



Degradation of a model naphthenic acid by nitrilotriacetic acid – modified Fenton process



Ying Zhang, Nikolaus Klamerth, Mohamed Gamal El-Din *

Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB T6G 2W2, Canada

HIGHLIGHTS

- NTA-modified Fenton process was very efficient in degrading CHA at pH 8.
- The second-order rate constants of $\cdot\text{OH}$ with CHA and with NTA at pH 8 were obtained.
- CHA degradation was closely related to the dose of H_2O_2 rather than $\text{Fe}^{\text{III}}\text{NTA}$ dose.
- $\cdot\text{OH}$ radical was mainly responsible for the CHA degradation, while $\cdot\text{O}_2^-$ radical played a minor role.
- Mechanisms for NTA-modified Fenton process were proposed and discussed for the first time.

ARTICLE INFO

Article history:

Received 27 November 2015

Received in revised form 23 January 2016

Accepted 14 February 2016

Available online 17 February 2016

Keywords:

Nitrilotriacetic acid

Fenton process

Cyclohexanoic acid

Naphthenic acids

$\cdot\text{OH}$ radical

$\cdot\text{O}_2^-$ radical

ABSTRACT

The degradation of cyclohexanoic acid (CHA) as a model compound of naphthenic acid (NA) was investigated in this study by a nitrilotriacetic acid (NTA) – modified Fenton process at pH 8. The optimum doses of hydrogen peroxide (H_2O_2) and $\text{Fe}^{\text{III}}\text{NTA}$ (NTA:Fe = 2:1) were 4.41 mM and 0.27 mM, respectively. CHA degradation reached a plateau within 4 h under these conditions. The degradation of CHA was influenced primarily by the dose of H_2O_2 , while the concentration of $\text{Fe}^{\text{III}}\text{NTA}$ complex primarily influenced the reaction time. The second-order rate constants of hydroxyl radical ($\cdot\text{OH}$) with CHA and with NTA were investigated using a competition-kinetics method and obtained as $4.09 \pm 0.39 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $4.77 \pm 0.24 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. $\cdot\text{OH}$ radical was the main responsible species for CHA degradation, while $\cdot\text{O}_2^-$ radical played a minor role. The reaction of CHA with $\cdot\text{O}_2^-$ radical generated by potassium superoxide (KO_2) in dimethyl sulfoxide (DMSO)/water solution was investigated for the first time. The reaction mechanisms of the NTA-modified Fenton process were proposed and discussed based on the discovery that no $\text{Fe}^{\text{II}}\text{NTA}$ was detected in the system.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Canada's oil sands in the northern Alberta region of Athabasca are the world's 3rd largest known oil deposits, with a volume of 170 billion barrels being currently considered as economically recoverable [1,2]. About 20% of the bitumen is surface mineable and is extracted from the oil sands by an alkaline hot water process at pH ~ 8 [3,4]. The produced suspension separates into three distinct layers of water, sands, and raw bitumen (also called bitumen froth) that is skimmed off the top to be further refined and upgraded to synthetic crude oil. Both the bitumen extraction and

froth treatment processes produce tailings with approximately 4 m^3 of fluid tailings per m^3 oil sands processed [5]. This process leads to the production of oil sands process-affected water (OSPW), which is highly saline, and shows acute and chronic toxicity to aquatic organisms [6]. Organic compounds in OSPW include unrecovered bitumen (oil and grease), naphthenic acids (NAs), polycyclic aromatic hydrocarbons (PAH), BTEX (benzene, toluene, ethyl benzene, and xylenes), and other organic acids such as fulvic and humic acids [3,7–10]. Tables S1 and S2 in the Supplementary Material present a summary of the inorganic and organic chemistry of OSPW, Athabasca River and regional lakes.

NAs are believed to be the main responsible compounds for OSPW toxicity. They are a group of aliphatic and alicyclic carboxylic acids with a general formula: $\text{C}_n\text{H}_{2n+z}\text{O}_x$, where n is the number of carbons, x is the number of oxygen, with $x = 2$ for classical NAs (c-NAs), $x \geq 3$ for oxidized NAs (oxy-NAs) which are formed after the oxidation of c-NAs [11], and z is zero or an even

* Corresponding author at: NSERC Senior Industrial Research Chair in Oil Sands Tailings Water Treatment, Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB T6G 1H9, Canada. Tel.: +1 780 492 5124; fax: +1 780 492 0249.

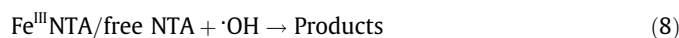
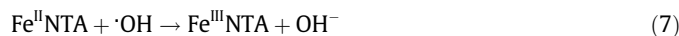
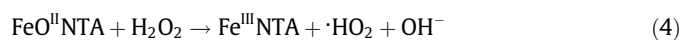
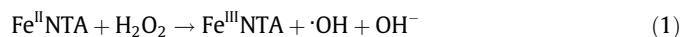
E-mail address: mgamalel-din@ualberta.ca (M. Gamal El-Din).

negative integer indicating the loss of hydrogen through either the formation of rings or the presence of double bonds [10]. NAs concentration in tailings ponds has been reported to be in a range of 40–130 mg/L, depending on pond age and extracted ore [3,12,13]. Due to the toxicity and recalcitrance of NAs to biodegradation, their removal from OSPW has been attracting attentions from researchers since 1980s [3,14].

Advanced oxidation processes (AOPs) have received much attention in the last decades for the treatment of recalcitrant contaminants due to their high oxidative ability promoted by the production of hydroxyl radicals ($\cdot\text{OH}$). AOPs have been proposed as a complementary technology to biological treatment of OSPW due to their ability to degrade recalcitrant NAs and reduce overall toxicity towards selected organisms [15–17]. $\cdot\text{OH}$ radical is a known oxidant, second to the strongest oxidant – fluorine, with a potential of 2.8 V versus normal H electrode. $\cdot\text{OH}$ radical is produced in the Fenton process through the reaction of hydrogen peroxide (H_2O_2) with Fe^{II} at acidic pH (around 3.0) [18–20]. This radical can oxidize almost any organic matter to short-chain organic acids, inorganic ions and CO_2 [21–23]. Fenton reactions have drawn lots of attention in the scientific community because they are fast, low cost, and easy to handle at room temperature [24–28]. However, the acidic condition requirement limits their application in the treatment of wastewaters.

Some researchers have studied modified Fenton processes at neutral pH by using chelating agents to prevent the precipitation of iron and to produce $\cdot\text{OH}$ radicals [29–35]. Due to their structure and properties, polycarboxylic acids and aminopolycarboxylic acids (APCAs) can chelate metal ions by the formation of complexes [36]. Several APCAs have been used as chelating agents in modified Fenton processes such as ethylenediaminetetraacetic acid (EDTA), ethylenediamine-*N,N'*-disuccinic acid (EDDS), and nitrilotriacetic acid (NTA). The use of EDTA considered as the most widely used chelating agent, has been limited due to its low biodegradability [36]. NTA has been proven to be one of the most active chelates by Sun and Pignatello [32] for the decomposition of H_2O_2 and the degradation of 2,4-dichlorophenoxyacetic acid among 50 chelating agents. NTA is biodegradable and the metal-NTA complexes have been reported to have rapid photodegradation [37,38]. Therefore, the contamination of NTA would not be an environmental concern. Actually, only very low level of NTA has been found in natural waters despite the use of NTA in industrial and consumer products [39]. NTA itself shows no adverse effects to aquatic life [39], and its by-products (iminodiacetic acid (IDA), glycine, oxalic acid, ammonia and carbon dioxide) would not cause a toxicity problem to the environment either. In this paper, NTA was used as a chelating agent to modify Fenton process at pH 8.

A reaction sequence was suggested for NTA-modified Fenton processes based on the reaction mechanisms between haem iron and H_2O_2 proposed by Petersen et al. [40] and by Gutteridge et al. [41] for the reaction between $\text{Fe}^{\text{III}}\text{EDTA}$ and H_2O_2 , as in the following equations (Eqs. (5)–(12) from De Laat et al. [42]):



Although several chelate driven Fenton processes have been described in the literature, there are no reports of these processes for the treatment of OSPW or NAs model compounds so far. Iron concentration in OSPW ranges from 0.8 to 3 mg/L [3], which can be used in Fenton processes, making the process more economically acceptable. Naphthenic acids with at least one ring are the main constituents in OSPW [14,43]. Cyclohexanoic acid (CHA), as one of the simplest cyclic NAs, was selected as a model compound to study the degradation mechanism of NAs by the NTA-modified Fenton process at pH 8 and ambient temperature. CHA was chosen as a model compound because it is one of the simplest cyclic NAs. Its structure is the typical structure of NAs and its reaction with radicals can represent the typical reaction between NAs and radicals. Moreover, CHA was used as a reference compound in some AOP papers and its degradation was well studied in previous studies [14,44]. To mimic the pH of real OSPW, the experiments were conducted using pH 8 buffer solution.

The parameters investigated in this study were as follows: the dose of H_2O_2 and $\text{Fe}^{\text{III}}\text{NTA}$, the ratio of NTA to Fe, the second-order rate constants of $\cdot\text{OH}$ with CHA and with NTA, the dosing mode of H_2O_2 , the oxidant species responsible for the degradation of CHA (tert-butyl alcohol (TBA) as a scavenger of $\cdot\text{OH}$ radical and chloroform (CHCl_3) as a scavenger of $\cdot\text{O}_2^-$ radical), and the reaction between CHA and $\cdot\text{O}_2^-$ radical generated by KO_2 dissolved in DMSO/water solution. Moreover, through the analysis of the species in the reaction, the reaction mechanisms proposed for NTA-modified Fenton process were discussed based on the results.

2. Materials and methods

2.1. Reagents and sample preparation

Cyclohexanoic acid (CHA) was purchased from TCI (Portland, OR, USA). NaOH, H_2O_2 (30%), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 98% H_2SO_4 , sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), 1,10-phenanthroline, acetic acid, dimethyl sulfoxide (DMSO) and sodium acetate were purchased from Fisher Scientific Co. Canada. Nitrilotriacetic acid (NTA) (99%), para-chlorobenzoic acid (pCBA), tetrabutylammonium bromide, and bovine catalase were purchased from Sigma Aldrich. KO_2 , tert-butyl alcohol (TBA), and chloroform were purchased from ACROS Organics. Titanium (IV) oxysulfate and ammonium acetate were purchased from Fluka Analytical. All chemicals were ACS grade. Filters used in the experiments were millex syringe-driven 0.2 μm nylon membrane filters provided by Thermo Scientific. All reagents for chromatographic analyses were HPLC grade (optima methanol and acetonitrile) purchased from Sigma Aldrich.

CHA stock solution (15.60 mM) was prepared in 18 M Ω MilliQ water (Millipore Corporation). 0.39 mM CHA test solution was prepared using the stock solution and a pH 8 buffer solution (0.05 M sodium tetraborate and 0.05 M sulfuric acid). Fe^{II} solution was prepared prior to Fenton reactions by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in MilliQ water at pH 3 to prevent any iron precipitation. The solution pH was adjusted using 0.1 M NaOH and 0.1 M H_2SO_4 . NTA stock

Download English Version:

<https://daneshyari.com/en/article/145675>

Download Persian Version:

<https://daneshyari.com/article/145675>

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