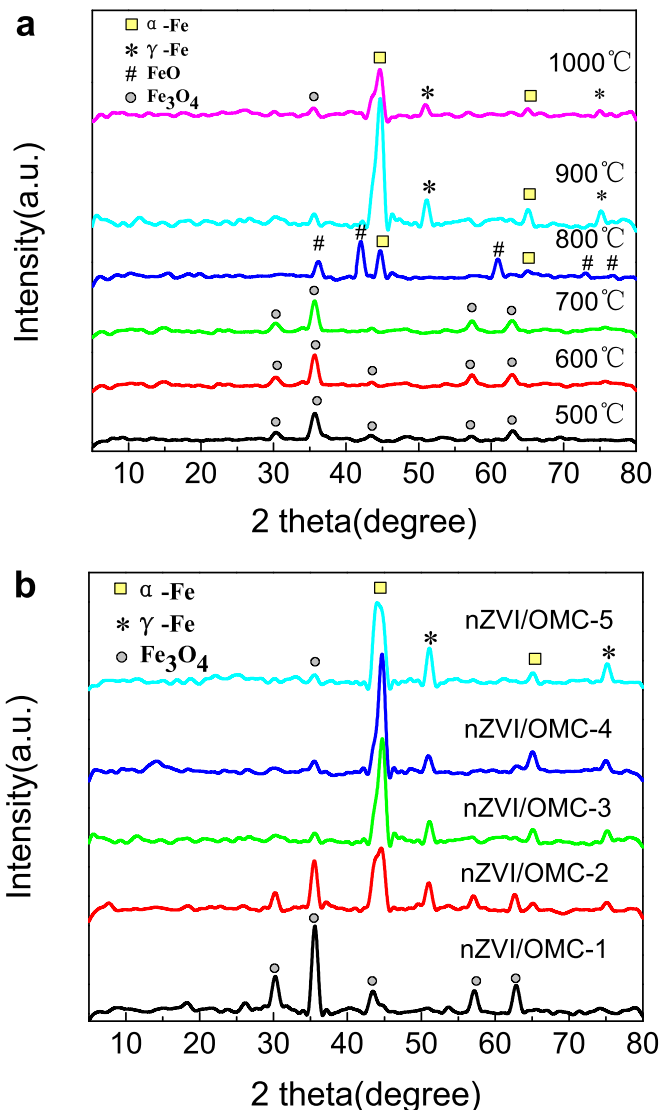


Fig. 1. XRD patterns of nZVI/OMC carbonized at different temperatures (a) and with different dosage of ferric nitrate (b).

under argon [19], Fe_3O_4/C and Fe^0/C composites can be obtained at $300\text{--}500^\circ\text{C}$ and $600\text{--}800^\circ\text{C}$, respectively. By pyrolyzing a mixture of the modified activated carbon colloid and iron salt, an Fe^0/C composite is obtained at 700°C [20] that still retains the colloidal characteristics and high reactivity. Using sucrose as the carbon source, the spherical Fe^0/C composites are obtained by using a two-step carbothermal reduction process [21]. The aerosol of Fe_3O_4/C composites is first synthesized at 1000°C , and then the Fe_3O_4 is converted to Fe^0 at 720°C [21]. The morphology of this Fe^0/C is regular (spherical) and the loading content of Fe^0 is higher than in other methods [21]. The carbon carriers used in the reported literature usually have the problems of small S_{BET} and pore volumes [16] and non-regular pore structure [19–21], which limits the

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