



# Dehalogenation of aromatic halides by polyaniline/zero-valent iron composite nanofiber: Kinetics and mechanisms



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## ARTICLE INFO

### Article history:

Received 7 June 2016

Received in revised form 21 August 2016

Accepted 13 September 2016

Available online 13 September 2016

### Keywords:

Reductive dehalogenation

Aryl halides

PANI/Fe<sup>0</sup> composite nanofibers

Grignard reagents

Heterogeneous catalyst

## ABSTRACT

Dehalogenation of aryl halides was demonstrated using polyaniline/zero valent iron composite nanofiber (termed as PANI/Fe<sup>0</sup>) as a cheap, efficient and environmentally friendly heterogeneous catalyst. The catalyst was prepared via rapid mixing polymerization of aniline monomers with Fe(III) chloride as an oxidant followed by reductive deposition of nano-sized Fe<sup>0</sup> onto the PANI nanofiber using the by-products (Fe(II)/Fe(III)) present in the polymerization system as the Fe precursor. The catalyst was characterized by various physico-chemical techniques: ATR-FTIR, FE-SEM, HR-TEM, XRD, XPS and VSM. A mild reductive dehalogenation process of a wide range of aromatic bromides was explored in the presence of PANI/Fe<sup>0</sup> catalyst. The catalyst was active and manifested a high reactivity (84% GC yield of naphthalene for 7 h at 40 °C) with four equivalents of *t*-BuMgCl. Deiodination reaction was proved to be more facile in comparison with their corresponding halides. Kinetic studies at different temperatures (30, 40, 50, and 60 °C) revealed an overall pseudo-first-order behaviour with rate constants 0.00281, 0.00893, 0.01137 and 0.02421 min<sup>-1</sup>, respectively. The reaction profile diagram of substrate consumption and the product formation rate indicated that there is no additional induction period was involved in the catalytic cycle. Activation energy (*E<sub>a</sub>*) was calculated to be 56.3 kJ/mol through Arrhenius plot. Several deuteration experiments were conducted with different Grignard reagents to understand the mechanism of the reaction. These studies explained that the hydride incorporated product was obtained through β-hydride elimination of *t*-BuMgCl. The catalyst was tested up to three cycles whereas the full conversion of the product was obtained for a prolonged period. PANI/Fe<sup>0</sup> could be an alternative suitable catalyst for dehalogenation of environmentally poisonous aromatic halides.

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## 1. Introduction

Halogenated organic compounds (HOCs) are mostly ubiquitous non-biodegradable pollutants in the environment [1–3]. A large number of HOCs are extensively used in chemical industry [1–3], and also naturally produced [4,5]. Typically, the majority of pernicious brominated compounds, due to their persistence and flame retardants in nature, are easily contaminated and often bioaccumulated in the food chain [1–3,6,7]. For the remediation of HOCs, it is very important to investigate the effective chemical pro-

cess for the reclamation of hazardous organic halides to less toxic hydrocarbon compounds, and to diminish the resistant waste in our eco-system.

In recent years, a considerable amount of work has been reported for dehalogenation of organic halides e.g. photochemical [8,9], oxidation [10,11], and biological processes [12,13]. Metal-catalyzed reductive dehalogenation is one of the most efficient and well-known alternative methods in organic synthesis with various available hydrogen sources. For examples, several methods have been performed with highly expensive, toxic metals (e.g. Ni, Pd, Rh, Ru), as well as environmentally noxious reductants (e.g. Bu<sub>3</sub>SnH, formate, N<sub>2</sub>H<sub>4</sub>, NaBH<sub>4</sub>, Et<sub>3</sub>SiH, Zn, H<sub>2</sub> gas, etc) [14–26]. Therefore, the development of cost effective, and practical catalytic methods are needed to be explored using cheap, and readily available reductant in combination with less toxic, and less expensive metal

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catalysts. Consequently, several research groups have been investigated the dehalogenation methods by employing iron as a catalyst [27–30]. However, iron-catalyzed dehalogenation is still to be a demanding task, owing to the issues of environment concern, as well as cost effectiveness of the catalyst.

The use of heterogeneous catalyst has aroused a lots of attention compared to homogeneous catalyst with regard to catalyst stability, handling and recyclability [31,32]. In recent years, nano-size metal catalysts are powerful effective tools in the catalytic organic transformation reactions [33–35]. However, the catalyst incorporated with nanofiber supported matrix enhances excellent recycling efficiency [36]. In the development of sustainable catalyst [37], current research trends have fascinated ample attention to find out alternative ways by using cheap, large-abundant, and non-toxic supported metal catalyst. On that note, iron-based nanomaterials are generally recovered from the reaction mixture through simple magnetic separation [38,39]. It is noteworthy that all these properties of iron based magnetic nanoparticles offer unique advantages over their inorganic salts and complexes [40,41].

Furthermore, PANI/Fe<sup>0</sup> or Fe<sub>3</sub>O<sub>4</sub> nanocomposite particles, due to its high surface area, have found potential application in water treatment [42–46], corrosion resistance [47,48], fuel cell [49–51], electronic device manipulation [52,53], sensor [54,55], and fabrication [56]. Recently, Fe-PANI/SiO<sub>2</sub> core-shell supported metal nanoparticles have shown their catalytic efficiency and recyclability in organic synthesis [57]. Bhaumik et al. reported that PANI/Fe<sup>0</sup> nanofibers could be used for the removal of Cr(VI), As(V) and Congo red (CR) dye [44–46]. The kinetics result followed the pseudo-second-order model whereas isotherm results fitted well with Langmuir model. The following two mechanisms for the removal of As(V) were proposed: (i) the adsorption process and (ii) the substitution of surface bonded OH<sup>-</sup> ligands produced by the reaction of Fe<sup>0</sup> and H<sub>2</sub>O/O<sub>2</sub>, whereas both adsorption and reduction mechanisms associated with the removal of Cr(VI). For CR dye removal, the degradation mechanism involved through reductive cleavage of the azo linkage of dye by nano-Fe<sup>0</sup> [46]. Haspulat et al. [43] disclosed the photocatalytic degradation mechanism for the decolorization of textile dyes using Fe ions doped PANI film, whereas Yue et al. [42] explained that the oxidation degradation process involved for the removal of Rhodamine B. Bhaumik et al. [45] also investigated the adsorption behaviour using PANI nanofibers as a highly effective reusable adsorbent. The kinetic data fitted well with pseudo-second-order and adsorption mechanism involved the ionic interaction between positive charge adsorbents and negative charge dye. However, to the best of our knowledge, no scientific study has been reported on the catalytic reactivity of PANI/Fe<sup>0</sup> composite nanofibers material for the dehalogenation of aryl halides in the literature. Hence, iron(0)-catalyzed transformations are still to be established for further applications in catalysis. This interest prompted our search to explore whether iron(0) decorated PANI nanofibers would be a potential recyclable catalyst for reductive dehalogenation of aryl halides.

As part of our current efforts aimed at developing the economical metal nanomaterials [45,58], herein, we report these findings for reductive dehalogenation of aromatic halides using PANI/Fe<sup>0</sup> composite nanofibers. In this work, PANI/Fe<sup>0</sup> composite nanofibers, heterogeneous catalyst, were prepared via reductive deposition of nano-sized Fe<sup>0</sup> onto the PANI nanofibers matrix for the dehalogenation of aromatic halides. The catalytic activity was tested on different Fe<sup>0</sup> loading catalyst, substrates, time and temperature. The leaching and reusability tests were also conducted to know the feasibility of the catalyst. Finally, a plausible mechanism was established for the catalytic cycle.

## 2. Experimental

### 2.1. Chemicals

Aniline (ANI, 99%) monomer, anhydrous iron (III) chloride (FeCl<sub>3</sub>) and sodium borohydride (NaBH<sub>4</sub>) were purchased from Sigma-Aldrich, USA. The monomer was purified by vacuum distillation prior to use and kept in the refrigerator. Ultrapure water was collected from an EASY pure<sup>®</sup> II, UV-ultrapure water system, for the preparation of catalyst and for the preparation of all experimental solutions. Aryl halides, Grignard reagents and Bromoethane-2,2,2-D<sub>3</sub> were bought from Sigma-Aldrich, USA. All other chemicals used were of reagent grade. All solvents used were dried according to the standard procedures for the catalytic experiment.

### 2.2. Preparation of catalyst

The catalyst, PANI/Fe<sup>0</sup> composite nanofiber with different Fe<sup>0</sup> loadings, was prepared using our previously reported method [44,58]. Firstly, the PANI nanofibers (PANI NFs) were prepared by rapid mixing technique using FeCl<sub>3</sub> as an oxidant at room temperature. In briefly, 0.8 mL of ANI monomer was syringed rapidly in 80 mL of anhydrous FeCl<sub>3</sub> solution in a 250 mL conical flask. The reaction mixture was stirred for 5 min to evenly distribute the oxidant and monomers to prevent the secondary growth of the polymer. Then, the reaction mixture was kept without stirring for 2 days and followed by filtered, washed with water and acetone, and finally dried at 60 °C.

Secondly, to support the Fe<sup>0</sup>, the prepared PANI nanofibers were used as support without removing them from the polymerization medium and polymerization by-products (FeCl<sub>2</sub> and/or any remaining FeCl<sub>3</sub>) as the source of Fe<sup>0</sup>. To prepare PANI/Fe<sup>0</sup> composite nanofibers, a freshly prepared sodium borohydride (NaBH<sub>4</sub>) solution (100 mL) was added dropwise to the PANI-polymerization system by mechanical stirring under a N<sub>2</sub> atmosphere for 10 min. The reaction mixture was stirred for another 20 min and the product (PANI/Fe<sup>0</sup>) was filtered, washed with water and ethanol and dried at 60 °C. To know the content of Fe<sup>0</sup> in the composite, leached solution (con. HCl) was analysed using ICP-OES technique and it was found to be 4.9% Fe<sup>0</sup> loading in the composite. To prepare other compositions of Fe<sup>0</sup> loading the same preparative methods were conducted using different concentrations of NaBH<sub>4</sub> solution. From now, we have labelled the catalyst as follows: PANI/Fe<sup>0</sup>-1(1.02%), PANI/Fe<sup>0</sup>-2(4.9%), PANI/Fe<sup>0</sup>-3(9.97%), PANI/Fe<sup>0</sup>-1(30.10%) and PANI/Fe<sup>0</sup>-1(70.06%). For catalytic activity test, it was found that PANI/Fe<sup>0</sup>-2 catalyst was performed better than other compositions. Therefore, PANI/Fe<sup>0</sup>-2 catalyst was selected for different characterizations.

### 2.3. Characterization

The morphology and size of the PANI and PANI/Fe<sup>0</sup>-2 were investigated by an Auriga Field Emission Scanning Electron Microscope (FE-SEM; Carl Zeiss, Germany) and a JEOL JEM-2100 High Resolution Transmission Electron Microscope (HR-TEM; JEOL, Japan). A JEOL JEM-2100 HR-TEM instrument with a LaB<sub>6</sub> filament operated at 200 kV was used to obtain TEM images. Specimen for HR-TEM was prepared by placing a drop of a dilute suspension of the sample in 2-propanol on a copper grid. X-ray diffraction (XRD) pattern of the PANI/Fe<sup>0</sup>-2 was performed using an X-ray powder diffractometer with Cu anode (PANalytical Co. X'pert PRO, UK), running at 40 kV and 30 mA, scanning from 10° to 80° with a scan speed of 1°/min. An Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectrum 100 Spectrometer (Perkin-Elmer, USA), with a germanium crystal was employed to record the IR spectrum of the PANI/Fe<sup>0</sup>-2. For the IR mea-

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