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Low temperature synthesis of highly stable and reusable CMC-Fe^{2+}(-nZVI) catalyst for the elimination of organic pollutants

Selvaraj Ambika, Indumathi Manivannan Nambi *, Jaganathan Senthilnathan

Environmental and Water Resources Division, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India

HIGHLIGHTS

- Synthesis of highly stable and reusable CMC-Fe^{2+}(-nZVI) hybrid (>7 nm) at 10 °C.
- Central Fe^{2+} ions sandwiched between CMC and nZVI in CMC-Fe^{2+}(-nZVI) hybrid.
- CMC-Fe^{2+}(-nZVI) removed organic pollutant for >50 cycles and stable at all pHs.
- Central $Fe^{2+/3+}$ show redox property forming $.OH/.OH_2$ radicals, limits Fe ion release.
- CMC-Fe^{2+}(-nZVI) catalyst of this kind can be used for drinking water applications.

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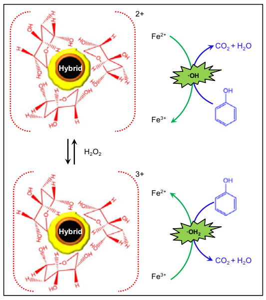
GRAPHICAL ABSTRACT



ABSTRACT

Removal of organic pollutants in Fenton process using nano zero valent iron (nZVI) has certain drawbacks such as formation of sludge, difficulty in recovery/reuse of nZVI and high concentration of Fe^{2+}/Fe^{3+} ions into the final effluent. The challenge is to stabilize the nZVI and control leaching of Fe^{2+}/Fe^{3+} ions without compromising the primary objective of removal of organic pollutants. This study demonstrates low temperature synthesis of carboxymethyl cellulose (CMC) stabilized nZVI hybrid (CMC-Fe^{2+}(-nZVI)). In this hybrid, Fe^{2+} ion present on the surface of nZVI is sandwiched between CMC and nZVI. At low temperature (~10 °C), CMC provides excellent control over the size (<7 nm) of CMC-Fe^{2+}(-nZVI). The new orientation of peaks in the UV–Vis absorbance spectra of CMC, Fe^{2+}-CMC and CMC-Fe^{2+}(-nZVI) further supported the formation of CMC-Fe^{2+}(-nZVI) hybrid. Similarly, ATR-FTIR spectra of CMC and CMC-Fe^{2+}(-nZVI) showed significant shift in the functional groups of –C=O and OH and confirmed their chelation with Fe^{2+} central ion. Redox properties of CMC-Fe^{2+}(-nZVI) when evaluated with cyclic voltammetry (CV) showed distinct oxidation and reduction peaks due to the formation of Fe^{2+} and Fe^{3+} ions. Furthermore, the redox properties and performance of CMC-Fe^{2+}(-nZVI) catalyst was assessed in Fenton process using phenol as a representative pollutant. Cyclic stability of CMC-Fe^{2+}(-nZVI) was performed at the scan rate of 60 mV/s and only less than 1% reduction in stability was observed at the end of 100 cycles. The Fe^{2+}(-nZVI) particle was effectively stabilized by CMC and only trace amount of Fe^{2+} was observed in solution at the end of the reaction. In addition, reuse of CMC-Fe^{2+}(-nZVI) led to complete phenol removal and this sustained for more than 50 cycles.

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* Corresponding author.
E-mail address: indunambi@iitm.ac.in (I.M. Nambi).

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1. Introduction

Nanotechnology is a rapidly emerging technique that is being explored in sustainable environmental applications including wastewater treatment, in-situ and ex-situ remediation of contaminants [1,2]. Different nanomaterials such as TiO_2, ZnO, CeO_2, and Fe_3O_4 have been extensively studied for the transformation of toxic contaminants into non-toxic forms [3–5]. Over the past decade, nano zero-valent iron (nZVI) has gained recognition as one of the most promising nanomaterials for remediation of contaminated groundwater/soil, chlorinated organic compounds, toxic metal ions, pesticides and organic dyes [6–11]. It has been well established that size of nanoparticles inversely correlated to its reactivity [1,2]. Our literature research indicates that the nanoparticles less than 10 nm in size are very effective for application in biomedical and environmental engineering [12–16].

The high surface to volume ratio along with quantum size effects of nZVI introduces unique chemical, electronic, magnetic and mechanical properties [17–19]. The superior properties of nZVI is a function of size and morphology of the particles, which tend to agglomerate rapidly to form larger aggregates due to van der Waals and magnetic forces of attraction, rendering them inapplicable for the targeted purposes [20,21]. It is of utmost importance to prevent agglomeration of nZVI and control the particle size for its successful application. There is also a concern about release of nanoparticles into the environment after the treatment process. It is therefore important to immobilize nZVI in a matrix. Efforts have been made to reduce the agglomeration of nanoparticles by adding stabilizer and/or templating agents [22–24]. Table 1 shows different stabilizers used for nZVI synthesis and the corresponding nZVI size. Some of the templating and/or stabilizing agents such as poly acrylic acid (PAA), polystyrene sulfonate, triblock, xanthan, acetylacetone and surfactants that are currently used for nanoparticles synthesis are either expensive or toxic and may pose additional burden to the treatment system [22–24]. Hence, there is an urgent need to develop a cheap and eco-friendly stabilizer. Recently, sodium carboxymethyl cellulose (CMC) has emerged as a pre-agglomeration stabilizer to obtain highly dispersed nZVI particles [25]. CMC molecules act as multidentate ligands, forming strong coordination bonds with nZVI to overcome the van der Waals or magnetic forces of attraction between the nZVI and reduce particles growth [26]. The advantage of CMC over other stabilizers is that it is non-toxic, biodegradable, biocompatible, economic, eco-friendly and applicable to diverse environments [27–29]. Most of the studies on nZVI synthesis using CMC were carried out at either high or ambient temperature, resulting in formation of larger sized (>10 nm) nZVI particles [30]. The activation energy of ZVI is inversely proportional to the temperature. When temperature is increased, activation energy decreases and particles tend to form a rapid agglomeration which leads to formation of larger particles [31,32]. Hence, it is hypothesized that if temperature is lowered during the synthesis, it may be possible to get a smaller sized nZVI particle. Furthermore, the interaction of CMC with nZVI at low temperature and its role in stepwise particle growth mechanism like formation of initial nuclei seed, nanocluster and nanoparticles have not been discussed in detail [33,34]. Further study to understand the stepwise formation of nZVI and role of CMC at low temperature is highly essential for large-scale synthesis and field application. Use of nZVI catalyst for the degradation of organic pollutants by Fenton's advanced oxidation process has been extensively studied by various research groups [35,36]. Formation of hydroxide radicals from ZVI for the degradation of organic pollutants in Fenton process is given below in Eqs. (1)–(3) [35,36].

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2H_2 + 2OH^- \quad (1)$$

$$Fe^{2+} + H_2O \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(II) + {}^{\cdot}OH_2/{}^{\cdot}O_2^- \quad (3)$$

The key obstacle in the use of Fenton process for drinking water or wastewater treatment is the post-treatment for removal of $Fe^{2+/3+}$ ions from treated water, which ultimately resulted in additional sludge handling costs. Moreover, recovery of nZVI from sludge and reuse is not possible due to the irreversible agglomeration of nano catalyst. Also, larger scale synthesis of nZVI particles is quite difficult in the absence of stabilizer or templating agent [37]. As a summary, size and stability of nZVI determine its reactivity and longevity in remediation systems. In addition, synthesis of stable and smaller sized (<10 nm) nZVI is still an emerging area of research.

Table 1
Size of nZVI with various stabilizers and synthesizing conditions.

Stabilizer	Size (nm)	Synthesizing conditions	Temperature	Reference
CMC	6.8	$FeSO_4 \cdot 7H_2O$ = 0.1 g/l CMC/Fe(II) ratio = 0.0301 M	10 °C	Present study
CMC	80 to 120	Fe = 2.5 g/L CMC = 0.5 g/L	Ambient temp	[60]
Starch	14.1 ± 11.7 Fe-Pd	Fe = 0.1 to 1 g/L Starch = 0.2% or 0.8% (w/w)	Ambient temp	[61]
CMC	<17.2	Fe = 0.1 or 1 g/L CMC = 0.2% or 0.8% (w/w)	Ambient temp	[25]
CMC	Not mentioned	Fe = 0.04 to 0.12 g/L CMC = 0.2% (w/w)	Ambient temp	[62]
CMC	15 ± 4	CMC = 0.5% (w/w)	Ambient temp	[63]
PAA	173 ± 40	30% (v/v) methanol/deoxygenated water	Ambient temp	[63]
CMC	11.2 ± 7.9	$FeSO_4.7H_2O$ = 0.1 to 0.2 M CMC = 1%	Ambient temp	[64]
PAA	9–15	PAA = 8% (v/v)	Ambient temp	[50]
CMC	40–100	CMC = 2% (w/w) Room temperature	Ambient temp	[50]
CMC	77 ± 15	CMC = 0.5% (w/w) Room temperature	Ambient temp	[65]
CMC	13.2 ± 2.3	Fe = 0.1 g/L CMC = 0.2% (w/w)	8 °C	[31]
CMC	70.2 ± 62.9	Ethanol solution = 30%	Ambient temp	[49]
CMC	15.9	$FeCl_3$ solution = 0.05 M CMC = 0.8%	Ambient temp	[51]