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Comparison of classical fenton, nitrilotriacetic acid (NTA)-Fenton, UV-Fenton, UV photolysis of Fe-NTA, UV-NTA-Fenton, and UV-H$_2$O$_2$ for the degradation of cyclohexanoic acid

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HIGHLIGHTS

- UV-NTA-Fenton at pH 3 presented the highest CHA degradation among seven processes.
- Fe-NTA species reacted faster with H$_2$O$_2$ than free iron.
- Fe-NTA photodegradation limited its application in the UV-related processes.
- H$_2$O$_2$ formed an adduct with Fe(III)NTA helping to prevent Fe precipitation.
- Borate ion helped to keep iron soluble; however, retarded the CHA degradation.

ARTICLE INFO

ABSTRACT

The treatment of a naphthenic acid model compound, cyclohexanoic acid, with classical Fenton, UV-H$_2$O$_2$, UV-Fenton, nitrilotriacetic acid (NTA)-Fenton, UV-NTA-Fenton, and UV photolysis of Fe-NTA processes at pHs 3 and 8 was investigated. At 1.47 mM H$_2$O$_2$, 0.089 mM Fe, and 0.18 mM NTA, the UV-NTA-Fenton process at pH 3 exhibited the highest H$_2$O$_2$ decomposition (100% in 25 min), CHA removal (100% in 12 min) with a rate constant of 0.27 ± 0.025 min^{-1}, and NTA degradation (100% in 6 min). Due to the formation of H$_2$O$_2$-Fe(III)NTA adduct, the total Fe concentration in the UV-NTA-Fenton system (0.063 mM at the end of the reaction) at pH 8 was much higher than that in the UV photolysis of Fe(III)NTA process (0.024 mM). The co-complexing effect of borate buffer helped to keep iron soluble; however, it imposed a negative influence on the CHA degradation in the UV-NTA-Fenton process (68% CHA removal in 60 min in the borate buffer compared to 92% in MilliQ water). The results demonstrated that the most efficient process for the CHA degradation under the experimental conditions was the UV-NTA-Fenton process at pH 3.

1. Introduction

The bitumen extraction from oil sands results in the production and storage of oil sands process-affected water (OSPW) in Alberta, Canada, which is alkaline, slightly brackish, and acutely toxic to aquatic biota (Allen, 2008). Naphthenic acids (NAs), a group of aliphatic and alicyclic carboxylic acids, are considered to be mainly responsible for the OSPW toxicity (Nelson et al., 1993; Allen, 2008). Up to date, no viable economical and practical treatment approach can be applied to treat OSPW efficiently (Pourrezaei, 2013). Because of the complexity of the OSPW matrix, cyclohexanoic acid (CHA) as a model NA compound was used to investigate the reaction mechanisms and kinetics in this study before applying the processes on the OSPW remediation. CHA was chosen because it is one of the simplest cyclic NAs, and its structure is the typical structure of NAs. The reaction between CHA and radicals can represent the typical reactions between NAs and the radicals (Zhang et al., 2016c).

Based on the production of hydroxyl radical (•OH), advanced oxidation processes (AOPs) are capable of degrading recalcitrant NAs and reducing the overall toxicity toward selected organisms (Fu et al., 2008; Scott et al., 2008; Wang, 2011). Fenton and photo-Fenton as very common AOPs have very limited application on the OSPW treatment (Zhang et al., 2016a, 2016b, 2016c). As Fe(III) precipitates at pH > 3 due to the formation of insoluble Fe-

hydroxides, chelating agents have been adopted to enable Fenton at natural pH (Gutteridge et al., 1990; Nam et al., 2001; Li et al., 2010; Huang et al., 2013). Nitrilotriacetic acid (NTA) as a chelating agent forms complexes with divalent and trivalent metal cations and can be used to prevent Fe precipitation in NTA modified Fenton process (NTA-Fenton) at high pH values.

The reaction rate of classical Fenton is limited by the reduction of Fe(III) to Fe(II) by H_2O_2. The efficiency of Fenton and NTA-Fenton can be significantly accelerated by the presence of natural sunlight (Vermilyea and Voelker, 2009; Klamerth et al., 2012, 2013) or UV light (Kušić et al., 2006; De la Cruz et al., 2012). The dominant monomeric Fe(III)-hydroxyl complex between pH 2.5 to 5 is $Fe(OH)^{2+}$ (Faust and Hoigné, 1990) with a charge transfer band between 290 nm and 400 nm (Weschler et al., 1986; Faust and Hoigné, 1990; Feng and Nansheng, 2000). UV irradiation is also known to be able to reduce Fe(III)L to Fe(II)L at high pH (Herney-Ramirez et al., 2010). Therefore, UV irradiation can greatly accelerate the reduction of Fe(III) to Fe(II) and Fe(III)NTA to Fe(II)NTA, leading to more •OH production in the UV irradiation of Fenton and NTA-Fenton processes. Fe(III)NTA has been reported to undergo rapid photolysis and generate •OH at the same time (Trott et al., 1972; Stolzberg and Hume, 1975). The major degradation products of NTA are iminodiacetic acid (IDA), formaldehyde, and CO_2 (Bunescu et al., 2008).

pH has a significant effect on the reactivity of compounds, the formation of by-products, and the efficiency of AOPs (Panadés et al., 2000; Bojanowska-Czajka et al., 2006; Homlok et al., 2010; Afzal et al., 2012). The reactivity of α carbon next to a carboxylic group is partly dependent on whether the group is protonated or dissociated (Hewgill and Proudfoot, 1976; Afzal et al., 2012). However, the information of pH influence on the decomposition of NAs in AOPs is very limited. Only one literature reported the decomposition of CHA as a model compound for NAs in the UV-H_2O_2 process at two different pHs 3 and 9 under a low-pressure UV lamp irradiation (Afzal et al., 2012).

No research has been reported on the comparison of classical Fenton, UV irradiation of Fenton (UV-Fenton), NTA-Fenton, UV irradiation of NTA-Fenton (UV-NTA-Fenton), UV photolysis of Fe-NTA (UV-Fe-NTA), and UV photolysis of H_2O_2 (UV-H_2O_2) in the contaminant removal, which makes our study using these processes to degrade CHA at two different pHs (3 and 8) very interesting and important. A medium-pressure (MP) UV lamp was used to provide UV irradiation in this study. The decomposition of CHA, NTA, and H_2O_2 in different processes under different conditions were recorded and compared. Reaction kinetics were compared to understand the degradation mechanisms. Fe concentration in the UV-Fe-NTA and UV-NTA-Fenton processes at pH 8 was recorded and compared to show the effect of the Fe(III)NTA-H_2O_2 adduct on the Fe precipitation.

The borate buffer was widely used in the Fenton systems (Dubinina et al., 2002; White et al., 2003; Lee et al., 2008; Lee and Sedlak, 2009) to keep pH stable in the reactions. In spite of so many uses of the buffer solution, none of these researchers studied the influence of borate ion on the processes. The influence of borate buffer on the reactivity of Fe(III)NTA complex and the efficiency of the UV-NTA-Fenton process was investigated in this study for the first time.

2. Materials and methods

2.1. Chemicals and sample preparation

Cyclohexanoic acid was purchased from TCI (Portland, OR, USA). Sodium hydroxide, hydrogen peroxide (30 wt%), Iron(II) sulfate heptahydrate, H_2SO_4 (98%), sodium tetraborate, 1,10-phenanthroline, acetic acid, and sodium acetate were purchased from Fisher Scientific Co. Canada. Nitrilotriacetic acid (99%), bovine catalase, optima methanol, and acetonitrile (HPLC grade) were purchased from Sigma Aldrich. Titanium (IV) oxysulfate and ammonium acetate were purchased from Fluka Analytical. Filters used were millex syringe-driven 0.2 μm nylon membrane filters provided by Thermo Scientific.

A CHA test solution of 0.39 mM was prepared by diluting a CHA stock solution (15.6 mM in MilliQ water (Millipore Corporation)). A 47.6 mM Fe(II) stock solution was prepared by dissolving FeSO$_4$·7H$_2$O in MilliQ water at pH 3 prior to Fenton reactions. A 0.18 M NTA stock solution was prepared by dissolving NTA in MilliQ water at pH 4 [45]. Concentration of CHA, Fe and NTA was chosen based on our previous study (Zhang et al., 2016c). Fe-NTA complex was prepared by adding NTA stock solution to samples first and then adding Fe stock solution slowly under gentle shaking. Afterwards, the pHs of the samples were adjusted to 8 (over 98% Fe was bound in the form of Fe-NTA at NTA:Fe of 2:1). pH 8 borate buffer solution was prepared by mixing 0.05 M sodium tetraborate and 0.05 M sulfuric acid at a ratio of 1.25:1.

2.2. Experimental design

An 80 mL sample solution was placed in a 100-mL beaker (5.4-cm diameter) with on a magnetic stirrer under a collimated beam UV apparatus (Model PSI-I-120, Calgon Carbon Corporation, USA) equipped with a 1-kw medium-pressure (MP) Hg-lamp (Calgon Carbon, Pittsburgh, PA, USA). The emission of the lamp was from 200 nm to 530 nm. Samples were taken periodically. Bovine catalase (1 g L^{-1}) was used to destroy excess H_2O_2. Control experiments were conducted under UV irradiation only. Classical Fenton and NTA-Fenton experiments were carried out under the same conditions without UV irradiation. Experiments were carried out in duplicates.

2.3. Analytical methods

H_2O_2 was measured by titanium (IV) oxysulfate method (DIN 38402H15) at 410 nm (GENESYS™ 10S UV−Vis spectrophotometer) [31, 49]. Fe was measured by 1,10-phenanthroline (ISO 6332) method at 510 nm [21]. The pH was controlled with a pH meter (Fisher Scientific, AR 50) using 0.1 M NaOH and H_2SO_4. NTA was analyzed by HPLC-UV (Agilent Technologies, 1260 Infinity) equipped with a C18 column (Phenomenex, 5 μm, 150 mm × 4.6 mm). CHA measurement was done by HPLC-ion trap MS (Agilent Poroshell 120 SB) with a C18 column, 2.7 μm, 50 mm × 2.1 mm (HPLC solvent gradient for the CHA detection given in Table S1). Details of the measurement are included in the Supplementary Material.

3. Results and discussions

3.1. CHA degradation and H_2O_2 decomposition at pH 3 and pH 8

CHA and H_2O_2 decomposition was investigated at pHs 3 and 8 under UV irradiation (blank), in the UV-H_2O_2, Fenton, NTA-Fenton, UV-Fenton, UV-Fe-NTA, and UV-NTA-Fenton processes. pH 8 was chosen for the experiments because the pH of real OSPW is around 8. pH 3 was chosen to compare the efficiency of Fenton processes at this pH with that at pH 8 due to the fact that classical Fenton is most effective at pH around 3. The reactions were stopped at the complete degradation of CHA/H_2O_2 or at maximum reaction time of 60 min.

Fe dose was chosen based on natural Fe concentration of 0.8−3 mg L^{-1} in OSPW (Allen, 2008). NTA dose was chosen based on the ratio of NTA to Fe used in our previous study (Zhang et al.,