



# Heterogeneous Fenton decontamination of organoarsenicals and simultaneous adsorption of released arsenic with reduced secondary pollution

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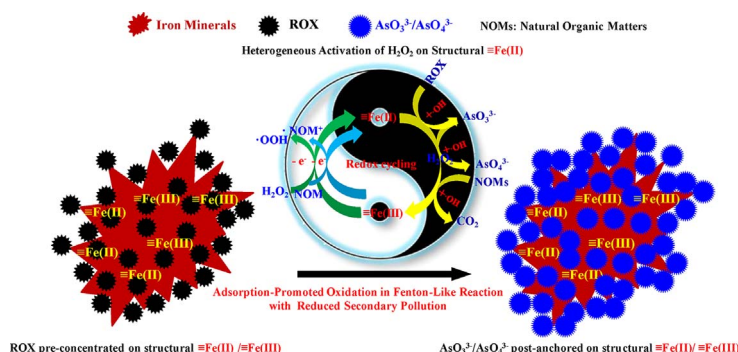
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## HIGHLIGHTS

- A simple strategy was proposed to refine organoarsenicals decontamination.
- Iron-based Fenton system was designed and estimated using typical Roxarsone.
- FeOOH-based Fenton system exhibited good capacity and stability with much reduced secondary pollution.
- The decontamination mechanisms were elucidated and clearly presented.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Organoarsenicals are widely used as antibiotics in the livestock industry and largely discharged into water environment directly, their safe, efficient and cost-effective treatment are actively perused. Herein, a heterogeneous iron-based Fenton-like technology was designed and validated with much reduced secondary pollution, mainly attributed to the bi-functional properties of both Fenton-active and arsenic-affinitive iron oxides. This simple one-step strategy not only exhaustively degraded organoarsenicals, but also selectively adsorbed the released high-toxicity arsenic from treated water. With Roxarsone as target, the FeOOH-based Fenton-like system exhibited a much superior capacity for both Roxarsone degradation and arsenic adsorption in various water matrices, compared to typical homogeneous systems under similar conditions. More than 80% of Roxarsone was degraded after 3.0 h, and most of the released AsO<sub>4</sub><sup>3-</sup> was removed simultaneously, without any additional post-treatment. The superior capacity of FeOOH might be mainly attributed to its strong redox-cycling capacity of surface central Fe atoms from their thermodynamically favorable electronic structure. Taking the important advantages of iron oxides and Fenton technology into account, our findings might provide a new chance to develop simple and efficient technologies for organoarsenicals removal from water with much reduced secondary pollution at a low cost.

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## 1. Introduction

Organoarsenicals are widely used in the livestock industry to control coccidial intestinal parasites, promote growth and improve meat pigmentation [1]. Approximately 90% of these wastes are directly applied as a fertilizer in agricultural, with a secondary environmental pollution of local soil, surface water and ground water [2,3]. What's more, these organoarsenic compounds can be converted by biotic or abiotic processes into inorganic arsenic with a much higher toxicity and mobility [1–3]. Thus, the effective, safe and exhaustive treatment of organoarsenicals before their final discharge is of considerable interest for controlling arsenic pollution in ecological environment. However, it is much more difficult to remove organoarsenicals by the usual adsorption, precipitation or coagulation, compared to inorganic arsenic [4–7].

Exhaustive decontamination of organoarsenicals from water usually needs two simultaneous processes. The one is the chemical liberation of high-toxicity arsenic from organoarsenic framework into the treated water by an oxidation strategy; the other is the adsorptive removal of released arsenic from the treated water [8]. Up to now, such a two-step synergistic combination of “oxidation + adsorption” has been mainly used for the efficient As(III) removal from ground water [9–20]. However, in general, the effective treatment of organoarsenicals is much more difficult than As(III), since their molecular structures are much larger and complicated and thus more resistant to be adsorbed and degraded on solid catalysts, and their diverse degradation intermediates might also exhibit large inhibiting effects [21–23]. In addition, the matrices of surface water with organoarsenicals are much more complicated than ground water containing As(III), this further raises the difficultness of organoarsenicals decontamination [24]. Thus, their safe and efficient treatments are actively perused, and it is of considerable interest if the oxidation of organoarsenicals and the adsorption of arsenic could be effectively combined into one single unit for practical applications at a low cost [25–28].

Heterogeneous Fenton-like catalysis exhibits great potentials to align with the “zero” waste scheme in water industry [29]. This advanced oxidation technology is widely used to remove a wide range of persistent organic pollutants, microorganisms and viruses from water and wastewater, in which the generated hydroxyl radicals ( $\cdot\text{OH}$ ,  $E^0 = 2.83 \text{ eV}$ ) is the most powerful oxidizing species in aqueous environment [29]. As the most important heterogeneous catalyst, various iron oxides ( $\text{FeO}_x$ ) receive the greatest interest, and have been widely used for advanced water treatment owing to their unique physical and chemical properties [30–32]. Thus, the iron-based Fenton catalysis can be anticipated to efficiently degrade the refractory organoarsenicals and to liberate arsenic from their organic framework into treated water. On the other hand, these Fenton-reactive iron oxides are also widely reported to be good adsorbents for the high-toxicity arsenic removal [33]. In principle, the superior arsenic adsorption capacity of iron oxides can be mainly attributed to the surface Fe-As coordination complex on the lattice Fe(III) active sites [34–38]. Moreover, the strong As adsorption onto iron oxides is highly stable regardless of the solution pH, indicating this iron-based Fenton-like system could further be efficient for the adsorption removal of inorganic arsenic from organoarsenicals degradation [39–41]. Thus, the synergistic combination of organoarsenicals degradation and arsenic adsorption could be realized on the both Fenton-active and As-affinitive iron oxides, and their heterogeneous Fenton-like systems might be a simple and efficient strategy for exhaustive organoarsenicals decontamination from water.

In this work, organoarsenicals removing tests were carried out by the synergistic Fenton-like system on three iron oxides with the typical Roxarsonic (3-nitro-4-hydroxyphenylarsonic acid, ROX) as target pollutant, and the fates of released arsenic were comprehensively investigated in details. ROX is widely used as chicken feed additive, while most of them are excreted into manure without chemical structural change [4,7,8]. Experimental results indicated a good technical

feasibility of the bifunctional iron-based Fenton-like system for exhaustive ROX decontamination in various water matrices, and its efficiency, properties and mechanism were clearly elucidated. Our findings might provide a new chance to develop more simple and efficient technologies for practical organoarsenicals decontamination from water.

## 2. Materials and methods

### 2.1. Synthesis of $\text{Fe}_2\text{O}_3$ , $\text{Fe}_3\text{O}_4$ and $\text{FeOOH}$

$\text{FeOOH}$  was synthesized by dissolving  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled water and the obtained solution pH was adjusted to 7.0–7.5 by adding  $\text{NaOH}$  aqueous solution (1.0 M). The solid was separated by centrifugation at 12,000 rpm for 15 min and washed three times with deionized water, then freeze-dried and stored at 4 °C until usage (Figs. S1–S5).  $\text{Fe}_2\text{O}_3$  was thermally prepared by the high-temperature treatment of as-prepared  $\text{FeOOH}$  at 250 °C for 3.0 h in air atmosphere accordingly.

$\text{Fe}_3\text{O}_4$  nanoparticles were prepared from ferric salt (Figs. S1–S5). In a typical procedure, 1.299 g of  $\text{FeCl}_3$ , 0.5 g of trisodium citrate and 2.0 g of  $\text{NaAc}$  were dissolved in 40 mL of ethylene glycol with continuous magnetic stirring. The obtained homogeneous yellow solution was then transformed into a 100 mL Teflon-lined stainless-steel autoclave, heated at 200 °C for about 10.0 h, and then naturally cooled to room temperature. The as-prepared black products were thoroughly washed by ethanol and distilled water for three times and dried in a vacuum at 70 °C for 10.0 h.

### 2.2. Iron-based Fenton removal of ROX

Adsorption and catalysis tests were carried out in a glass beaker with effective volume of 150 mL. The adsorption experiments were conducted in comparison by adding  $0.1 \text{ g L}^{-1}$  catalyst into 100 mL aqueous solution of ROX ( $10.0 \text{ mg L}^{-1}$ ) with constant stirring (160 rpm) at room temperature (22–25 °C) in dark. After shaken for 1.0 h in dark to reach the adsorption-desorption equilibrium with the residual ROX concentration of  $\sim 10.0 \text{ mg L}^{-1}$ , a given amount of  $\text{H}_2\text{O}_2$  was added for the Fenton-like degradation. ROX removal tests were also carried out in different water matrices, humic acids,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  were selected as typical background contaminants in surface water.

The 5-run cyclic tests were carried out under the typical conditions, and the three iron oxides were regularly eluted by 0.1 M  $\text{NaOH}$  aqueous solution. For sample analysis, the elution of adsorbed As species from iron oxides surface by  $\text{NaOH}$  was done with aliquots.

### 2.3. Analysis

At regular intervals, 2 mL of ROX was sampled and filtered by a  $0.22 \mu\text{m}$  membrane to remove solid catalyst. ROX was measured by high-performance liquid chromatography (LC-20 AD, Shimadzu Ltd., Japan) with a diode array detector (SPD-20A) using a C18 column ( $4.6 \text{ mm} \times 150 \text{ mm}$ ,  $5 \mu\text{m}$ , GL Sciences Inc., Japan). The concentration of inorganic arsenic,  $\text{AsO}_3^{3-}$  and  $\text{AsO}_4^{3-}$ , was measured by atomic fluorescence spectrometry (AFS-8220, Beijing Titan Ltd., China). In the recycling runs, 10 mL of 0.1 M  $\text{NaOH}$  aqueous solution was used for arsenic leaching, with the volume/solid ratio of 1:1 (ml: mg) much lower than that in the adsorption step, 10:1 (ml: mg). In addition, residual ROX was found in  $\text{NaOH}$  solution used to desorb arsenic species.  $\cdot\text{OH}$  was analyzed by electron spin resonance (ESR) spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide recorded on a Bruker EPR300 spectrometer, with settings as follow: center field = 3512 G, microwave frequency = 9.86 GHz and power = 6.36 mW.  $\text{Fe}^{2+}/\text{Fe}^{3+}$  were measured by a 1,10-phenanthroline method using a UV-vis spectrophotometer at 510 nm (U-3310, HITACHI). All tests were repeated in

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