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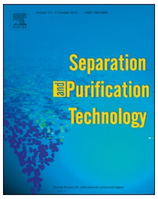

Application of glutamate to enhance carbon tetrachloride (CT) degradation by Fe(II) activated calcium peroxide in the presence of methanol: CT removal performance and mechanism

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ABSTRACT

In this study, we examined the effects of chelators on reductive degradation of carbon tetrachloride (CT) in Fe(II) activated CaO_2 system in the presence of methanol (MeOH). The results suggested that glutamate (Glu) could significantly enhance CT degradation percent with around 25.9% increase in 20 min at the initial CaO_2/Fe(II)/MeOH/Glu/CT molar ratios of 20/20/10/10/1. In the system, MeOH and Glu acted through different mechanisms, in which MeOH was used to directly stimulate the reductants formation and its reactivity, whereas Glu was acted to keep relatively high soluble iron and thus promote Fenton reaction. The results of scavenging tests suggested that $O_2^{\cdot -}$ was one of the reductive radicals for CT depletion and the mechanism of CT degradation was significantly distinguished from trichloroethene (TCE) degradation which was primarily through oxidation by $OH^{\cdot}$. CH_2Cl_2, C_2Cl_4, and C_2Cl_6 were detected as the intermediates accompanied by CT destruction, and a reduction mechanism for CT degradation by the CaO_2/Fe(II)/MeOH/Glu process was proposed accordingly. Finally, the simultaneous removal of CT and TCE was achieved in the CaO_2/Fe(II)/MeOH/Glu system, indicating a potential technique for complex contaminated sites remediation.

1. Introduction

Over these years, chlorinated organic compounds (COCs), which were widely utilized in many industrial fields including metal degreasing and dry cleaning, etc., were frequently detected in the environment worldwide [1,2]. These organics possess high solubility, volatility, toxicity and strong environmental persistence, indicating that COCs can last many years and cause wide–spreading distribution and persistent pollution [3]. Therefore, these contaminates have drawn significant public attention and it is urgent to develop an effective technology for COCs contaminated site remediation.

Various techniques have been applied for COCs remediation so far, in which advanced oxidation processes (AOPs) with oxidants of permanganate, persulfate, ozone, and hydrogen peroxide (H_2O_2) have received much investigation and, to some extent, demonstrated high effectiveness [4]. The main principles in these AOPs are owed to the generation of reactive oxygen species (ROSs) including MnO_4^- [5], $S_2O_8^{2-}$ [6], O_3 [7], $OH^{\cdot}$ [8] from oxidants. These ROSs with high redox potentials are relatively nonspecific and these strong oxidants can react with most unsaturated COCs including chlorinated aliphatics and aromatics, fuel hydrocarbons, polycyclic aromatic hydrocarbons, and pesticides [3,4]. Among these AOPs, catalytic hydrogen peroxide (CHP) process is the most employed technique for contaminant remediation. In most cases, various approaches, such as transition metals, ultraviolet irradiation, electricity, ultrasound, etc., are applied to activate H_2O_2 and develop the reactive species, primary $OH^{\cdot}$ and others in relatively low levels [8–12]. Upon $OH^{\cdot}$ generation in CHP process, it is capable of destructing a wide variety of unsaturated/reductive contaminants such as perchloroethylene [13], trichloroethylene [14], and dichloroethylene [15]. However, $OH^{\cdot}$ is considered not reacting with highly oxidized organic compounds including perhalogenated aliphatics like hexachlorobenzene, bromotrifluoromethane, and carbon tetrachloride (CT). These compounds have a positive carbon oxidation state and are considered to be preferentially destructed by reductive species rather than oxidative ones. Beside $OH^{\cdot}$, CHP process can generate superoxide radical ($O_2^{\cdot -}$) (reactions (1)–(3)) [16] which has a

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redox potential of −2.4 V and is documented to have the potential transferring an electron to oxidized compounds, resulting in efficient degradation of highly oxidized organic compounds [17,18]. However, since the quantity of $O_2^{\cdot -}$ generated through CHP process is in an extremely low level and its life–time is very short in aqueous solution, $O_2^{\cdot -}$ is considered incapable of reacting with the highly oxidized compounds at low H_2O_2 concentration. Various modification options for enhancing $O_2^{\cdot -}$ reactivity in CHP process included the usage of excess H_2O_2 [19], addition of aliphatic alcohols [20], or increase of solid surfaces [18]. Since high H_2O_2 concentration is typically difficult to maintain in subsurface environment, and expanding the reaction surface is also more difficult in actual practice, adding aliphatic alcohols seems to be more suitable in actual contaminated site remediation. The modified system by aliphatic alcohols was demonstrated to significantly increase the reactivity of $O_2^{\cdot -}$ even at low H_2O_2 concentration according to our previous works, in which methanol (MeOH) and ethanol were chosen to enhance CT degradation [21,22]. Beside hyperactive $O_2^{\cdot -}$, the addition of aliphatic alcohols could generate α–hydroxyalkyl radical ($R^{\cdot}CHOH$) through the reaction between alcohols and $OH^{\cdot}$ (reaction (4)), which is an organic reductant and able to offer an electron to C−Cl bonds [23,24]. According to the reactions (1)–(4), $OH^{\cdot}$ is a typical controlling factor in reductants formation. Therefore, increasing $OH^{\cdot}$ production is speculated to be benefit for the reductant generation, thus enhancing contaminant removal efficiency.

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + OH^{\cdot} + OH^{-} \quad k = 63\,M^{-1}\,s^{-1} \tag{1}$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \quad k = 3.3 \times 10^{7}\,M^{-1}\,s^{-1} \tag{2}$$

$$HO_2^{\cdot} \leftrightarrow H^{+} + O_2^{\cdot -} \quad k = 1.58 \times 10^{5}\,M^{-1}\,s^{-1} \tag{3}$$

$$RCH_2OH + OH^{\cdot} \rightarrow R^{\cdot}CHOH + H_2O \tag{4}$$

Chelate–based CHP process, in which metal chelating agents are utilized to combine with Fe(II) or Fe(III), has been confirmed to significantly enhance $OH^{\cdot}$ production. Citric acid (CIT) [15], oxalic acid (OA) [25], ethylenediaminete–traacetic (EDTA) [26] and glutamate (Glu) [27], ascorbic acid (ASC) [28] have been commonly used in enhancing $OH^{\cdot}$–based COCs remediation efficiency. On one hand, the introduction of chelating agents could prevent soluble iron from precipitation and thereby be beneficial for Fenton reaction. On the other hand, the cycles of Fe(III)/Fe(II) with the presence of chelating agents would become difficult due to the low redox potentials of Fe(III)/Fe(II)–chelators and need stronger reductants such as $O_2^{\cdot -}$ rather than H_2O_2 for Fe(II) regeneration from Fe(III) [29]. For reductant–based highly oxidized organic contaminants remediation, the roles of chelators would differ from those in $OH^{\cdot}$–based COCs remediation. Hence, the purpose of this work was to investigate the degradation performance of highly oxidized contaminant in the modified Fenton system in the presence of aliphatic alcohol and chelator.

Calcium peroxide (CaO_2), as a solid H_2O_2, possesses more advantages compared with the liquid H_2O_2 [30], therefore, in this work, CaO_2 activated by Fe(II) was applied to produce $OH^{\cdot}$. MeOH, as the simplest aliphatic alcohol, would minimize the intermediates and total organic carbon (TOC) at the same enhancement on CT degradation according to our previous works [21,22], therefore it was selected as the stimulant in enhancing reductant reactivity and meanwhile some chelators were adopted to increase the precursor of $OH^{\cdot}$ production. In order to evaluate the effects of MeOH and chelators on contaminant remediation, CT and trichloroethene (TCE) were selected as the representatives of oxidized and reduced contaminants, respectively.

2. Materials and methods

2.1. Materials

Carbon tetrachloride (CCl_4, CT, 99.5%), trichloroethene (C_2HCl_3, TCE, 99.0%), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99.5%) and *n*–hexane (C_6H_{14}) were supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$, CIT, 99.0%), oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$, OA, 99.0%), ethylenediaminete–traacetic ($C_{10}H_{16}N_2O_8$, EDTA, 99.0%), glutamate ($C_5H_9NO_4$, Glu, 99.0%), ascorbic acid ($C_6H_8O_6$, ASC, 99.0%), trisodium citrate dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, CIT–3Na, 99.0%) and 5,5–dimethyl–1–pyrroline N–oxide (DMPO) were provided by Sigma–Aldrich Co. Ltd. (Shanghai, China). Methanol (CH_4O, MeOH, 99.7%), nitrobenzene ($C_6H_5NO_2$, NB, 99.0%) were obtained from Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). Calcium peroxide (CaO_2, 75.0%), isopropanol (C_3H_8O, IPA, 99.0%) and chloroform ($CHCl_3$, CF, 99.0%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). A Milli–Q water system was used to purify double deionized water (Classic DI, ELGA, Marlow, UK).

2.2. Experimental procedures

To characterize the degradation of CT and to identify the primary radicals in the modified system, batch experiments were carried out in a cylindrical glass reactor (250 mL, 6.0 cm inner diameter × 9.0 cm height) equipped with a thermostat circulating water bath (DC, Ningbo, China) to control the constant temperature at 20 ± 0.5 °C. A magnetic stirrer was inserted into the reactor to ensure the solution homogeneous and no headspace was allowed to avoid CT evaporation. Stock solution of CT was equilibrated with Milli–Q water under gentle magnetic stirring (500 rpm) in dark for 2 h. Reports indicated that commonly detected concentrations of CT in contaminated sites were almost at an average level of 0.016–3.909 $mg\,L^{-1}$ in China [31], hence the initial concentration of CT in this study was fixed on 20 $mg\ L^{-1}$ (0.13 $mmol\,L^{-1}$, 5–fold of the actual average level). Especially, several types of controls (only CT, CT + CaO_2, CT + Fe(II), CT + chelated–Fe(II)) were conducted to check any possible loss of CT caused by volatilization, adsorption, and oxidation during the each experiment. The designed amounts of all the chemicals (i.e. ferrous sulfate, chelators, MeOH) except CaO_2 were added simultaneously to the reactor containing CT for homogeneous condition. After 10 min mixing, CaO_2 was added to initiate the reaction. The initial molar ratio of CaO_2/Fe(II)/MeOH/CT (initial CT = 0.13 $mmol\,L^{-1}$) was set as 20/20/10/1 for CT removal after several attempts and other experimental molar ratios were changed on this base. At the required time intervals, 1.0 mL samples were taken and immediately mixed with 1.0 mL *n*–hexane to cease the reaction and extract CT before gas chromatography (GC) analysis. The initial and final pHs in each experiment were recorded (Table S1). Each test was conducted at least in triplicate with the standard deviations below 5%. The average values were used for all presentations and discussions.

Batch experiments were firstly conducted to compare the degradation of CT by CaO_2/Fe(II)/MeOH and CaO_2/Fe(II)/MeOH/chelators processes. And then experiments were carried out to evaluate the individual effect of MeOH or chelators dosage on CT degradation by the CaO_2/Fe(II)/MeOH, CaO_2/Fe(II)/chelators and CaO_2/Fe(II)/MeOH/chelators processes, respectively. In order to identify the precursor $OH^{\cdot}$ generation during the reaction, probe tests were conducted in accordance with CT degradation procedure and CT was instead of by NB ($OH^{\cdot}$ probe, $k_{OH^{\cdot}} = 3.9 \times 10^{9}\,M^{-1}\,s^{-1}$) [32]. Furthermore, the electron paramagnetic resonance (EPR) experiments, in which 5,5–dimethyl–1–pyrroline N–oxide (DMPO) was used as spin trap agent, was employed to evaluate the radical intensity. Total soluble iron was measured to assess the impact of Glu in Fenton reaction. To illustrate the different mechanism of the degradation of potential different contaminants, both CT (representative of oxidative contaminants) and TCE (representative of reductive contaminants) scavenging experiments were carried out by adding an extra amount of CF ($O_2^{\cdot -}$ scavenger, $k_{O_2^{\cdot -}} = 3 \times 10^{10}\,M^{-1}\,s^{-1}$) [33] or IPA ($OH^{\cdot}$ scavenger, $k_{OH^{\cdot}} = 3 \times 10^{9}\,M^{-1}\,s^{-1}$) [32] which might support reductants formation while scavenging $OH^{\cdot}$ [20]. The chloride ion released and