Hydroxylamine promoted Fe(III) reduction in H₂O₂/soil systems for phenol degradation

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Abstract
Production of hydroxyl radicals (•OH) upon the oxidation of solid Fe(II) by O₂ or H₂O₂ in soils and sediments has been confirmed, which benefits in situ remediation of contaminants. However, Fe(III) reduction by H₂O₂ is rate-limiting. Accelerating the Fe(III)/Fe(II) cycle could improve the efficiency of remediation. This study intended to use hydroxylamine to promote Fe(III)/Fe(II) cycle during 100 g/L soil oxidation by H₂O₂ for phenol degradation. The removal of phenol was 76% in 3 h during soil oxidation with 1 mM H₂O₂ in the presence of 1 mM hydroxylamine but was negligible in the absence of hydroxylamine. Fe(III) in the soil was reduced to 0.21 mM Fe(II) by 1 mM hydroxylamine in 30 min. The accelerated cycle of Fe(III)/Fe(II) in the soil by hydroxylamine could effectively decompose H₂O₂ to produced •OH, which was responsible for the effective enhancement of phenol degradation during soil oxidation. Under the conditions of 1 mM H₂O₂ and 100 g/L soil, the pseudo-first-order kinetic constant of phenol degradation increased proportionally from 0.0453 to 0.0844 min⁻¹ with the increase of hydroxylamine concentrations from 0.5 to 1 mM. The kinetic constant also increased from 0.0041 to 0.0111 min⁻¹ with H₂O₂ concentration increased from 0.5 to 2 mM, while it decreased from 0.0100 to 0.0051 min⁻¹ with soil dosage increased from 20 to 200 g/L. In addition, column experiments showed that phenol (10 mg/L) degradation ratio kept at about 48.7% with feeding 2 mM hydroxylamine and 2 mM H₂O₂ at 0.025 PV/min. Column experiments suggested an optional application of hydroxylamine and H₂O₂ for in situ remediation. The output of this study provides guidance and optional strategies to enhance contaminant degradation during soil oxidation.

Keywords Hydroxylamine · Chemical oxidation · Hydrogen peroxide · Phenol · Fe cycle · Soil remediation

Introduction
Oxidation of Fe(II) in soils and sediments by O₂ or H₂O₂ can produce hydroxyl radicals (•OH), the most powerful reactive oxygen species (ROS) in the environment (Tong et al. 2016; Cheng et al. 2016; Du et al. 2021; Liao et al. 2019; Chen et al. 2020). Because of the strong oxidizing ability, oxidation by •OH has been proposed as an important strategy for contaminant remediation in soil, groundwater, and sediments. For instance, researchers proved that half-lives of abiotic trichloroethylene (TCE) dechlorination in sediments were decreased significantly from 60 to 0.25 years in the presence of O₂, and the oxidative degradation was driven by •OH (Schaefer et al. 2018). Phenol could be degraded by •OH produced from oxygenation of different sediments (Xie et al. 2020). These results indicated that iron-bearing minerals in soils and sediments could be the intrinsic iron source to activate O₂ or H₂O₂ for contaminant degradation without extra iron injection (Yan et al. 2019; Matta et al.)
The use of abundant iron minerals existing in soils or aquifer sediments is a promising solution to develop in situ chemical oxidation method for engineering remediation of organic contaminated soil or groundwater. However, the efficiencies of •OH production and contaminant degradation were relatively low (Tong et al. 2016; Xie et al. 2020; Du et al. 2021; Liao et al. 2019; Chen et al. 2020; Schaefer et al. 2018). Therefore, new strategies are needed to enhance the production efficiency of •OH for contaminant remediation upon soil/sediment oxidation.

Based on our early recognition, the capacity of •OH production depends on Fe(II) content and speciation in soils and sediments (Xie et al. 2020). The addition of ligands (such as sodium ethylene diamine tetraacetate (EDTA), sodium tripolyphosphate (TPP), nitritolriacetic acid (NTA), oxalate, and citrate) to change Fe(II) speciation during sediment oxygenation enhanced TCE degradation (Xie et al. 2021). The efficiency of TCE degradation increased by up to 6 times by ligand addition. Even so, the number of electrons in Fe(II) is limited in soils and sediments. When Fe(II) was consumed, the activation efficiency of O2 or H2O2 would decrease and the production of •OH would be lowered. The reduction of Fe(III) by H2O2 is always the rate-limiting step with the low-rate constant (0.001–0.01 M−1 s−1) (He et al. 2016; Qiu et al. 2015; Pham et al. 2012). Therefore, artificially accelerating the redox cycle of Fe(III)/Fe(II) to regenerate active Fe(II) for •OH production upon soil or sediment oxidation by O2 or H2O2 is the key to enhance the efficiency of pollutant degradation.

\[
\text{Fe(II)} + O_2 \rightarrow \text{Fe(III)} + O_2^{-} \quad (1)
\]

\[
\text{Fe(II)} + O_2^{-} \rightarrow \text{Fe(III)} + H_2O_2 \quad (2)
\]

\[
\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(III)} + \cdot\text{OH} \quad (3)
\]

\[
\text{Fe(III)} + H_2O_2 \rightarrow \text{Fe(II)} + \cdot\text{HO}_2 + H^+ \quad (4)
\]

Based on earlier summarization about homogeneous or heterogeneous Fenton reaction (Eqs. (1)–(4)), nZVI, carbon materials, metal sulfides, and other reducing agents have been used to accelerate Fe(II) regeneration (Duesterberg and Waite 2007; Paciolla et al. 2002; Chen et al. 2011, 2015; Zou et al. 2013; Wu et al. 2015; Fukuchi et al. 2014; He et al. 2020; Hou et al. 2017, 2016; Wang et al. 2021). Some of the reductive species would react with H2O2 or •OH, which may decrease the efficiency of Fenton reaction for contaminant degradation (Duesterberg and Waite 2007; Paciolla et al. 2002; Chen et al. 2011; Zou et al. 2013). Wu et al. investigated the acceleration of the Fe(III)/Fe(II) cycle by different reducing agents, including hydroxylamine, sodium thiosulfate, ascorbic acid, sodium ascorbate, and sodium sulfite, in the persulfate/ferrous ion system and found that hydroxylamine was the most efficient species (Wu et al. 2015). A recent study conducted by He et al. found that benzoic acid degradation by Fenton reaction followed the order of hydroxylamine > ascorbic acid > cysteine (He et al. 2020). Hydroxylamine is more effective than other promoters in homogeneous Fenton reaction because of (1) it has a strong reactivity and activates H2O2 directly (Chen et al. 2015), and (2) the weak •OH consumption in weak acidic conditions (Buxton et al. 1988). For heterogeneous Fenton reaction, Hou et al. found that hydroxylamine could enhance the alachlor degradation efficiency in goethite/H2O2 system. Its degradation was attributed to the acceleration of the iron cycle on goethite surface (Hou et al. 2017). Lorenzo proved the abatement of several chlorobenzenes by catalytic wet peroxide oxidation using goethite as the catalyst for H2O2 decomposition to hydroxyl radicals and hydroxylamine as the promoter (Lorenzo et al. 2019). However, it is still unknown whether hydroxylamine can enhance the Fe(III)/Fe(II) cycle during real soil oxidation by H2O2 for contaminant degradation.

This study investigated contaminant degradation during a real soil oxidation by H2O2 in the presence of hydroxylamine. Phenol was chosen as a probe organic contaminant. A real acidic soil was chosen as a model soil because it is widely distributed on the earth surface in southern of China, and contains abundant iron oxides such as goethite. The goals of this study were to (1) evaluate phenol degradation efficiency during soil oxidation by H2O2 in the presence of hydroxylamine, (2) assess the effects of hydroxylamine and H2O2 concentrations and soil dosage on phenol degradation, and (3) test phenol degradation in simulated soil column fed with H2O2 and hydroxylamine.

**Experimental section**

**Chemicals and materials**

Hydroxylamine hydrochloride, phenol (> 99.5%), H2O2 (30 wt %), NaH2PO4, sodium ethylene diamine tetraacetate (EDTA), 1,10-phenanthroline, and 2,2′-bipyridine (BPY) were of analytical grade and bought from Medicines Corporation Ltd. China. N,N-Diethyl-p-phenylenediamine (DPD) and peroxidase (POD) were purchased from Sigma-Aldrich and the Shanghai Yuanye Bio-Technology Co., Ltd, China, respectively. Deionized (DI) water (18.2 MΩ cm) was obtained from a Heal Force NW ultra-pure water system and used in all experiments. All the other chemicals were of analytical grade.

The soil (as topsoil) was sampled from the earth surface at the base of Nanwang mountain (114.393889°E, 30.525556°N) in Wuhan city. The soil was excavated by...
a shovel and sealed in a plastic bag, and then transported to the laboratory. Plant residue and large particles such as stone and brick were removed. The soil sample was dried indoors, ground, and passed through a 100-mesh (0.147 mm) screen for all experiments. Soil particle distribution was determined by a laser particle analyzer (Mastersizer 3000). In detail, the organic matter in soil sample was removed by H₂O₂ and then, the inorganic carbon content was removed by HCl. The residual sample was dispersed with sodium hexametaphosphate for analysis. The bulk elemental composition of the soil was determined by X-ray fluorescence spectrometer (XRF, PANalytical Epsilon 3XLE) (Table S1). The XRD pattern was obtained on a D8-FOCUS X-ray diffractometer with Cu K radiation (Bruker AXS, Germany) at 40 kV, 40 mA, a scanning step size of 0.01°, and a step time of 0.05 s.

**Phenol degradation experiments**

The degradation experiments were carried out in 100-mL glass bottles wrapped by tin foil to avoid photochemical reactions. The reaction glasses were conducted in a shaking table (220 rpm) at room temperature (25 °C). In a typical experiment, 5 g of soil was added into a 50 mL solution containing phenol (5 mg/L), hydroxylamine (1 mM), and H₂O₂ (1 mM). The pH was not conditioned during reactions. For anoxic control, the soil suspension (100 g/L soil) was purged by N₂ (99.999%) at a flow rate of 10 L/min for 30 min to remove dissolved oxygen (DO). Then, phenol, hydroxylamine, and H₂O₂ with the same concentration as the typical experiment were added into the reactor in order. Finally, the glass bottles were covered with the lid immediately to start the reaction. Quenching experiment was carried out by adding 100 mM 2-propanol (k₂-propanol, •OH = 1.9 × 10⁹ M⁻¹·s⁻¹) (Buxton et al. 1988) to evaluate the contribution of •OH to the degradation of phenol. To explore the effect of hydroxylamine concentration on phenol degradation, different initial concentrations of hydroxylamine (0.5, 0.75, 1 mM) were set based on the typical experiment. The effect of H₂O₂ concentrations (0.5, 0.75, 1, 2 mM) and the dosages of soil (20, 40, 50, 100, 200 g/L) were also investigated in the same mode. All the degradation experiments were sampled by syringe at predetermined time intervals (0–180 min), the suspension in the selected tubes was separated into solid and liquid phase for the analysis of Fe(II). The filtrate was analyzed directly and the Fe(II) in the residue was extracted by 10 mL 0.5 M HCl for 8 h. In order to explore Fe(II) speciation contributing to •OH production, 2 mM 1,10-phenanthroline was injected into the phenol degradation system to complex surface adsorbed Fe(II) (Viollier et al. 2000).

Column experiments were conducted to test the feasibility of hydroxylamine and H₂O₂ injection for in situ chemical oxidation (ISCO) of contaminated soil. The column reactor (5 cm inner diameter and 12 cm length) was filled with 350 g soil in the bath experiments (Fig. 1). At the top and bottom of the column, 0.5-cm thickness of quartz sand was laid to prevent blocking. The porosities of soil column were determined to be about 50%, giving liquid volume of 120 mL. The column was operated in an up-flow mode. The fed solution was pumped from the glass bottle into the bottom of the column by a peristaltic pump (BS100-1A, Baoding Signal Fluid Technology Co., Ltd.) at 3 mL/min. The influent and effluent were sampled per pore volume (PV) and kept monitoring for 8 PV. Note that each PV needed to feed for 40 min (120 mL/3 ml/min = 40 min). The fed solution was prepared by DI water containing phenol (10 mg/L), H₂O₂ (2 mM), and hydroxylamine (2 mM) in a glass bottle. To simplify, hydroxylamine was abbreviated as HA in figures.
and equations. Liquid samples (1.5 mL) were collected from the influent and effluent ports by syringe. After filtration through a 0.22 μm filter, 500 μL of filtrate was mixed with 500 μL of methanol immediately to quench reactions for phenol measurement.

**Analytical methods**

Phenol was measured by an LC-15C HPLC (Shimadzu) equipped with a UV detector and an Inter Sustain C18 column (4.6 × 250 mm). The mobile phase was a mixture of acetonitrile and water (45:55, v/v) at a flow rate of 1 mL/min, and the detection wavelength was 210 nm. Total iron in the soil was extracted by 6 M HCl (total iron refers to the iron extracted by 6 M HCl). In brief, 0.5 g of soil was mixed with 10 mL HCl (6 M) and then shaken for 12 h. The concentration of dissolved Fe(II) was determined by the 1.10-phenanthroline method at 510 nm. Total Fe was measured after the reduction of Fe(III) by 10% hydroxylamine (Tamura et al. 1974). H₂O₂ was analyzed by a modified DPD method (Katsyoianis et al. 2008). In detail, 0.1 mL of filtrate was added into the premixed tube containing 0.1 mL BPY (10 mM), 0.1 mL EDTA (100 mM), 0.4 mL phosphate buffer (0.5 M, pH 6.0), and 3.3 mL DI water. Then, 20 μL DPD (1% in 0.1 M H₂SO₄) and 10 μL POD (100 unit/mL) were added in order. The absorbance of H₂O₂ was measured by UV detector (UV-1800 PC, Shanghai Mapada Instruments Co., Ltd.) at 551 nm within 45 s. Hydroxylamine was analyzed by indirect spectrophotometry (Yang 1999). In detail, 0.1 mL of filtrate was mixed with 0.2 mL of BPY-Fe(III) complex (10 mM BPY, 8 mM Fe(III), 20 mM HCl) and 0.5 mL acetate buffer (pH 5.2). The solution was kept in the dark for 15 min and then, the absorbance was measured at 520 nm. Soil pH was determined by a pH meter at a ratio of soil to water at 1:2.5 (w/w).

**Results and discussion**

**Soil properties**

Particle size analysis of the soil showed that the sandy, silty, and clayey contents were 27.56%, 69.10%, and 3.78%, respectively. The silty part could be further divided into coarse silt (27.56%), powder (21.80%), and fine silt (19.74%), respectively. The surface area of soil used in batch experiments was 0.72 m²/g. The soil pH was 4.6, which belongs to acid-soil. The Fe(II) and total Fe extracted by 6 M HCl were 4.49 mg/g and 33.98 mg/g in the soil. Based on XRD results (Fig. S1), the soil chemical composition consisted mainly of quartz, goethite, and lepidocrocite. Peaks of clay minerals were not detected probably because they may have been overlapped by those iron oxides.

**Phenol degradation during soil oxidation with H₂O₂ and hydroxylamine**

Phenol was negligibly degraded during soil oxidation with hydroxylamine or H₂O₂ alone (Fig. 2a), while 76% of phenol was degraded during soil oxidation with 1 mM hydroxylamine and 1 mM H₂O₂ in 3 h. Phenol degradation was only 19% by hydroxylamine and H₂O₂ without soil, which indicated the coupling effects of soil, hydroxylamine, and H₂O₂ on phenol degradation. The slight difference in phenol degradation in the presence and absence of O₂ suggested that H₂O₂ was the key oxidant during soil oxidation in the presence of hydroxylamine. The presence of 100 mM 2-propanol suppressed the degradation of phenol significantly (Fig. 2b), which further suggested that •OH was the major reactive species for phenol degradation during soil oxidation by H₂O₂ in the presence of hydroxylamine. As a reductant, hydroxylamine could react with H₂O₂, with •OH produced only at high concentration (H₂O₂, hydroxylamine > 10 mM) (Chen et al. 2015). The slight decrease of phenol by hydroxylamine and H₂O₂ (1 mM) also proved the little •OH production without iron (soil as iron source) (Fig. 2a). The cumulative •OH was 130 μM during the soil oxidation in 3 h with HA by H₂O₂, which further illustrates the degradation mechanism of phenol by •OH (Fig. S2). Therefore, •OH was mainly produced from H₂O₂ decomposition by soil components in the presence of hydroxylamine. As phenol degradation was enhanced when hydroxylamine was present in the reaction system, hydroxylamine might have played a significant role in the reaction. Hydroxylamine can reduce Fe(III) in goethite to produce Fe(II), which decomposes H₂O₂ to •OH for contaminant degradation (Hou et al. 2017). Therefore, it can be speculated that hydroxylamine reduced Fe(III) to Fe(II) in soils, which might have activated H₂O₂ to •OH for phenol degradation.

To confirm our hypothesis, the variations of H₂O₂ and hydroxylamine during soil oxidation were compared. H₂O₂ decomposition by the soil was negligible in 3 h. H₂O₂ was quickly decomposed and decreased to 15% in 3 h by the mixture of soil and hydroxylamine (Fig. 3a). In contrast, only 15% of H₂O₂ was decomposed by hydroxylamine in 3 h. As H₂O₂ was more quickly decomposed by Fe(II) than Fe(III), the increased decomposition of H₂O₂ could be attributed to the recycling of Fe(III)/Fe(II) during soil reaction with hydroxylamine. The decrease of hydroxylamine was 10% by the reaction of H₂O₂, while hydroxylamine decreased to 35% by the reaction of soil and H₂O₂ in 3 h (Fig. 3b). The increased decomposition of hydroxylamine could be attributed to the reduction of Fe(III) during soil reaction with H₂O₂. The oxidation of hydroxylamine by the produced •OH might have also accelerated the decomposition of hydroxylamine. Hydroxylamine could be oxidized to NO₃⁻ by •OH (Hou et al. 2017), which might increase nitrogen fertilizer in...
Fig. 2 Variations of phenol concentrations a under different reaction conditions and b in the absence and presence of 100 mM 2-propanol. The initial concentrations of hydroxylamine, H$_2$O$_2$, and phenol were 1 mM, 1 mM, and 53 μM (or 5 mg/L), respectively. The dosage of soil was 100 g/L. The initial pH was 4.9 and the variation was 0.2.
Fig. 3  Decomposition of a H$_2$O$_2$ and b hydroxylamine in the specific experiment. The initial concentrations of hydroxylamine, H$_2$O$_2$, and phenol were 1 mM, 1 mM, and 53 μM (or 5 mg/L), respectively. The dosage of soil was 100 g/L. The initial pH was 4.9 and the variation was 0.2.
topsoil during the remediation. For remediation purpose, the decomposition of hydroxylamine by $\cdot$OH might decrease the efficiency of contaminant degradation. On the other hand, the added hydroxylamine could be removed synchronously by the produced $\cdot$OH, which benefits remediation without secondary pollution. The complete removal of hydroxylamine was confirmed in 24 h oxidation (Fig. S3).

To further confirm the reduction of Fe(III) in the soil by hydroxylamine, the soil was reduced by hydroxylamine under anoxic conditions to measure the variation of Fe(II) in solid and aqueous solution. The concentration of solid Fe(II) increased from 0.03 mg/g to 0.25 mg/g in 30 min and kept at 0.24 ± 0.01 mg/g (0.21 mM) (Fig. 4a). Dissolved Fe(II) was not detected in soil suspensions, suggesting that hydroxylamine did not promote the Fe release from the surface of the soil. Therefore, solid Fe(III) in the soil, mainly goethite and lepidocrocite, was reduced to surface adsorbed or structural Fe(II) by hydroxylamine. The presence of 2 mM 1,10-phenanthroline inhibited the degradation of phenol (Fig. 4b), suggesting that the reduced Fe(II) might be on the solid surface rather than in the structure. As dissolved Fe(II) was not detected in the experiments (data not shown), the complexation of surface Fe(II) with 1,10-phenanthroline inhibited Fe(II) oxidation. Hou et al. found the surface reduction of goethite in the presence of hydroxylamine could be explained by two steps (Eqs. (5) and (6)) (Hou et al. 2017). We supposed the interaction between hydroxylamine and soil was also attributed to the surface reduction of Fe minerals.

\[
\equiv \text{Fe(III)} \cdot \text{OH}_2 + \text{HA} \rightarrow \equiv \text{Fe(III)} \cdot \text{HA} + \text{H}_2\text{O} \quad (5)
\]

\[
\equiv \text{Fe(III)} \cdot \text{HA} + \text{H}_2\text{O} \rightarrow \equiv \text{Fe(II)} \cdot \text{OH}_2 + \cdot\text{HA} \quad (6)
\]

### Effects of hydroxylamine, H$_2$O$_2$ and soil dosage on phenol degradation

To get more implications for engineering application, the effects of hydroxylamine and H$_2$O$_2$ concentrations and soil dosage on phenol degradation were explored. Phenol removal increased with the increase of hydroxylamine concentration. The removal ratios of phenol were 45%, 55%, 73%, and 82% at 0.5-, 0.75-, 1-mM, and 2-mM hydroxylamine, respectively (Fig. 5a). The pseudo-first-order kinetic model properly fitted the degradation kinetics of phenol at different hydroxylamine concentrations (Table S2). The rate constant increased from $4.28 \times 10^{-3}$ to $16.45 \times 10^{-3}$ min$^{-1}$ when the concentration of hydroxylamine was increased from 0.5 to 1 mM. The rate constants correlated linearly with hydroxylamine concentrations (Fig. 5d). The linear correlation indicated that the concentration of HA was the key factor for phenol degradation. Higher concentration of hydroxylamine would enhance phenol degradation rate. Higher concentrations of hydroxylamine could reduce more Fe(III) to Fe(II) in the soil, which enhanced H$_2$O$_2$ decomposition to produce more $\cdot$OH. The heterogeneous reaction was limited by the surface reactive sites. What’s more, hydroxylamine could compete with phenol for $\cdot$OH consumption. However, the results indicated no significant inhibition in the presence of 2 mM hydroxylamine. Hydroxylamine might be insufficient to reduce all of the solid Fe(III) and compete with phenol oxidation, while higher concentration would cause higher cost, which should be considered during remediation.

The increase of H$_2$O$_2$ concentration from 0.5 to 2 mM increased phenol degradation from 48 to 84% (Fig. 5b). The rate constants of phenol degradation also increased with the increase of H$_2$O$_2$ concentration but reached to a saturation pattern from 1 to 2 mM H$_2$O$_2$ (Fig. 5e). That meant there was a maximum kinetic constant for phenol degradation by H$_2$O$_2$ in the system. When the maximum reaction rate was reached, it did not become a factor to affect the degradation rate of phenol even the concentration of hydrogen peroxide increased. The reason was that the concentration of H$_2$O$_2$ was also related to the $\cdot$OH consumption (Eqs. (7) and (8)) apart from the production of $\cdot$OH. However, the self-scavenger caused by H$_2$O$_2$ at higher concentration (2 mM) seems to be significant during the oxidation, which can lead to the deceleration of phenol degradation kinetics.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \cdot\text{OH} & \rightarrow \cdot\text{HO}_2 + \text{H}_2\text{O} \quad (7) \\
2\text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (8)
\end{align*}
\]

Phenol degradation was similar under different soil dosages less than 100 g/L. The results indicated that the soil dosage less than 100 g/L was not the limiting factor for phenol degradation. With increasing the soil dosage from 100 to 200 g/L, the degradation rate decreased from 76 to 62% in 3 h (Fig. 5c). However, phenol degradation within 60 min was quick and higher for 200 g/L soil. The decrease of kinetics rate constant correlated linearly with the soil dosage (Fig. 5f). Appropriate soil dosage should be considered during ex situ remediation. The higher dosage of soil would enhance the reduction of Fe(III) by hydroxylamine and catalytic decomposition of hydrogen peroxide by Fe(II), which might enhance phenol degradation, while other factors would affect phenol degradation. On one hand, the higher dosage of soil led to the excess solid Fe(II) formed from soil reduction. The role of Fe(II) was as important as hydroxylamine might be insufficient to reduce all of the solid Fe(III) and compete with phenol oxidation, while higher concentration would cause higher cost, which should be considered during remediation.
Fig. 4  a Fe(II) production in solid and aqueous solution during soil reduction by hydroxylamine under anoxic conditions. The dosage of soil was 50 g/L and the concentration of hydroxylamine was 1 mM.  

b Phenol degradation by soil/H$_2$O$_2$/hydroxylamine in the presence of 2 mM 1,10-phenanthroline. The initial concentrations of hydroxylamine, H$_2$O$_2$, and phenol were 1 mM, 1 mM, and 53 μM (or 5 mg/L), respectively. The dosage of soil was 100 g/L. The initial pH was 4.9 and the variation was 0.2.
rate constant. Moreover, the organic matter in the soil will also scavenge •OH. Higher soil dosages with more organic matter would decrease phenol degradation due to its competition for •OH. Therefore, soil dosage was not the key factor to enhance or deduce the degradation rate of phenol, which meant iron source was enough in the soil.

To sum up, the relationship between concentration cost and degradation rate should be considered in actual remediation. Appropriate dose of hydroxylamine, hydrogen peroxide, and soil dosage should be tested before remediation. Because of no selection of hydroxyl radicals, the degradation of target pollutants (phenol) by hydroxyl radicals would be influenced by other organic matters in the actual wastewater. Many other studies verified the degradation effect of target pollutants in actual wastewater by hydroxyl radicals produced from activating oxygen was very good (Lai et al. 2021; Wei et al. 2022; Li et al. 2022). Therefore, further configuration was not designed to test degradation effect of actual water. The feasibility of the system in the actual soil remediation process was verified by column experiment.
Column experiment

Column experiment was carried out to explore the practical application potential of the heterogeneous Fenton oxidation in the presence of hydroxylamine. The concentration of phenol was between the influent and effluent sample, which meant phenol accomplishes a breakthrough in the soil column. The adsorption in the soil column was 0.004 mg/g calculated by the breakthrough curves. Without H$_2$O$_2$ in the fed solution, phenol increased quickly within 3 PV. The degradation of phenol was negligible in the fed solution without H$_2$O$_2$ according to the stable concentration of phenol in the effluent water (Fig. 6). The concentration of phenol in effluent with 2 mM H$_2$O$_2$ in fed solution was lower than that in the absence of H$_2$O$_2$ (Fig. 6). With continuous pumping, the concentration of phenol in the effluent water increased gradually. After feeding for 3 PV, the concentration of phenol in the influent and effluent solution was kept 5.13 mg/L, which was equivalent to 48.7% phenol degradation. The column experiment results suggested that the simultaneous injection of hydroxylamine and H$_2$O$_2$ is a promising way for the in situ chemical oxidation remediation of organic contaminated soil.

Conclusion

Compared with traditional Fenton oxidation remediation, in situ activation of O$_2$/H$_2$O$_2$ by iron minerals in intrinsic soils could reduce the additional cost for extra injection of iron or other catalysts. However, soils or aquifer sediments could not efficiently decompose H$_2$O$_2$ because of their poor Fe(III)/Fe(II) cycle. Here we demonstrated the degradation of phenol was enhanced during soil oxidation by H$_2$O$_2$ in the presence of hydroxylamine in batch and column experiments. Hydroxylamine accelerated solid surface Fe(III)/Fe(II) recycling efficiency and then promoted H$_2$O$_2$ decomposition and •OH production. Phenol (10 mg/L) degradation ratio was kept at 48.7% with H$_2$O$_2$ and hydroxylamine fed in column experiments. These results suggest that hydroxylamine-promoted soil oxidation by O$_2$ or H$_2$O$_2$ has the potential to achieve efficient in situ remediation for phenol or other organic pollutants. What’s more, hydroxylamine could be degraded simultaneously without secondary pollution. The effectiveness of in situ remediation by hydroxylamine/soil/H$_2$O$_2$ will be influenced by numerous factors related to the contaminated site, such as iron content and iron spcies of soil. A smaller scale of field test is also required to confirm the practicability for filed remediation.

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Availability of data and materials The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.
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