



Short communication

Cavity-confined acceleration of iron cycle for the Fenton-like reaction by β -CD-benzoquinone host–guest complex under visible irradiation

Litong Fu^a, Zhenwen Zhao^b, Jiahai Ma^{a,*}, Xuefeng Hu^{c,*}^a School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, PR China^b Beijing Mass Spectrum Center, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China^c Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, Shandong 264003, PR China

ARTICLE INFO

Article history:

Received 18 December 2014

Received in revised form 30 January 2015

Accepted 9 February 2015

Available online 17 February 2015

Keywords:

Host–guest complex

Iron cycle

Visible irradiation

Fenton

ABSTRACT

The catalyst (CDBQ) that was prepared from β -cyclodextrin (β -CD) and 2,5-dihydroxy-1,4-benzoquinone (2,5-DBQ) achieved the cavity-confined acceleration of iron cycle under visible irradiation. The semi-quinone-like (SQ) radical was generated from photoexcitation of 2,5-DBQ within the β -CD's cavity. The SQ radical as an electron donor could coordinate with iron ions, and thus 2,5-DBQ shuttled one electron between Fe^{3+} and Fe^{2+} via Fe–dihydroxybenzoquinone complex process. In Fenton reactions, CDBQ greatly increased the HO^\bullet yield, and thus significantly accelerated the degradation of dyes. The cavity-confined acceleration of iron cycle has promising applications in photo-Fenton system for the efficient decontamination for wastewater.

© 2015 Elsevier B.V. All rights reserved.

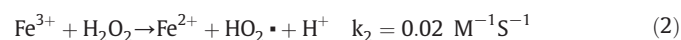
1. Introduction

There is no doubt that iron plays an irreplaceable role in industrial, chemical and biological systems [1–3]. Fe^{3+} and Fe^{2+} are the dominant forms of iron, and the cycle between them contributes to many significant redox reaction in environmental and chemical systems, for instance, the oxidation of S(IV) to S(VI) [4,5] and the redox cycle of As(III)/As(V) and Cr(III)/Cr(VI) [6,7]. The cycle can also generate and deplete the reactive oxygen species [8–11] and degrade the dissolved organic matter [12,13] in natural water, influencing the global carbon cycle. The redox cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ can be driven by several methods, including photocatalysis [14–16], chemical catalysis [17] and sonoprocessing [18,19]. Hydroquinone/quinone analogues [14,20–22] have also been utilized to accelerate the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle through the reversible conversion of the Q/SQ from the quinone structure unit. The unprotected Q/HQ molecules play the sacrificing co-catalysts to accelerate the iron cycle in that they will be attacked by HO^\bullet . Consequently, quinones were loaded onto the anion-exchange resin, which made the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle happen at the solid/liquid interface and HO^\bullet produced in the homogeneous solution, preventing Q/SQ from deactivation successfully [23].

Being non-toxic, edible, and chemically stable, β -CD possesses a hydrophilic outer surface and a fairly hydrophobic inner cavity with

suitable size [24], which is suitable for the inclusion of various organic molecules by formation of a reversible host–guest complex [25]. Cyclodextrin complexation reactions are adopted in many applications like drug delivery system technology, and the reactions are frequently used to the separation and food industries [26]. If selected as catalyst container, β -CD may provide advantages of microheterogeneous reaction [23] in inner-cavity in homogeneous system. In this study, β -CD was selected to coat 2,5-DBQ to explore a cavity-confined reaction category of β -CD-benzoquinone host–guest complex (CDBQ): β -CD provided microreaction space, and 2,5-DBQ catalyzed the iron cycle within the β -CD's cavity, which protected and enhanced the catalytic activity of 2,5-DBQ for the redox cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in reaction solution under visible irradiation.

Fenton and Fenton-like processes are promising water treatment technologies, due to their high performance, simplicity, and low cost of the reagents [27,28]. The key free radical chain is outlined below [14,22], and the slow reaction [Eq. (2)] is the rate-determination step in Fenton system.



Any factor that promotes the reduction of Fe^{3+} to Fe^{2+} would promote the Fenton reaction. Consequently, the CDBQ's cavity-confined acceleration of iron cycle under visible irradiation, in comparison with the

* Corresponding authors.

E-mail addresses: majia@ucas.ac.cn (J. Ma), xphu@yic.ac.cn (X. Hu).

control Fenton system and Fenton system with sacrificial 2,5-DBQ, greatly promoted the Fenton degradation of dye pollutants.

2. Experimental

2.1. Materials

5,8-Dihydroxy-naphthoquinone and 2,5-dihydroxy-1,4-benzoquinone were purchased from J&K. Anthraquinone-1,5-disulfonic acid sodium salt, anthraquinone-2,6-disulfonic acid sodium salt, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and β -cyclodextrin were purchased from TCI. Benzoquinone was purchased from Alfa Aesar. Malachite green (MG), Rhodamine B (RhB), hydrogen peroxide, $\text{Fe}(\text{ClO}_4)_3$, HClO_4 , ethylenediaminetetraacetic acid sodium salt (EDTA), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 1,10-phenanthroline, methanol, HAc, NaAc, NaF, H_2SO_4 , AgSO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ were of analytical grade. Milli-Q water was used throughout this study. All CDBQ samples used in this study were prepared by a simple process: an appropriate amount of 2,5-DBQ solid was dissolved into the equal molar β -CD solution. For example, CDBQ in Fig. S4 was prepared by adding 0.01135 g β -CD (10^{-5} mol) and 0.0014 g 2,5-DBQ (10^{-5} mol) solids into 50 mL water.

2.2. Reaction systems

All experiments were conducted in aerated solutions in a cylindrical Pyrex vial (10 or 50 mL) under visible irradiation (500 W Xe lamp, with a cut-off filter placed outside the Pyrex jacket to completely remove wavelengths shorter than 420 nm). The initial pH around 2.9 was adjusted with HClO_4 . Reaction solutions were freshly prepared from stock solution of $\text{Fe}(\text{ClO}_4)_3$ (1 mM) and dye (0.1 mM).

2.3. Analysis

The degradation of dye MG was determined by UV/Vis spectroscopy (UV-2550, SHIMADZU). Fe^{2+} concentration was determined by 1,10-phenanthroline method (monitored at 510 nm), with excess F^- to suppress any further reduction of Fe^{3+} after reaction.

An AB Sciex QTrap 4500 tandem mass spectrometer (Foster City, Ca, USA) operated with a turbo-V IonSpray source was used to obtain the mass spectra. IronSpray voltage and declustering potential were set to 4.5 keV and 60 eV in the negative ion mode. The sample solution was directly injected into the ESI source. The CDBQ solution, in this analysis, was mixed with 50% methanol before injection. ^1H NMR spectra were recorded on a Bruker Avance III 500 MHz instrument in D_2O at 296.5 K.

The electron paramagnetic resonance (EPR) experiments were recorded on a Bruker ER200D-SRC X-band spectrometer equipped with a 100 kHz field modulation, and the magnetic fields were calibrated by using a Bruker ER 035 M NMR Gaussmeter. The experimental temperature of 123 K or 298 K was controlled by a Bruker ER 4111VT variable temperature unit. The EPR (123/298 K) instrument was operated in the following parameters: microwave power 4.00000/0.99800 mW, microwave frequency 9044.066 MHz/0.99800 mW, sweep time 240.0/30.0 s, center field 323.2/323.1 mT, sweep width $7.5 \times 1/5 \times 1$ mT and 4096/4096 data points.

The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALAB 250Xi using Al $K\alpha$ radiation. The solid samples in XPS experiment were prepared with freeze-drying. The micro-Raman spectroscopy was performed on a Renishaw inVia plus, and it carried out under ambient conditions by using an argon ion laser ($\lambda = 514.5$ nm). Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker VERTEX 70. All the solid samples for FTIR were prepared as the notes in Fig. 1 in liquid, and then treated the liquid sample with freeze-drying for 36 h.

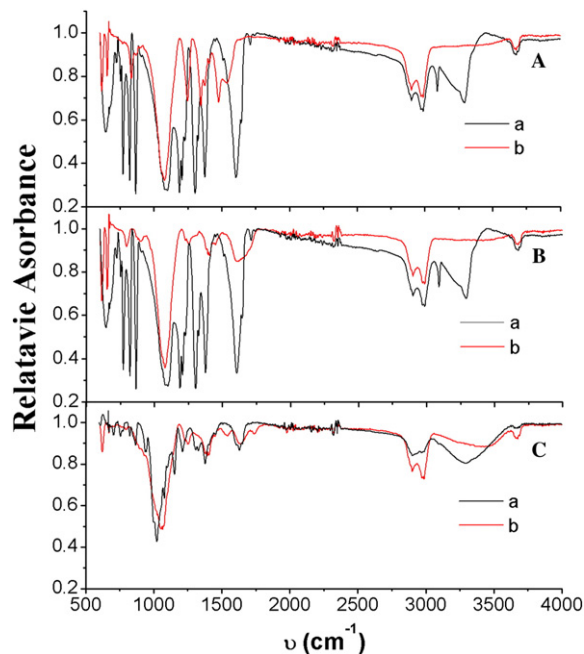


Fig. 1. (A) Infrared spectra of (a) 2,5-DBQ and (b) 2,5-DBQ mixed with Fe^{3+} : 7.5 mM $\text{Fe}(\text{ClO}_4)_3$, 7.5 mM 2,5-DBQ. (B) Infrared spectra of (a) 2,5-DBQ and (b) 2,5-DBQ reacted with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ for 5 min: 7.5 mM $\text{Fe}(\text{ClO}_4)_3$, 75 mM H_2O_2 , 7.5 mM 2,5-DBQ. (C) Infrared spectra of (a) CDBQ and (b) CDBQ reacted with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ for 10 min: 7.5 mM $\text{Fe}(\text{ClO}_4)_3$, 75 mM H_2O_2 , 7.5 mM 2,5-DBQ. All the reactions were proceeded at pH = 2.9 under visible irradiation.

3. Results and discussion

3.1. Choice in guest molecule of β -CD

Owing to the corresponding reduction ability for Fe^{3+} under irradiation, five quinones were selected as guests of β -CD, including 5,8-dihydroxy-naphthoquinone, anthraquinone-1,5-disulfonic acid sodium salt, benzoquinone, 2,5-dihydroxy-1,4-benzoquinone, anthraquinone-2,6-disulfonic acid sodium salt. Then the catalytic activity of these quinones was studied by comparing their degradation of MG in Fenton-like reaction under visible irradiation. Fig. S1 revealed that 2,5-DBQ was the best co-catalyst in the photo-Fenton reaction among the five quinones, so 2,5-DBQ was selected as β -CD's guest molecule.

A result from a typical titration experiment monitored by ^1H NMR was showed in Fig. S2. This figure showed how the β -CD protons shift in the presence of varying amounts of 2,5-DBQ. The downfield shifts of H-3' and H-5' were obvious, and the band shape alteration of H-5' was apparent. H-3' and H-5' are the protons located in the interior of the cavity. The significant modifications of these protons are usually considered as a support for the complexation process [29,30]. This observation indicated that 2,5-DBQ was included in the β -CD cavity.

The successful coating was also evidenced by ESI-MS. In Fig. S3, the ion corresponding to the CDBQ's supramolecular complex was clearly observed, compared with those corresponding to uncomplexed β -CD and 2,5-DBQ in the mass spectra. For the complex of β -CD with 2,5-DBQ, the ion at m/z 1273 corresponded to $[\text{CDBQ-H}]^-$, and the ion at m/z 1133 and 139 were also assigned as the peak corresponding to $[\beta\text{-CD-H}]^-$ and $[\text{2,5-DBQ-H}]^-$. The results confirmed the supramolecular interactions between β -CD and 2,5-DBQ.

3.2. The function of β -CD for iron cycle

Fe^{3+} is more thermodynamically stable than Fe^{2+} in most environmental and chemical systems. Therefore, the key to attain $\text{Fe}^{3+}/\text{Fe}^{2+}$ effectively proceeding is to substantially enhance the Fe^{3+} reduction rate.

Download English Version:

<https://daneshyari.com/en/article/50283>

Download Persian Version:

<https://daneshyari.com/article/50283>

[Daneshyari.com](https://daneshyari.com)