



Simple colorimetric assay for dehalogenation reactivity of nanoscale zero-valent iron using 4-chlorophenol



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ARTICLE INFO

Article history:

Received 5 August 2014

Received in revised form 14 October 2014

Accepted 22 October 2014

Available online 1 November 2014

Keywords:

Nanoscale zero valent iron

4-Chlorophenol

Indophenol reaction

Dehalogenation reactivity

Colorimetric assay

ABSTRACT

Despite the wide application of nanoscale zero valent iron (nZVI) for the treatment of a plethora of pollutants through reductive reactions, reactivity evaluation of nZVI toward dehalogenation has not been standardized. In this light, it was desired to develop a simple colorimetric assay, for versatile laboratory application, using merely a spectrophotometer for color intensity determination. A modification of the indophenol reaction, which is well known for its use in ammonia detection, is suggested for this color assay. Being that 4-chlorophenol can be reduced to phenol by nZVI but cannot react according to the indophenol reaction, as its para-position is blocked; the simple colorimetric assay for reducing reactivity determination of nZVI to organically bound halogens was developed, using 4-chlorophenol as the model substrate that is selectively reduced to phenol by nZVI. The sensitivity and selectivity of the color assay for phenol detection was initially investigated. Since a shift of the peak absorbance was observed at higher concentrations of indophenol formed from phenol, the appropriate concentration range for analysis was determined as 0–50 μM , with a peak absorbance at 680 nm. The suggested color assay showed superior selectivity toward phenol in the presence of 4-chlorophenol. However, the high concentration of soluble iron ions produced throughout the reaction caused positive interference on absorbance. Addition of NaCO_3 for the pre-treatment of samples was suggested to eliminate the effect of residual iron ions and acidity from buffers used in nZVI reactivity tests. Several types of nZVI were investigated with the reaction, including monometallic nZVI and bimetallic nZVIs of Ni/Fe and Cu/Fe; and only Ni/Fe particles were able to produce phenol, indicating the reducing reactivity of Ni to produce atomic hydrogen along with an electron supplied by the core of nZVI. Throughout this study, the 4-chlorophenol based reactivity assay, using the modified indophenol reaction, successfully determined reducing reactivity of nZVI in varied experimental conditions.

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1. Introduction

Zero valent iron (ZVI), by utilizing reductive reaction mechanisms, has been applied in the removal of a wide variety of pollutants, especially halogenated organics, including chlorinated hydrocarbons, chlorinated phenols, polychlorinated biphenyls (PCBs), etc. [1]. In particular, it has been found that nanoscale ZVI (nZVI) exhibited much higher activity for dehalogenation than commercially available micro-iron powder, due to the difference in specific surface area [2]. Moreover, the further enhancement of nZVI reactivity has been intensively investigated. A wide range of stabilizers, e.g. surfactant [3], sodium carboxymethyl cellulose [4],

starch [5], and guar gum [6], have been applied to prevent aggregation of nZVI, although this can lead to a decrease in actual surface area available for reaction [7]. The application of a second metal is another approach for enhancement of nZVI reactivity. In bimetallic materials, the primary metal, having a lower standard redox potential, Fe, acts as an electron donor to reduce the contaminants; while the secondary metal (Pd, Pt, Ag, Ni, Cu, etc.), acting as a catalyst and having a high standard redox potential, promotes the reactivity via hydrogenation and accelerates corrosion [8–10].

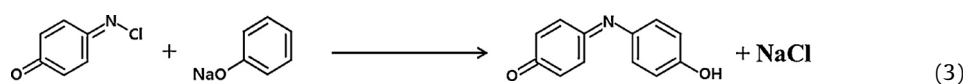
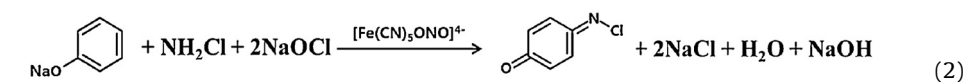
However, the evaluation of nZVI reactivity toward dehalogenation has not yet been standardized in previous studies. The use of advanced chromatographic techniques has mostly been applied to determine the parent compound and subsequent degradation products [11,12]. These techniques are powerful tools to analyze the compounds both qualitatively and quantitatively. Nevertheless, it generally requires long analysis times and complicated set-ups. In

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this light, a simple color assay for use in laboratories, requiring only a basic spectrophotometer, for determining color intensity should be developed.

Chlorinated phenols, which are broadly used as wood preservatives, anti-rust agents, and pesticides, have become a note-worthy contaminant in the environment [13], being that most of them are toxic, carcinogenic, and intractable [14]. Due to the aryl structure and presence of the chlorine atom, chlorinated phenols are exceptionally recalcitrant toward chemical reactions aimed at their reduction [15]. In the last decade, application of ZVI for reduction of chlorophenols has been extensively studied [8,15–18]. Chlorophenol can be reduced to phenol via dehalogenation, driven from electron transfer, and it is generally accepted that phenol is the only product during this process [16,17].

The indophenol reaction is the name given to the reaction of monochloramine and a phenol, which, under suitable conditions, results in the formation of a blue indophenol dye, which can be determined spectrophotometrically [19]. This reaction is highly specific for ammonia, and in the presence of a suitable catalyst, extremely high sensitivity is attainable. The reaction mechanism, as it's understood, is outlined below in Eqs. (1)–(3) [20]



The produced monochloramine in Eq. (1) reacts with the para position of phenol, and N-chloro-p-hydroxybenzoquinone monoamine is produced. This intermediate reacts with phenolate to produce a blue colored indophenol. Since the para position of phenol is involved in this reaction, it is generally accepted that only phenols with un-substituted para-positions can make this reaction [19]. Therefore, it can be hypothesized that phenols with a substituted para position will not be detected by this reaction; whereas the reduction product of it, phenol, will produce color. Because it is known that para-chlorophenol (4-chlorophenol) is able to be reduced to phenol by the reaction with nZVI; in this study, 4-chlorophenol is chosen as a target compound for the development of a color assay.

Herein, the simple colorimetric assay for reducing reactivity determination of nZVI to organically bound halogens was developed, using 4-chlorophenol as the model substrate that is selectively reduced to phenol by nZVI. Firstly, the sensitivity of the color assay was optimized for phenol quantification. Secondly, the selectivity of the color assay toward phenol, in the presence of 4-chlorophenol, was investigated to test the feasibility of the assay. Several types of nZVI and bimetallic nZVI (Ni/Fe, Cu/Fe) were tested for degradation of 4-chlorophenol to phenol; in order to demonstrate the applicability of the method and the feasibility to distinguish reducing reactivity. The matrix effect, namely pH and residual iron ions concentration, was investigated and carbonate addition is applied to eliminate any interferences. Based on the overall results of bimetallic nZVI reactivity and the selectivity of the color assay, a simple and effective assay to determine reactivity of nZVI is suggested.

2. Methods

2.1. Chemicals

Ferrous sulfate heptahydrate (>99%, Fluka), sodium borohydride (>98%, Sigma–Aldrich), copper sulfate pentahydrate (>99%, Fluka)

and nickel sulfate hexahydrate (>99%, Sigma–Aldrich), ethanol (>99.9%, Sigma–Aldrich) were used for nZVI synthesis. Phenol (>99%, Fluka), 4-chlorophenol (>98%, Merck), sodium hypochlorite solution (10%, Fluka), ammonium chloride (>99.5%, Sigma–Aldrich), sodium nitroprussid (>99%, Merck) were used for the modified indophenol reaction. Hydrochloric acid (37%, Sigma–Aldrich), sodium hydroxide (>98%, Sigma–Aldrich), sodium citrate (>98%, Sigma–Aldrich), citric acid (>99.8%, Fluka), and acetate (>99.8%, Sigma–Aldrich) were used for pH adjustment. Ferric chloride hexahydrate (>98%, Sigma–Aldrich) was used for investigating effect of residual iron ions in the sample. Sodium carbonate (>99%, Sigma–Aldrich) was used for sample pretreatment. Unless otherwise stated, all of the chemicals were used as received from the supplier. All solutions were prepared using degassed deionized water (DDIW) by purging with nitrogen gas for 3 h.

2.2. Reagents and optimized assay procedure

Typical reaction conditions for ammonium measurement using the indophenol reaction had ammonium as the limiting reagent, and excess amounts of phenol and hypochlorite

were applied to ensure all ammonium forms indophenol, catalyzed by sodium nitroprusside. In this study, phenol was chosen as the limiting reagent, in order to have the color development dependent on the concentration of phenol.

In this study, reagent A, hypochlorite-NaOH solution, and reagent B, ammonium-sodium nitroprusside solution, were prepared for the suggested color assay. Reagent A was prepared by diluting 1 mL of 10% hypochlorite solution and 66 mL of 0.5 M NaOH solution to 100 mL with DDIW. Reagent B was prepared as 1250 mg-N/L of ammonium chloride (4.78 g NH₄Cl/L) and 0.3 g/L of sodium nitroprusside in DDIW. A drop of hydrochloric acid was added to minimize ammonia stripping to the headspace in the reaction vessel. Reagent C was prepared by dissolving 106 g/L Na₂CO₃ to make a 1 M solution. Reagent C is used to neutralize any acidic buffer that might be used in the experiments with nZVI reactivity and to precipitate residual soluble iron ion (Fe²⁺ or Fe³⁺) produced throughout reaction, in order to remove interferences with the color reading.

The following procedure was used to quantify phenol in the reaction mixture: 5 mL of homogenized samples were pre-treated by 250 μL of carbonate solution (reagent C) to neutralize the acidic buffer and to precipitate interfering iron ions. Produced iron carbonate was well precipitated in 30 min, and the supernatant was taken for phenol analysis. Equal volumes of reagents A and B were mixed to make the reagent AB, prior to sample addition. Then, 2.3 mL of diluted sample, having an expected phenol concentration range of 0–50 μM, was transferred into a tube, and 0.2 mL of reagent AB was added to the diluted sample. The mixture was gently shaken and allowed to react in the dark for 2 h and subsequently quantified with a photometer at 680 nm in 1.0 cm polycarbonate cuvette. Depending on the desired precision of quantification, a 5 point calibration curve (Blank, 5, 10, 25 and 50 μM of phenol) was obtained in parallel. If a high precision is not required (kinetic or competitive studies), quantification is performed using the determined calibration curve: [phenol, μM] = (Abs – 1.43 × 10⁻² cm⁻¹) / (7.62 × 10⁻³ cm).

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