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# α-Hydroxy acids modified β-cyclodextrin capped iron nanocatalyst for rapid reduction of nitroaromatics: A sonochemical approach

Falguni Shukla [a], Twara Kikani [a], Anisha Khan [a], Sonal Thakore [a,b,*]

[a] Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390002, India
[b] Institute of Interdisciplinary Studies, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390002, India

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ABSTRACT

This study reports a sonochemical approach for the synthesis and catalytic performance of zerovalent iron nanoparticles (nZVI) capped with two cyclodextrin (CD) crosslinked polymers derived from Lactic acid and Citric acid (CDLA and CDCA respectively). The polymers and the catalysts were characterized by NMR, FTIR, HRTEM, DLS, Zeta potential, FESEM, EDAX, VSM, XRD, XPS, TGA analysis. The catalysts proved to be sustainable and recyclable for rapid sonochemical reduction of nitroaromatics under ambient conditions. The isolated yield of the derivatives was found to be greater than 90%. The results suggest excellent dispersibility, stability, high iron content and smaller size of CDLA polymer capped nZVI compared to CDCA capped nZVI, leading to two-fold higher catalytic activity. The effect of various crucial catalysis parameters was investigated and optimized. The scope of the reaction was extended to other nitroaromatics under the optimized conditions. Being magnetically separable, the cost effective and non-toxic catalysts exhibited high recycling efficiency (~13 cycles), high turnover number (TON) and turnover frequency (TOF). The recyclable catalysts could be low-cost and sustainable options for organic transformation in water via sonochemical approach in aqueous medium.

## 1. Introduction

Nanocatalysts adorned with nanoparticles (NP) have shown a big improvement over past decade. They are chemically stable, cheap and contribute to design a route to cleaner chemical processes with reduced environmental impact [1]. Moreover, engineered nanocatalysts represent a promising avenue to enhanced catalytic activity, selectivity, tunability and recovery. Despite these improvements, their development at breakneck speed has been associated with toxicity, recovery of the catalyst from the mixture. Majority of the nanocatalysts reported in literature are derived from nanoparticles in either metallic, metal oxides or organic forms [2].

Among these, nano-engineered catalysts magnetic nanoparticles have been of major interest to researchers in area of catalysis owing to its ability to heterogenize the nanoparticles in addition to providing ease of catalyst separation via magnetic decantation. In the class of magnetic nanoparticles, specifically iron oxide nanoparticles have been widely explored for various applications such as catalysis, drug delivery, adsorption etc. [3–5]. Recently it is reported that iron is considered as "metal with minimum safety concern" by regulatory authorities [6].

Besides iron oxide nanoparticles, elemental zerovalent iron existing in a bcc crystal structure as alpha-Fe has very reactive surface sites in its nano state.

Elemental zerovalent iron nanoparticles (nZVI) have been the subject of considerable research as they can play vital role in aiding greener synthesis, minimizing environmental contaminants, sustainable catalysis. They are earth abundant, non-toxic, biocompatible, adorned with excellent electron donating capability and have high potential to behave as catalysts [7]. In this regard, an excellent opportunity comes into light for application of nZVI in the field of catalysis. Excellent catalytic activity of iron nanoparticles in zero valent state (nZVI) has been reported for few reactions like Fenton process as well as for dehalogenation of aromatic halides [2]. They can be synthesized at ease and demonstrate large surface to volume ratio. For the synthesis of zerovalent iron nanoparticles, a significant amount of research has been done and well documented so far. [8]. The physical methods for preparation of nZVI are not cost effective and chemical methods are simple due to homogeneity and ease of operation.

Although the emergence of zerovalent iron nanoparticles is rapidly progressing due to its various advantages but they associated with various factors such as high aggregation rate, surface oxidation and interaction with the environment are the limitations responsible for

* Corresponding author.
*E-mail addresses:* chemistry2797@yahoo.com, drsonalit@gmail.com (S. Thakore).

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