

Efficient arsenic removal by a bifunctional heterogeneous catalyst through simultaneous hydrogen peroxide (H₂O₂) catalytic oxidation and adsorption

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Abstract

Arsenic (As) is a toxic contaminant in surface waters and groundwater. Oxidation of arsenite (As(III)) to less toxic arsenate (As(V)) by hydrogen peroxide (H_2O_2) is desirable for enhancing the immobilisation of Arsenic (As). However, this As(III) oxidation process is constrained by the strong pH dependence and the generated As(V) must also be removed for complete As remediation. This study developed and evaluated a novel heterogeneous catalytic system using manganese-doped Lanthanum oxycarbonate (MnL) to catalyse the oxidation of As(III) by H_2O_2 and simultaneously adsorb the generated As(V). The presence of MnL enhanced the removal rate of As(III) by 35 times compared with systems utilising H_2O_2 alone. Additionally, this superior performance was observed over a wide pH range (5-9), which demonstrated this approach could bypass the well-known pH restriction on oxidation by H_2O_2 . Mechanistic studies revealed that the long-lived superoxide radicals ($\cdot\text{O}_2^-/\cdot\text{OOH}$), present on the particle surfaces and derived from the dissociation of the Lewis acid-base adduct (La-OOH^*), were the dominant active species for As(III) oxidation. Mn atoms with low valence states played a crucial role in As(III) oxidation through the provision of extra active sites to facilitate radical production. The La and Mn sites in MnL could rapidly immobilize the generated As(V) by forming precipitates, resulting in a final As removal efficiency of 99% even after three cycles of reutilisation. Overall, this study demonstrates the viability of the proposed novel multifunctional catalyst for efficient As remediation from aqueous environments.

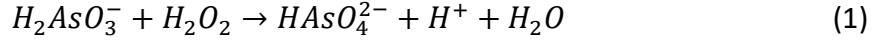
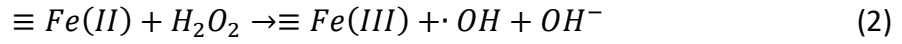
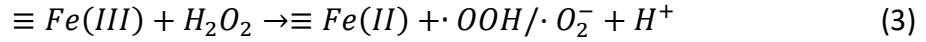
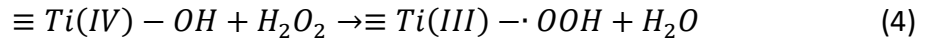
Keywords: Arsenic; Sustainable catalyst; Advanced oxidation; Pollutant adsorption; Lewis acid-base adduct.

1. Introduction

Arsenic (As) is one of the most widespread heavy metal contaminants in both surface and groundwater systems and poses a severe risk to the aquatic environment and to human health (Argos et al. 2012, Su et al. 2018). Related human disease and mortality have been reported in many countries (Ahmad et al. 2018, Smith et al. 2012), thus the World Health Organization (WHO) has set a safety level of $10 \mu\text{g L}^{-1}$ As in drinking waters (Wei et al. 2019). In solution under anoxic and anaerobic conditions, As mainly exists as the trivalent species As(III) (Shan et al. 2019a), which has substantially greater toxicity than As(V) (Qiu et al. 2020). Moreover, As(III) shows much less affinity for adsorbents, compared with As(V), due to it mainly existing as a non-ionic molecule (H_3AsO_3) in water (Shan et al. 2019b). Therefore, the development of As(III) decontamination technology from aqueous environments has drawn particular attention.

Hydrogen peroxide (H_2O_2) has been used as a benign oxidant to convert As(III) to less toxic As(V) in water and wastewater treatment processes (Eq. 1) due to its superior oxidation potential (Wei et al. 2019). However, the oxidative activity of H_2O_2 is strongly pH-dependent and functionality is significantly inhibited under non alkali condition (Shan et al. 2019b). To broaden the applicable pH range of H_2O_2 and to increase oxidation efficiency, some catalysts have been suggested to stimulate the reaction. The most common method has been to apply Fenton-like catalysts, e.g. Fe, Cu and Mn-based (hydro)oxides, which could act as an electron shuttle to accelerate the dissociation of H_2O_2 and produce more powerful reactive oxygen species (ROSs), e.g. $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ (Eq. 2-3) (Wang et al. 2015, Weng et al. 2017, Yang et al. 2019). Recently, another effective approach of using transition metal (hydro)oxides, e.g. Ti, Ce, and Zn, to form Lewis-acid centres on the material surface in H_2O_2 solution during oxidation reactions has been discovered (Chen et al. 2012, Fernandes et al. 2020, Kim et al. 2015). Such Lewis acid catalysis could complex with H_2O_2 and withdraw electrons from its O-O bond, thus leading to the generation of the strong oxidative radicals (Eq. 4), e.g. $\cdot\text{OOH}$, $\cdot\text{OH}$ or $^1\text{O}_2$, facilitating As(III) oxidation (Corma and Garcí'a 2002, Wang et al. 2018). Nevertheless,

simply oxidising As(III) only decreases the toxicity of the As contaminated water. The subsequent removal through adsorption, coagulation, or ion exchange is needed to completely remediate the environmental risk of As (Manning et al. 2002, Nicomel et al. 2016).



We have previously synthesised a novel manganese-doped Lanthanum oxycarbonate (MnL) adsorbent and demonstrated its superior As(V) adsorption ability of 555.6 mg g⁻¹ (Su et al. 2020). This adsorption capability was significantly higher than that (26.3-454.9 mg g⁻¹) of most reported adsorbents, such as Fe-La hydroxide (Zhang et al. 2014), Cu doped Fe₃O₄ (Wang et al. 2015), and Ce doped TiO₂ (Li et al. 2011). Interestingly, the Lanthanum (La) sites in this La-based compound could act as Lewis acids, which have been applied as complexation agents for many anions (Muthu Prabhu et al. 2018, Wahlen et al. 2005). Thus, we hypothesized that MnL could not only adsorb As(V) but also accelerate As(III) oxidation through catalytic activities in generating ROSs by forming Lewis acid-base adducts with H₂O₂. The application of MnL during As(III) oxidation by H₂O₂ may form a heterogeneous catalytic system to fulfil the dual functions of catalysed oxidation of As(III) and adsorption of the generated As(V), however, the performance and underlying mechanisms have hitherto not been studied.

Therefore, this study aimed to develop and evaluate a potential multi-functional catalyst for effective removal of As from aqueous environments through simultaneous H₂O₂ catalytic oxidation of As(III) and adsorption of As(V), over a wide pH range. Firstly, the capabilities of synthesised MnL materials with different relative percentage compositions of Mn and La, on As(III) oxidation and on the total As removal in H₂O₂ solutions, were evaluated. Then, the potential effects of experimental factors, including pH conditions and the dosage of H₂O₂ and MnL, on the oxidation of As(III) were investigated. Furthermore, mechanistic studies were conducted to determine the

potential roles of specific reactive oxygen species on As(III) oxidation, and the functionality of La and Mn lattice sites on the overall As removal. After understanding the mechanisms, the potential application of MnL in H₂O₂ catalytic oxidation processes for As removal was further examined in the presence of other interfering ions. Finally, the reusability of MnL was investigated by subjecting the catalyst to several cycles of use and regeneration.

2. Materials and Methods

2.1. Chemicals and materials

Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, 99%), hydrogen peroxide (H₂O₂, 30%), sodium arsenate dodecahydrate (Na₃AsO₄·12H₂O, 99%) and sodium arsenite (NaAsO₂, 99%) were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). Manganese nitrate solution (Mn(NO₃)₂, 50%), citric acid monohydrate (AM, C₆H₇O₇·H₂O, 99%), polyethene glycol 6000 (PEG-6000, 99%), ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, 99%), ascorbic acid (AA, C₆H₈O₆, 99%), tertiary butanol (TBA, C₄H₁₀O, 99%), p-benzoquinone (p-BQ, C₆H₄O₂, 99%) and the spin-trapping agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 99%) were purchased from Sinopharm Co. Ltd. (Shanghai, China). Ultrapure water (18 MΩ·cm) was used in all experiments.

2.2. Preparation and characterization of Mn-doped La₂O₂CO₃ (MnL)

Mn-doped La₂O₂CO₃ (MnL) was synthesised via a facile sol-gel method that has been reported by Su et al. (2020). Briefly, a certain amount of Mn(NO₃)₂ and La(NO₃)₃·6H₂O, with molar ratios of Mn/(La+Mn) equal to 2.56%, 5.26%, 25% and 50%, were dissolved in ultrapure water (20 mL) and stirred vigorously for 30 min. Then, the mixtures were added into an aqueous solution (20 mL) composed of C₆H₇O₇·H₂O (0.01 mol) and PEG-6000 (6 g). The solutions were heated to 85°C with continuous stirring until the formation of a wet gel. After drying overnight at 85 °C, the gels were calcined in the air (600°C for 120 min; heating rate of 5°C/min). After cooling, the solid samples were finely ground to produce target materials. Our previous study has also demonstrated losses of Mn and La following this preparation process are negligible

(Table S1) (Su et al., 2020). Pure $\text{La}_2\text{O}_2\text{CO}_3$ was prepared by the same process but without $\text{Mn}(\text{NO}_3)_2$ addition.

The crystal structures of MnL before and after reaction were determined by X-Ray diffraction (XRD) using a PANalytical X'Pert PRO powder diffraction system (Malvern Panalytical, Cambridge, UK) with Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) from 5° to $90^\circ/2\theta$ at a scan speed of $5^\circ/\text{min}$. The morphology of the samples and their microstructure were recorded by Environmental Scanning Electron Microscope (ESEM, Su-8020, Hitachi, Japan). The valences of Mn2p, O1s, C1s and As 3d in MnL before and after oxidation were recorded by the X-ray Photoelectron Spectra (XPS; SCALAB250Xi, Thermo Fisher Scientific, USA), which was operated under a monochromatic Al K α radiation source (1486.6eV). All binding energies were calibrated by contaminant carbon (C1s, B.E= 284.8 eV). To determine the existence of peroxide species on the material's surface, diffuse reflectance UV-visible spectra of MnL and H_2O_2 -pretreated MnL was recorded using a UV-visible spectrophotometer (DR-UVS; Cary 500 UV-Vis, Varian Inc., Palo Alto, CA. USA), equipped with a diffuse reflectance accessory. The formation of surficial complexation was also investigated by Raman spectroscopy (LabRAM HR Evolution, HORIBA, France) using the excitation wavelength of 785 nm.

2.3. Experiments and sample analysis

2.3.1. The performance of MnL/ H_2O_2 coupling treatment

Different MnL materials with differing Mn contents (2.56%, 5.26%, 25% and 50%) and the pristine LaMnO_3 were firstly evaluated for potential catalysis of the H_2O_2 oxidation of As(III) under neutral conditions. The same dosage of different MnL (0.2 g L^{-1}) was added into NaAsO_2 solutions (60 mL) with an initial As(III) concentration of 15 mg L^{-1} . The pH was adjusted to 7 using 0.1-1 M HNO_3/NaOH . The mixture was continuously stirred in the dark and the oxidation reaction was initiated by the addition of H_2O_2 (0.534 mM). The experiment was conducted at room temperature ($25 \pm 2^\circ\text{C}$) for 360 min. Each treatment was carried out in triplicate.

At given time intervals, an aliquot (2.5 mL) of the suspensions were withdrawn from each group. The removed samples were then mixed with ascorbic acid (10 g L^{-1} ; 200

μL) to quench the reactions, and filtered immediately through a cellulose acetate membrane (0.22 μm) for determination of the concentrations of total As, As(V), and As(III). The concentration of As(V) in each sample was determined colorimetrically by the molybdenum blue method (Kim et al. 2015) using a UV/visible spectrometer (870 nm; 756 PC, Hong Ji Instrument. Co., Ltd., Shanghai). For determination of total As, KMnO₄ solution (1 mL; 2 mM) was added into the sample to oxidise As(III) to As(V) before the detection of the latter. The concentrations of As(III) were determined by subtraction between total As and As(V). The pseudo-first-order model (Eq. 5) was used to simulate the dynamics of As(III) removal (Wang et al. 2020).

$$-\ln \left(\frac{C_t}{C_0} \right) = k_{obs} t \quad (5)$$

Where C_t was As(III) concentration (mg L^{-1}) versus time (min), C_0 was initial As(III) concentration (mg L^{-1}). k_{obs} was rate constant of the first-order kinetic (min^{-1}).

2.3.2. The effect of H₂O₂ and MnL dosage

The best-performing MnL adsorbent, containing 5.26% Mn, was used to further investigate the influence of H₂O₂ and MnL dosage on As(III) oxidation. To study the effect of the H₂O₂, experiments were conducted with dosages of 0.267, 0.534, 1.335, 2.67 and 5.34 mM of H₂O₂. For the investigation into MnL dosing, experiments were conducted with MnL dosages at 0.1, 0.2, 0.5 and 1 g L⁻¹. Experimental conditions and sample analysis were the same as the aforementioned batch experiment. The pseudo-first-order model (Eq. 5) was again applied to evaluate the removal rate of As(III) under the different treatments.

2.3.3. The effect of pH

The removal of As(III), As(V) and total As, were investigated in MnL/H₂O₂ coupling treatment systems under different pH conditions (3, 5, 7, 9 and 11). The initial As(III) concentration was set at 20 mg L⁻¹, and the dosages of MnL and H₂O₂ were 0.2 g L⁻¹ and 0.534 mM, respectively. The experiments were conducted at room temperature (25 ± 2°C) and sample collection and analysis were the same as previously described. The amounts of Mn²⁺ and La³⁺ liberated were detected by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; Optima 8300, Perkin Elmer Inc., USA) with a

limit of detection (LOD) of 0.2 mg L⁻¹. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; 7500a, Agilent Inc., USA) was used to confirm results when concentration levels were found to be below 0.2 mg L⁻¹.

2.3.4. The generation and role of ROSs on As(III) oxidation

During the MnL/H₂O₂-coupled treatment at pH 7, the ESR spectra of the generated reactive oxygen species ($\cdot\text{OH}$, and $\cdot\text{O}_2^-/\cdot\text{OOH}$) were investigated using a Bruker microESR (Bruker BioSpin GmbH, Rheinstetten, Germany). DMPO was used as a radical trapping agent and the equipment was operated to accumulate three scans with the microwave frequency of 9.817 GHz and power of 19.88 mW. Five mg of catalyst was dispersed into 25 mL of pure water, followed by adding 1 mM of H₂O₂. Then 10 μL of DMPO were added into 1 mL of the mixed solution, which was then immediately placed into a glass capillary sealed with plasticine at one side, for $\cdot\text{OH}$ detection. The detection procedure for $\cdot\text{O}_2^-$ was similar to that of $\cdot\text{OH}$ except replaced the solvent of pure water with absolute methanol. After confirming the existence of the ROSs, the role of each on As(III) oxidation was further studied through active species trapping experiments. The performances for As removal were investigated by addition of the corresponding scavengers (Kim et al. 2015), i.e. TBA (100 mM) for $\cdot\text{OH}$ and p-BQ (5 mM) for $\cdot\text{O}_2^-/\cdot\text{OOH}$, to the mixture. The results were compared with those from the control group without the addition of the scavengers.

To verify the generation of $\cdot\text{O}_2^-/\cdot\text{OOH}$ derived from the surface complex and define its effect on As(III) oxidation, diffuse reflectance UV-visible spectra (DR-UVS) and Raman spectra of MnL, before and after the treatment, were acquired (Tang et al. 2021). The contribution of dissolved oxygen to the generation of $\cdot\text{O}_2^-/\cdot\text{OOH}$ and As(III) oxidation was evaluated by conducting the experiment under O₂ and N₂ aeration at 5 mL min⁻¹. Experimental conditions, sample collection and analysis were the same as previously described. To further investigate the role of La lattice sites on H₂O₂ dissociation and As(III) oxidation, NaF (2 mM) was added to the solution which was further stirred in the dark for 3 h to ensure La sites were completely occupied (Wu et al. 2018). H₂O₂ (0.534 mM) was then added to initiate the oxidation reaction and the oxidation performance was

subsequently determined.

In order to evaluate the function of Mn lattice sites on As(III) oxidation and As(V) adsorption, the different valence states of Mn (Mn(II), Mn(III) and Mn(IV)) were determined at the end of this MnL/H₂O₂ coupling treatment. For the comparison, La₂O₂CO₃, instead of MnL, was used in the control groups. The concentration of H₂O₂ was determined by titanium potassium oxalate spectrophotometry at 400 nm (Shan et al. 2019b). The electronic transport capability of materials could be reflected by current density during the oxidation/reduction processes. Thus, cyclic voltammetry (CV) measurements were conducted using an electrochemical work station in a standard three-electrode configuration, with N₂-purged Na₂SO₄ (50 mL, 0.5 M) containing H₂O₂ (0.534 mM) as the electrolyte (Tian et al. 2019). The MnL electrode was prepared by dispersing MnL (5 mg) in ethanol (1mL) which contained PTFE solution (50 μ L; 5%), and then dried under vacuum before coating onto the pretreated FTO surface. The potential range was between -1.2 and 1.5 V (vs. Ag/AgCl) and the scan rate was 500 mV s⁻¹.

2.3.5. The reusability of MnL and the influence of coexisting ions

The regeneration of MnL was investigated by immersing the used catalysts into a NaOH solution (1 M) for 24 h, to ensure that all the As(V) adsorbed on MnL was eluted out. The refreshed material (0.2 g L⁻¹) and H₂O₂ (0.534 mM) were then added to As(III) solution (20 mg L⁻¹). This procedure was repeated 3 times. Moreover, the effect of typical coexisting ions (Xu et al. 2020), i.e. Fe³⁺, Mn²⁺, Cl⁻, H₂PO₄⁻ and HCO₃⁻, on the As(III) oxidation process was also evaluated. MnL/H₂O₂ coupling treatments were separately conducted at initial ionic concentrations of 0, 0.2 and 2 mmol L⁻¹. After a 360 min reaction time, 5 mL aliquots were collected from each group for As(III) determination. All of the aforementioned experiments and each sample analysis were conducted in triplicate.

3. Results and Discussion

3.1. Characterization of Mn-doped La₂O₂CO₃ (MnL) composites

The XRD patterns of the pristine La₂O₂CO₃ (Fig. 1a) indicated that it existed as a

monoclinic structure (JCPDS card No. 48-1113). Doping of a small amount of Mn ($\leq 5.26\%$) on $\text{La}_2\text{O}_2\text{CO}_3$ improved the crystal symmetry and resulted in a crystal structure similar to that of tetragonal $\text{La}_2\text{O}_2\text{CO}_3$ (JCPDS card No. 23-0320). After further increasing the amount of Mn doped into MnL to 25% and 50%, clear characteristic peaks of LaMnO_3 (JCPDS card No. 01-089-2470) were observed (Fig. 1a). Such a new phase of manganese oxide precipitation on the surface of $\text{La}_2\text{O}_2\text{CO}_3$ may have been due to the introduction of excess Mn in its lattice cells (Xuan et al. 2018). ESEM images of MnL indicated a rod-like morphology with a rod length of 1.7-4 μm (Fig. 1b-c), and element mapping of MnL suggested that both La and Mn were uniformly distributed on the material's surface (Fig. 1d-g). Characterisation confirmed that Mn atoms had successfully entered into $\text{La}_2\text{O}_2\text{CO}_3$ lattices, giving rise to the formation of $(\text{La}_x\text{Mn}_{1-x})_2\text{O}_2\text{CO}_3$ solid solution (Wang et al. 2018).

3.2. H_2O_2 activation by MnL for As(III) oxidation and further As(V) adsorption

3.2.1. The role of Mn content

The catalytic efficiency of the synthesised MnL for As(III) removal was firstly evaluated under neutral conditions (Fig. 2a). In the treatment group without the addition of MnL, only 5% of As(III) was oxidised at the end of the study, which indicated the low capability of As oxidation by H_2O_2 under neutral conditions (Shan et al. 2019b). It is well-known that it is difficult to absorb As(III) onto adsorbents due to it mainly existing as a non-ionic molecule (H_3AsO_3) in water (Shan et al. 2019b). Thus, the application of 5.26%-MnL alone, without H_2O_2 , only removed approximately 3.5% of As(III) through adsorption (Fig. S1), which also demonstrated that As(III) removal in the H_2O_2 /MnL-coupled treatment systems are mainly through the oxidation process. Fig. 2a shows that the coupling H_2O_2 /MnL treatments achieve As(III) oxidation of up to 90% within 360 min. The pure $\text{La}_2\text{O}_2\text{CO}_3$ without Mn doping showed 70% As(III) removal, which was higher than those of 25%-MnL and 50%-MnL. This showed that La is also crucial for As(III) removal during the oxidation process by H_2O_2 , and the roles of La and Mn are explored in the mechanistic studies (Section 3.3).

The dynamics of As(III) oxidation could be well described ($R^2 > 0.95$) by the pseudo-first order model (Fig. S2a). Both removal efficiency (Fig. 2a) and removal rate (k value,

Fig. S2a) of As(III) increased to 90% and 0.0044 min^{-1} , respectively, with increasing Mn doping of $\text{La}_2\text{O}_2\text{CO}_3$ from 0 to 5.26%. This might be attributed to the presence of variable-valence Mn atoms in the lattice structure of MnL, which could act as active sites and accelerate the electron transfer for As(III) oxidation (Li et al. 2020, Tian et al. 2019, Zhou et al. 2020). However, both the As(III) removal efficiency and removal rate gradually reduced to 30% and 0.001 min^{-1} , respectively, under the higher Mn doping regime of 50% on $\text{La}_2\text{O}_2\text{CO}_3$. The excess Mn might have formed a new phase of LaMnO_3 in the lattice cell (Fig. 1), causing a lack of exchangeable ligands (e.g. CO_3^{2-} , O^{2-} and $-\text{OH}$) between H_2O_2 and catalysts and resulting in decreased As(III) oxidation efficiency (Su et al., 2020). This was supported by the observation that pure LaMnO_3 showed negligible catalytic effects on the oxidation of As(III) (Fig. S2b).

The surface of MnL is positively charged under pH 7 (Su et al. 2019), resulting in negligible electrostatic attraction between MnL and As(III) and consequently poor adsorption rate for As(III) (Fig. S1). Therefore, to completely remove As from contaminated water, further remediation of As(V) is necessary (Nicomel et al. 2016). The results of total As removal efficiencies (Fig. 2b) were identical to the As(III) oxidation efficiencies (Fig. 2a) in the corresponding H_2O_2 /MnL-coupled treatment system, indicating that the majority of the oxidation product of As(V) was adsorbed by MnL. This was supported by our previous study which determined that MnL can effectively adsorb As(V) through surface complexation, ion exchange and the formation of LaAsO_4 precipitates (Su et al. 2020). The results supported the hypothesis that the oxidation capability of As(III), rather than the adsorption of As(V), could be the control step for the removal of As. Overall, the results demonstrated that doping with Mn played a crucial role in H_2O_2 catalysis, and that the MnL material with Mn content of 5.26% performed the best at remediation of As through the synergistic functions of As(III) oxidation and As(V) adsorption.

3.2.2. The influences of H_2O_2 and MnL dosage

The best performance of As(III) removal was attributed to the MnL material doped with 5.26% Mn (Fig. 2a), which was therefore selected for further investigations to

evaluate the influence of other factors on the reactions. In the treatment system using $\text{H}_2\text{O}_2/\text{MnL}$ coupling, the removal rate of As(III) was found to increase dramatically when H_2O_2 concentration increased from 0.267 mM ($k=0.0018 \text{ min}^{-1}$) to 1.335 mM ($k=0.006 \text{ min}^{-1}$) (Fig. 2c). Correspondingly, the removal efficiency of As(III) increased from 73% to 99% within 480 min. However, with further increasing H_2O_2 dosage to 5.34 mM, the As(III) removal rate only exhibited slight improvement, to 0.0077 min^{-1} . This might have been due to the gradual saturation of sites for H_2O_2 adsorbed on the MnL, thus limiting As(III) oxidation (Gennari et al. 2015). Additionally, increasing the dosage of MnL was observed to improve As(III) oxidation (Fig. 2d). Unlike the scenario of limited increment of As(III) oxidation under the solely high addition of H_2O_2 , the removal efficiency of As(III) continued to increase from 51% to 98% within 360 min when the addition of MnL increased from 0.1 to 1 g L^{-1} (Fig. 2d). It might be partly due to the adsorption effect of As(III) by the MnL. As the adsorption capability is relatively low, the increased As(III) removal was likely due to the availability of more active surficial catalytic sites at higher dosages of MnL (Kim et al. 2015). Therefore, the optimum ratio of the H_2O_2 and MnL should be determined for As removal in order to achieve the best performance.

3.2.3. The influence of pH

It has been reported that pH is an important factor influencing As(III) oxidation by H_2O_2 . In this study, considerable oxidation of As(III) in the H_2O_2 -only treatment was only observed under pH 11, reaching similar removal efficiency ($\sim 90\%$ within 30 min) to that under MnL catalysis treatment (Fig. 3a). This agreed with previous work that showed direct oxidation by H_2O_2 only occurred under strongly alkaline conditions (Qian et al. 2015, Shan et al. 2019b). Significantly lower As(III) oxidation efficiencies ($<22\%$) were obtained under acid and neutral conditions (pH of 3-7).

By contrast, in $\text{H}_2\text{O}_2/\text{MnL}$ -coupled treatment systems, similar removal efficiencies of As(III) were achieved (88%) under neutral conditions (pH 7) when compared with the results under strongly alkaline conditions (pH of 11). At pHs of 5 and 9, the removal efficiencies were approximately 70% within 360 min. In strong acid conditions (pH 3), the removal efficiency (18.5%) of As(III) was much lower when compared with those

values obtained under other pH conditions. This might be due to the poor stability of MnL under strong acid, where the amount of La and Mn leaching at pH 3 were as high as 283 and 3.5 mg L⁻¹, respectively (Fig. 3b). These amounts were almost equal to the original contents of La and Mn in the studied MnL composites (Table S1).

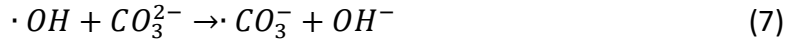
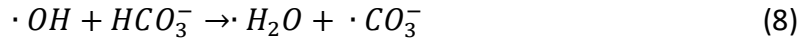
The production of As(V) has also been detected in the H₂O₂/MnL-coupled treatment system (Fig. 3c). In the pH 5-9 range, the concentrations of As(V) in solution increased within the initial 30 min and then decreased gradually, indicating that the removal process of As(III) by MnL was through the combination of As(III) oxidation and As(V) adsorption. However, As(V) in solution displayed a negligible decrease after 30 min at both pH =3 and 11, which may have been due to i) active surfaces on MnL being dissociated in the strong acid conditions and ii) MnL possessing poor adsorption qualities towards As(V) under strongly alkaline conditions (Xu et al. 2018). The total As removal performance of the proposed heterogenous catalytically treatment system (Fig. 3d), indicated that the MnL/H₂O₂ -coupled catalytic system could achieve both efficient As(III) oxidation and As(V) removal over the wide pH range of 5-9.

3.3. Mechanisms of As(III) oxidation in the MnL/H₂O₂ -coupled system

3.3.1. The functions of reactive species

Reactive oxygen species (ROSs), i.e. hydroxyl ($\cdot\text{OH}$), hydroperoxyl ($\cdot\text{OOH}$) and superoxide radicals ($\cdot\text{O}_2^-$), are recognized as important oxidants in catalysed H₂O₂ oxidation reactions (Watts and Teel 2019). In this study, ESR spectroscopy detected the four peaks typical of the DMPO-OOH adduct from samples collected from MnL/H₂O₂ -coupled treatment systems (Fig. 4a). The intensity ratio of these four peaks was approximately 1:1:1:1, supporting the formation of $\cdot\text{O}_2^-/\cdot\text{OOH}$ over the MnL. Notably, the steady-state concentration of $\cdot\text{O}_2^-/\cdot\text{OOH}$ would be relatively low due to the low signal intensities through current determinations (Fig. 4a), investigations through more precise analytical methodology should be conducted for further confirmation. The presence of the DMPO-OH adduct (intensity ratio of 1:2:2:1) was additionally observed within 2 min (Fig. 4b), which suggested the formation of $\cdot\text{OH}$, and this might be ascribed to a Fenton-like reaction, activated by $\equiv\text{Mn(II/III)}$ (Weng et al. 2017). However, after 2 min, the signal

for DMPO-OH disappeared, which might have indicated that $\cdot\text{OH}$ was quickly consumed by the excess of H_2O_2 (Eq. 6). Moreover, considerable CO_3^{2-} was released into the solution from the catalyst, in particular the system in the presence of H_2O_2 (Fig. S2), which would further quench $\cdot\text{OH}$ following equations 7 and 8 (Jiang et al. 2020, Zhou et al. 2020):



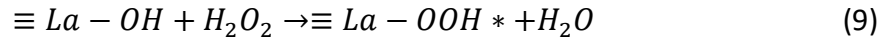
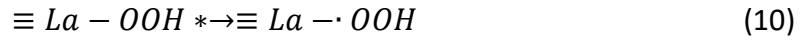
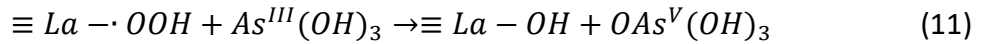
To evaluate the specific role of each radical, scavenging compounds, viz. tert-butyl alcohol (TBA) and p-benzoquinone (p-BQ) (Kim et al. 2015; Fan et al. 2021), were added to the MnL/ H_2O_2 system during the reaction (Fig. 4c). Following the addition of TBA (100 mM), the $\cdot\text{OH}$ scavenger ($k_{\cdot\text{OH}/\text{TBA}} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the As(III) removal efficiency did not show significant change when compared with the control group, which indicated that the $\cdot\text{OH}$ may not have been the main radical responsible for As(III) oxidation. By contrast, the removal efficiency of As(III) decreased from 90% to 53% within 360 min with the addition of 1 mM p-BQ ($k_{\cdot\text{O}_2^-/\text{BQ}} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), and this further decreased to 18% when the concentration of p-BQ was increased to 5 mM. From the ROSs scavenging experiments, it suggested that $\cdot\text{O}_2^-/\cdot\text{OOH}$ rather than $\cdot\text{OH}$ might play a major role in As(III) oxidation in the MnL/ H_2O_2 treatment system.

3.3.2. The origin of $\cdot\text{O}_2^-/\cdot\text{OOH}$

In addition to H_2O_2 , dissolved oxygen may be an important source for $\cdot\text{O}_2^-/\cdot\text{OOH}$ formation in some catalysis reactions (Exner and Over, 2019). To investigate this, the MnL/ H_2O_2 coupling treatments were conducted separately, in solutions that were aerated either by O_2 or N_2 (Fig. S4a). It was clear that the excess oxygen did not show a significant positive effect on As(III) oxidation. Meanwhile, there was only a slight suppression of efficiency of As(III) oxidation under N_2 conditions. These observations thus excluded the role of dissolved oxygen for $\cdot\text{O}_2^-$ production and contribution to As(III) oxidation.

It is known that La(III) could act as a Lewis acid-base adduct and form a peroxide

complex with H₂O₂, resulting in the generation of ROSs (Novikov et al. 2016). After treatment, the DR-UVS spectrum of MnL showed an obvious red shift (Fig. S4b), and a new characteristic band (1065 cm⁻¹) was observed in the Raman spectrum (Fig. 4d) that could be assigned to peroxide species (Shan et al. 2019b, Wang et al. 2018, Wei et al. 2019). The results suggested that H₂O₂ was substantially adsorbed onto MnL and formed a surficial Lewis acid-base adduct, i.e. La-OOH*, through the reaction in Eq. 9 (Corma and Garcí'a 2002). This Lewis acid-base complex would be then dissociated by donating electrons towards La(III) sites (Eq. 10), giving rise to the formation of surficial ·O₂⁻/·OOH species (Novikov et al. 2016), finally causing conversion of As(III) to As(V) (Eq. 11).



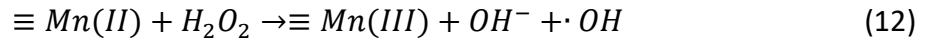
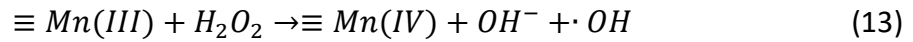
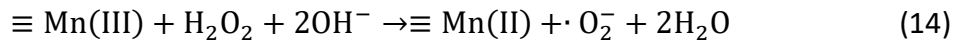
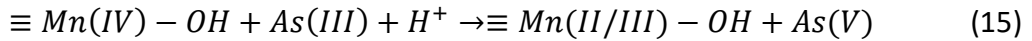
Further experimentation with the addition of NaF, acting as an inhibitor towards La(III) (Wu et al. 2018), greatly reduced As(III) oxidation (Fig. S4c), confirming the important role of $\equiv La(III)$ sites on H₂O₂ decomposition. It is hypothesised that, due to the effective complexation ability and the electrophilic properties of La(III), the surficial radical La-OOH was able to be stabilized and extended the lifetime of ·OOH to at least 60 minutes (Fig. 4a). During As(III) oxidation, the intensity of the peak attributed to La-OOH* in acquired Raman spectra (Fig. 4d) dramatically decreased, accompanied by an appearance of a signal due to the As-O species. It could thus be concluded that the surficial Lewis acid-base complex (La-OOH*) was an important precursor of ·O₂⁻/·OOH generation.

3.3.3. The effects of different-valent Mn

As an active transition metal with various valence states, Mn has been demonstrated to typically show a positive effect on both pollutant adsorption and catalytic oxidation reactions (Wen et al. 2017, Weng et al. 2017). During the H₂O₂ catalytic oxidation by MnL, the content of Mn(IV) in MnL increased from 36.5% to 44.8% while Mn(III) and Mn(II) decreased from 34.2% to 26.5% and 29.3% to 28.5%, respectively (Fig. 5a). However, during the As(III) adsorption reaction by MnL alone,

without the addition of H₂O₂, the contents of Mn(II), Mn(III) and Mn(IV) in MnL exhibited negligible change.

Since Mn can act as a typical active site for Fenton-like reactions, Mn with low valence states, i.e. Mn(II), Mn(III), could be oxidised by H₂O₂ accompanied by Mn(IV) and ·OH production (Eq. 12-13). Meanwhile, Mn(III), acting as Lewis acid might also complex and dissociate H₂O₂ to produce ·OOH (Eq. 14). Therefore, the decrease in Mn(III) content of the MnL would be significantly higher than that of Mn(II), when MnL was treated with H₂O₂. After oxidizing As(III), a small amount of Mn(IV) would have been reduced to Mn(II) and Mn(III) again (Eq. 15), which might be attributed to As(III) being directly oxidised by Mn(IV)-OH under the acidic conditions (Zhang et al. 2018). However, compared to ·OOH, the role of Mn(IV) for As(III) oxidation would be considered to be minor.



It should be noted that newly formed ·OH through a Fenton-like reaction would be quenched rapidly by CO₃²⁻/HCO₃⁻ (Eq. 7-8), thus the utilisation efficiency of H₂O₂ for As(III) oxidation in MnL activating system (52.5%-64.3%) was lower than that in pure La₂O₂CO₃ system (77.4%-91.5%) (Fig. S4d). Nevertheless, the adsorption efficiency of H₂O₂ on MnL was greatly improved, as shown in Fig. 5b-c, which would facilitate the formation of surficial Lewis acid-base complexes and favour ROS production. In addition, because of the valence state transformation between Mn(II)/Mn(III) and Mn(IV) during oxidation of As(III), interfacial electron transfer would have been accelerated and that gave rise to higher current density during the reaction (Fig. 5d), which efficiently promoted oxidation of As(III) (Tian et al. 2019).

3.3.3. The overall processes of As removal

XRD spectra of MnL clearly showed the formation of LaAsO₄ precipitates (JCPDS

card. No. 15-0756) after As(III) oxidation (Fig. 6a), consistent with the ESEM image that revealed wire-like species present on the MnL rod (Fig. S5), suggesting that La(III) sites also played an important role on As(V) immobilisation. The absence of manganese arsenic compounds in XRD spectra might be ascribed to the minor amount of Mn present in MnL, thus the corresponding peaks of products were not evident. XPS spectra of As3d (Fig. 6b) suggested that all of the immobilized arsenic on MnL, including the pre-adsorbed As(III) (44.5 eV), had been completely converted to As(V) (45.3 eV) (Ma et al. 2020) in the MnL/H₂O₂ -coupled system.

XPS spectra of C1s (Fig. 6c) supported that CO₃²⁻ (289.4 eV) (Liu et al. 2018) in MnL decreased from 22.6% to 19.1% after As(III) removal, indicating that the adsorption process of As(V) on MnL was accompanied by CO₃²⁻/HCO₃⁻ exchange (Su et al. 2020). The obvious shift of C=O (286.1 eV) was observed after As(III) oxidation, which may be due to the complexation effect of H₃AsO₄ with C=O (Li et al. 2019). For O1s (Fig. 6d), La/Mn-O peak (528.8 eV) decreased markedly, while the As-O signal (531.0 eV) was present after As(III) oxidation (Souza et al. 2021), supporting the fact that La/Mn were active sites for As(V) adsorption (Lv et al. 2019). It should be noted that the percentage ratio of surface oxygen, i.e. -OH/OOH (531.4 eV) in MnL increased from 59.5% to 60.9% after H₂O₂ treatment, confirming the formation of the lanthanum/peroxide complex, La-OOH*. However, the intensity of surface -OH/-OOH had decreased again to 49.6%, proving that the surface peroxide complex was consumed by arsenite during oxidation, which was in accordance with the result of Raman analysis (Fig. 4d).

The overall removal process of As in the MnL/H₂O₂ coupled system can be visualised in Fig.7. Only a small amount of As(III) can be directly oxidised to As(V) by H₂O₂ in particular under neutral and acid conditions. The majority of the As(III) is oxidised by the generated ROSs and the ·O₂⁻/·OOH is the dominant active species. La(III) sites in MnL play an important role in complexing with H₂O₂ to form surficial Lewis acid-base complex species, which are the precursors of ·OOH and produced the dominant effect on As(III) oxidation. Mn(III) ions in MnL can also act as activators to improve ·OOH production by adsorbing and dissociating H₂O₂. Meanwhile, Mn(II/III) can further accelerate charge

transfer processes during As(III) oxidation by a Fenton-like reaction. The As(V) oxidised from As (III) and original As(V) in the solution would be rapidly adsorbed on La and Mn lattice sites in MnL by precipitation, accompanied with exchange with $\text{CO}_3^{2-}/\text{HCO}_3^-$. Thus, this H_2O_2 catalysis system would finally achieve an effective removal of As in contaminated water.

3.4. The effect of coexisting ions on As(III) removal and reusability of MnL

The removal efficiency of As(III) increased from 92% to 98% when 0.2 mM Fe^{3+} was present in the MnL/ H_2O_2 -coupled reaction solution, indicating that an appropriate amount of Fe^{3+} was conducive to As(III) oxidation (Fig. 8a). It is known that the combination of the transition metal ions Fe^{3+} and Mn^{2+} could catalyse H_2O_2 to generate $\cdot\text{OOH}$ and accelerate electron transfer and facilitate ROS production (Zhou et al. 2020). In this study, the Mn^{2+} in MnL decreased from 29.3% to 28.5% (Fig. 5a), which represented its synergetic contribution with Fe^{3+} on the improved oxidation of As(III). Meanwhile, Fe^{3+} could rapidly capture the oxidation product of HAsO_4^{2-} and form precipitates of FeAsO_4 (Zhang et al. 2019), further contributing to the highly-efficient removal of As(III). However, when increasing the concentration of Fe^{3+} to 2 mM, the removal efficiency of As (III) sharply decreased to 10%, probably because the strongly acidic conditions (pH 2.98) under a high concentration of Fe^{3+} would destabilize the catalyst and lead to a significant loss of active sites (Fig. 3b).

When Mn^{2+} or Cl^- were present in the solution, the removal efficiency of As(III) was maintained between 92% to 94%, indicating that these ions had little impact on As(III) removal. It could also be seen that the presence of H_2PO_4^- and HCO_3^- had little influence on As(III) oxidation at low concentration (0.2 mM) while showing substantial inhibitory effect at the higher concentration studied (2 mM). This might be attributed to the excess amount of phosphoric acid and carbonic acid competing with As(III) for La lattice sites, thus hindering the adsorption of As(V) (Su et al. 2020), reducing the catalytic activity of MnL and decreasing the removal efficiency of As(III). Additionally, HCO_3^- , as a quencher of most ROSs (Eq. 7-8), further reduced the removal efficiency of As(III) to 65% when the concentration reached 2 mM.

The reusability of MnL as a catalyst of H_2O_2 oxidation, for the removal of As, was evaluated (Fig. 8b). After three cycles of As(V) desorption followed by MnL regeneration with NaOH (1 M), the catalyst could still achieve 99% removal of As within 8 h (Fig. 8b) and the remnant As(III) in solution was less than $10 \mu\text{g L}^{-1}$ from an initial As(III) concentration of 3.15 mg L^{-1} (Fig. S6). The stable removal rates of As in the second and third cycles were interpreted as a consequence of decreases in the CO_3^{2-} content of the MnL after successive regeneration treatments with NaOH. Since CO_3^{2-} showed an adverse effect on ROS production and As(V) adsorption, the presence of less CO_3^{2-} would conceivably increase As(III) removal. It should be emphasised that the performance of the As removal will ultimately decrease due to the decrease in active sites after a certain amount of reuse, however, the extent of the reusability needs to be further investigated.

4. Conclusions

In this study, Mn-doped $\text{La}_2\text{O}_2\text{CO}_3$ (MnL) was proved to be a good catalyst for oxidation of As(III) by H_2O_2 , over a wide pH range of 5-9, which greatly broadens the applicability of this oxidant. Mechanistic studies revealed that La lattice sites played an important role in generating surficial superoxide radicals ($\cdot\text{O}_2^-/\cdot\text{OOH}$) by forming an active Lewis acid-base adduct (La-OOH^*) with H_2O_2 , and persistent surficial $\cdot\text{O}_2^-/\cdot\text{OOH}$ was confirmed to be the dominant active species available for As(III) oxidation. Meanwhile, the low-valent states of Mn (Mn(II/III)) not only accelerated charge transfer during the oxidation, but also improved $\cdot\text{OOH}$ production and the adsorption of H_2O_2 on the surface of MnL, which resulted in higher oxidation efficiency of As(III). The oxidation product As(V) would then be rapidly immobilized on the La and Mn sites by forming precipitates. This work thus provides a new strategy by which to develop other Lanthanum-based catalysts for environmental remediation by advanced oxidation processes. Moreover, the excellent reusability of the MnL material and the levels of remnant As well below the permissive value ($10 \mu\text{g L}^{-1}$) after treatment, further suggest that remediation by the MnL/ H_2O_2 -couple is a great prospect for the effective and simultaneous oxidation of As(III) and

adsorption of As(V) towards complete As elimination.

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Reference

- Ahmad, S.A., Khan, M.H. and Haque, M. 2018. Arsenic contamination in groundwater in Bangladesh: implications and challenges for healthcare policy. *Risk Manag. Healthc. Policy*. 11, 251-261. <https://doi.org/10.2147/RMHP.S153188>
- Argos, M., Ahsan, H. and Graziano, J.H. 2012. Arsenic and human health: epidemiologic progress and public health implications. *Rev. Environ. Health* 27(4), 191-195. <https://doi.org/10.1515/reveh-2012-0021>
- Chen, F., Shen, X., Wang, Y. and Zhang, J. 2012. CeO₂/H₂O₂ system catalytic oxidation mechanism study via a kinetics investigation to the degradation of acid orange 7. *Appl. Catal. B: Environ.* 121-122, 223-229. <https://doi.org/10.1016/j.apcatb.2012.04.014>
- Corma, A. and García, H. 2002. Lewis Acids as Catalysts in Oxidation Reactions From Homogeneous to Heterogeneous Systems. *Chem. Rev.* 102, 3837-3892. <https://doi.org/10.1021/cr010333u>
- Exner, K.S. and Over, H. 2019. Beyond the rate-determining step in the oxygen evolution reaction over a single-crystalline IrO₂(110) model electrode: kinetic scaling relations. *ACS Catal.* 9(8), 6755-6765. <https://doi.org/10.1021/acscatal.9b01564>
- Fan, W., Cui, J., Li, Q., Huo, Y., Xiao, D., Yang, X., Yu, H., Wang, C., Jarvis, P., Lyu, T. and Huo, M., 2021. Bactericidal efficiency and photochemical mechanisms of micro/nano bubble-enhanced visible light photocatalytic water disinfection. *Water Res.* 203, 117531. <https://doi.org/10.1016/j.watres.2021.117531>
- Fernandes, C.I., Vaz, P.D., Nunes, T.G. and Nunes, C.D. 2020. Zinc biomimetic catalysts for

- epoxidation of olefins with H_2O_2 . *Appl. Clay Sci.* 190, 105562
<https://doi.org/10.1016/j.clay.2020.105562>
- Gennari, M., Brazzolotto, D., Pécaut, J., Cherrier, M.V., Pollock, C.J., DeBeer, S., Retegan, M., Pantazis, D.A., Neese, F. and Rouzières, M. 2015. Dioxygen activation and catalytic reduction to hydrogen peroxide by a thiolate-bridged dimanganese (II) complex with a pendant thiol. *J. Am. Chem. Soc.* 137(26), 8644-8653. <https://doi.org/10.1021/jacs.5b04917>
- Jiang, W., Dionysiou, D.D., Kong, M., Liu, Z., Sui, Q. and Lyu, S. 2020. Utilization of formic acid in nanoscale zero valent iron-catalyzed Fenton system for carbon tetrachloride degradation. *Chem. Eng. J.* 380, 122537. <https://doi.org/10.1016/j.cej.2019.122537>
- Kim, D.H., Bokare, A.D., Koo, M. and Choi, W. 2015. Heterogeneous catalytic oxidation of As(III) on nonferrous metal oxides in the presence of H_2O_2 . *Environ. Sci. Technol.* 49(6), 3506-3513. <https://doi.org/10.1021/es5056897>
- Li, H., Gao, Q., Wang, G., Han, B., Xia, K. and Zhou, C. 2020. Unique electron reservoir properties of manganese in Mn(II)-doped CeO_2 for reversible electron transfer and enhanced Fenton-like catalytic performance. *Appl. Surf. Sci.* 502, 144295. <https://doi.org/10.1016/j.apsusc.2019.144295>
- Li, Z., Qu, J., Li, H., Lim, T.C. and Liu, C. 2011. Effect of cerium valence on As (V) adsorption by cerium-doped titanium dioxide adsorbents. *Chem. Eng. J.* 175, 207-212. <https://doi.org/10.1016/j.cej.2011.09.096>
- Li, Z., Liu, X., Jin, W., Hu, Q. and Zhao, Y. 2019. Adsorption behavior of arsenicals on MIL-101(Fe): The role of arsenic chemical structures. *J. Colloid Interface Sci.* 554, 692-704. <https://doi.org/10.1016/j.jcis.2019.07.046>
- Liu, X., Zong, E., Hu, W., Song, P., Wang, J., Liu, Q., Ma, Z. and Fu, S. 2018. Lignin-derived porous carbon loaded with $\text{La}(\text{OH})_3$ nanorods for highly efficient removal of phosphate. *ACS Sustainable Chem. Eng.* 7(1), 758-768. <https://doi.org/10.1021/acssuschemeng.8b04382>
- Lv, Z., Fan, Q., Xie, Y., Chen, Z., Alsaedi, A., Hayat, T., Wang, X. and Chen, C. 2019. MOFs-derived magnetic chestnut shell-like hollow sphere $\text{NiO}/\text{Ni@C}$ composites and their removal performance for arsenic(V). *Chem. Eng. J.* 362, 413-421. <https://doi.org/10.1016/j.cej.2019.01.046>
- Ma, L., Cai, D. and Tu, S. 2020. Arsenite simultaneous sorption and oxidation by natural

- ferruginous manganese ores with various ratios of Mn/Fe. *Chem. Eng. J.* 382, 123040.
<https://doi.org/10.1016/j.cej.2019.123040>
- Manning, B.A., Fendorf, S.E., Bostick, B. and Suarez, D.L. 2002. Arsenic (III) oxidation and arsenic (V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* 36(5), 976-981.
<https://doi.org/10.1021/es0110170>
- Muthu Prabhu, S., Chuaicham, C. and Sasaki, K. 2018. A mechanistic approach for the synthesis of carboxylate-rich carbonaceous biomass-doped lanthanum-oxalate nanocomplex for arsenate adsorption. *ACS Sustainable Chem. Eng.* 6(5), 6052-6063.
<https://doi.org/10.1021/acssuschemeng.7b04678>
- Nicomel, N.R., Leus, K., Folens, K., Van Der Voort, P. and Du Laing, G. 2016. Technologies for arsenic removal from water: current status and future perspectives. *Int. J. Environ. Res. Public Health* 13(1), 62. <https://doi.org/10.3390/ijerph13010062>
- Novikov, A.S., Kuznetsov, M.L., Rocha, B.G.M., Pombeiro, A.J.L. and Shul'pin, G.B. 2016. Oxidation of olefins with H₂O₂ catalysed by salts of group III metals (Ga, In, Sc, Y and La): epoxidation versus hydroperoxidation. *Catal. Sci. Technol.* 6(5), 1343-1356.
<https://doi.org/10.1039/C5CY01367D>
- Qian, A., Yuan, S., Zhang, P. and Tong, M. 2015. A new mechanism in electrochemical process for arsenic oxidation: production of H₂O₂ from anodic O₂ reduction on the cathode under automatically developed alkaline conditions. *Environ. Sci. Technol.* 49(9), 5689-5696.
<https://doi.org/10.1021/acs.est.5b00808>
- Qiu, Z., Shi, S., Qiu, F., Xu, X., Yang, D. and Zhang, T. 2020. Enhanced As(III) removal from aqueous solutions by recyclable Cu@MNM composite membranes via synergistic oxidation and absorption. *Water Res.* 168, 115147. <https://doi.org/10.1016/j.watres.2019.115147>
- Shan, C., Dong, H., Huang, P., Hua, M., Liu, Y., Gao, G., Zhang, W., Lv, L. and Pan, B. 2019a. Dual-functional millisphere of anion-exchanger-supported nanocerium for synergistic As(III) removal with stoichiometric H₂O₂ Catalytic oxidation and sorption. *Chem. Eng. J.* 360, 982-989.
<https://doi.org/10.1016/j.cej.2018.07.051>
- Shan, C., Liu, Y., Huang, Y. and Pan, B. 2019b. Non-radical pathway dominated catalytic oxidation of As(III) with stoichiometric H₂O₂ over nanocerium. *Environ. Int.* 124, 393-399.
<https://doi.org/10.1016/j.envint.2019.01.014>

- Smith, A.H., Marshall, G., Liaw, J., Yuan, Y., Ferreccio, C. and Steinmaus, C. 2012. Mortality in young adults following in utero and childhood exposure to arsenic in drinking water. *Environ. Health Perspect.* 120(11), 1527-1531. <https://doi.org/10.1289/ehp.1104867>
- Souza, T.G., Freitas, E.T., Mohallem, N.D. and Ciminelli, V.S., 2021. Defects induced by Al substitution enhance As (V) adsorption on ferrihydrites. *J. Hazard. Mater.* 420, 126544. <https://doi.org/10.1016/j.jhazmat.2021.126544>
- Su, J., Lyu, T., Yi, H., Bi, L. and Pan, G. 2020. Superior arsenate adsorption and comprehensive investigation of adsorption mechanism on novel Mn-doped $\text{La}_2\text{O}_2\text{CO}_3$ composites. *Chem. Eng. J.* 391, 123623. <https://doi.org/10.1016/j.cej.2019.123623>
- Su, X., Kushima, A., Halliday, C., Zhou, J., Li, J. and Hatton, T.A. 2018. Electrochemically-mediated selective capture of heavy metal chromium and arsenic oxyanions from water. *Nat. Commun.* 9, 4701. <https://doi.org/10.1038/s41467-018-07159-0>
- Tang, Y., Zhang, M., Zhang, J., Lyu, T., Cooper, M. and Pan, G. 2021. Reducing arsenic toxicity using the interfacial oxygen nanobubble technology for sediment remediation. *Water Res.* 205, 117657. <https://doi.org/10.1016/j.watres.2021.117657>
- Tian, N., Tian, X., Nie, Y., Yang, C., Zhou, Z. and Li, Y. 2019. Enhanced 2, 4-dichlorophenol degradation at pH 3–11 by peroxymonosulfate via controlling the reactive oxygen species over Ce substituted 3D Mn_2O_3 . *Chem. Eng. J.* 355, 448-456. <https://doi.org/10.1016/j.cej.2018.08.183>
- Wahlen, J., De Vos, D., De Hertogh, S., Nardello, V., Aubry, J.M., Alsters, P. and Jacobs, P. 2005. Lanthanum-exchanged zeolites as active and selective catalysts for the generation of singlet oxygen from hydrogen peroxide. *Chem. Commun.* 7, 927-929. <https://doi.org/10.1039/B414597F>
- Wang, C., Yin, H., Bi, L., Su, J., Zhang, M., Lyu, T., Cooper, M. and Pan, G. 2020. Highly efficient and irreversible removal of cadmium through the formation of a solid solution. *J. Hazard. Mater.* 384, 121461. <https://doi.org/10.1016/j.jhazmat.2019.121461>
- Wang, T., Yang, W., Song, T., Li, C., Zhang, L., Wang, H. and Chai, L. 2015. Cu doped Fe_3O_4 magnetic adsorbent for arsenic: synthesis, property, and sorption application. *RSC Adv.* 5(62), 50011-50018. <https://doi.org/10.1039/C5RA03951G>
- Wang, W., Zhu, Q., Qin, F., Dai, Q. and Wang, X. 2018. Fe doped CeO_2 nanosheets as Fenton-like

- heterogeneous catalysts for degradation of salicylic acid. *Chem. Eng. J.* 333, 226-239.
<https://doi.org/10.1016/j.cej.2017.08.065>
- Watts, R.J. and Teel, A.L. 2019. Hydroxyl radical and non-hydroxyl radical pathways for trichloroethylene and perchloroethylene degradation in catalyzed H_2O_2 propagation systems. *Water Res.* 159, 46-54. <https://doi.org/10.1016/j.watres.2019.05.001>
- Wei, Y., Yu, X., Liu, C., Ma, J., Wei, S., Chen, T., Yin, K., Liu, H. and Luo, S. 2019. Enhanced arsenite removal from water by radially porous Fe-chitosan beads: Adsorption and H_2O_2 catalytic oxidation. *J. Hazard. Mater.* 373, 97-105. <https://doi.org/10.1016/j.jhazmat.2019.03.070>
- Wen, Z., Zhang, Y., Wang, Y., Li, L. and Chen, R. 2017. Redox transformation of arsenic by magnetic thin-film MnO_2 nanosheet-coated flowerlike Fe_3O_4 nanocomposites. *Chem. Eng. J.* 312, 39-49. <https://doi.org/10.1016/j.cej.2016.11.112>
- Weng, Z., Li, J., Weng, Y., Feng, M., Zhuang, Z. and Yu, Y. 2017. Surfactant-free porous nano- Mn_3O_4 as a recyclable Fenton-like reagent that can rapidly scavenge phenolics without H_2O_2 . *J. Mater. Chem. A* 5(30), 15650-15660. <https://doi.org/10.1039/C7TA04042C>
- Wu, P., Xia, L., Liu, Y., Wu, J., Chen, Q. and Song, S. 2018. Simultaneous sorption of arsenate and fluoride on calcined Mg-Fe-La hydrotalcite-like compound from water. *ACS Sustainable Chem. Eng.* 6(12), 16287-16297. <https://doi.org/10.1021/acssuschemeng.8b03209>
- Xu, H., Wang, D., Ma, J., Zhang, T., Lu, X. and Chen, Z. 2018. A superior active and stable spinel sulfide for catalytic peroxymonosulfate oxidation of bisphenol S. *Appl. Catal. B: Environ.* 238, 557-567. <https://doi.org/10.1016/j.apcatb.2018.07.058>
- Xu, R., Lyu, T., Zhang, M., Cooper, M. and Pan, G. 2020. Molecular-level investigations of effective biogenic phosphorus adsorption by a lanthanum/aluminum-hydroxide composite. *Sci. Total Environ.* 725, 138424. <https://doi.org/10.1016/j.scitotenv.2020.138424>
- Xuan, K., Zhu, X., Cai, Y. and Tu, X. 2018. Plasma oxidation of H_2S over non-stoichiometric La_xMnO_3 perovskite catalysts in a dielectric barrier discharge reactor. *Catalysts* 8(8), 317. <https://doi.org/10.3390/catal8080317>
- Yang, X., He, J., Yang, Q., Jiao, R., Liao, G. and Wang, D. 2019. Cu(I)-doped Fe_3O_4 nanoparticles/porous C composite for enhanced H_2O_2 oxidation of carbamazepine. *J. Colloid Interface Sci.* 551, 16-25. <https://doi.org/10.1016/j.jcis.2019.04.083>
- Zhang, W., Fu, J., Zhang, G. and Zhang, X. 2014. Enhanced arsenate removal by novel Fe-La

- composite (hydr) oxides synthesized via coprecipitation. Chem. Eng. J. 251, 69-79.
<https://doi.org/10.1016/j.cej.2014.04.057>
- Zhang, W., Liu, C., Zheng, T., Ma, J., Zhang, G., Ren, G., Wang, L. and Liu, Y. 2018. Efficient oxidation and sorption of arsenite using a novel titanium(IV)-manganese(IV) binary oxide sorbent. J. Hazard Mater. 353, 410-420. <https://doi.org/10.1016/j.jhazmat.2018.04.034>
- Zhang, W., Liu, F., Sun, Y., Zhang, J. and Hao, Z. 2019. Simultaneous redox conversion and sequestration of chromate(VI) and arsenite(III) by iron(III)-alginate based photocatalysis. Appl. Cat. B: Environmen. 259, 118046. <https://doi.org/10.1016/j.apcatb.2019.118046>
- Zhou, X., Xu, D., Chen, Y. and Hu, Y. 2020. Enhanced degradation of triclosan in heterogeneous E-Fenton process with MOF-derived hierarchical Mn/Fe@PC modified cathode. Chem. Eng. J. 384, 123324. <https://doi.org/10.1016/j.cej.2019.123324>

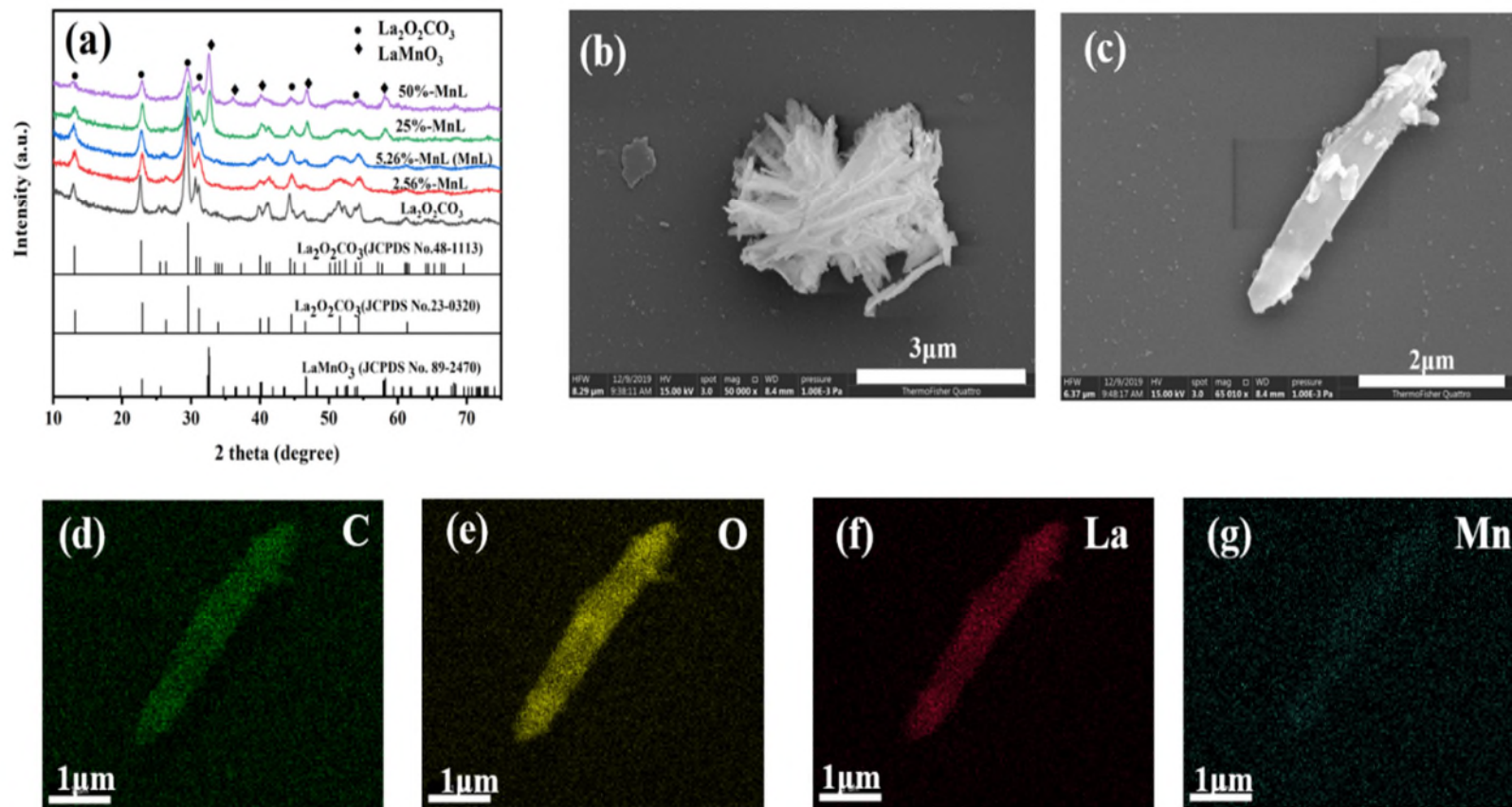


Fig. 1. (a) XRD patterns of Mn-doped La₂O₂CO₃ (MnL) with different amounts of Mn doping. (b-c) Representative ESEM images of MnL at different zoom levels, and element mapping images for (d) Carbon, (e) Oxygen, (f) Lanthanum and (g) Manganese, on MnL.

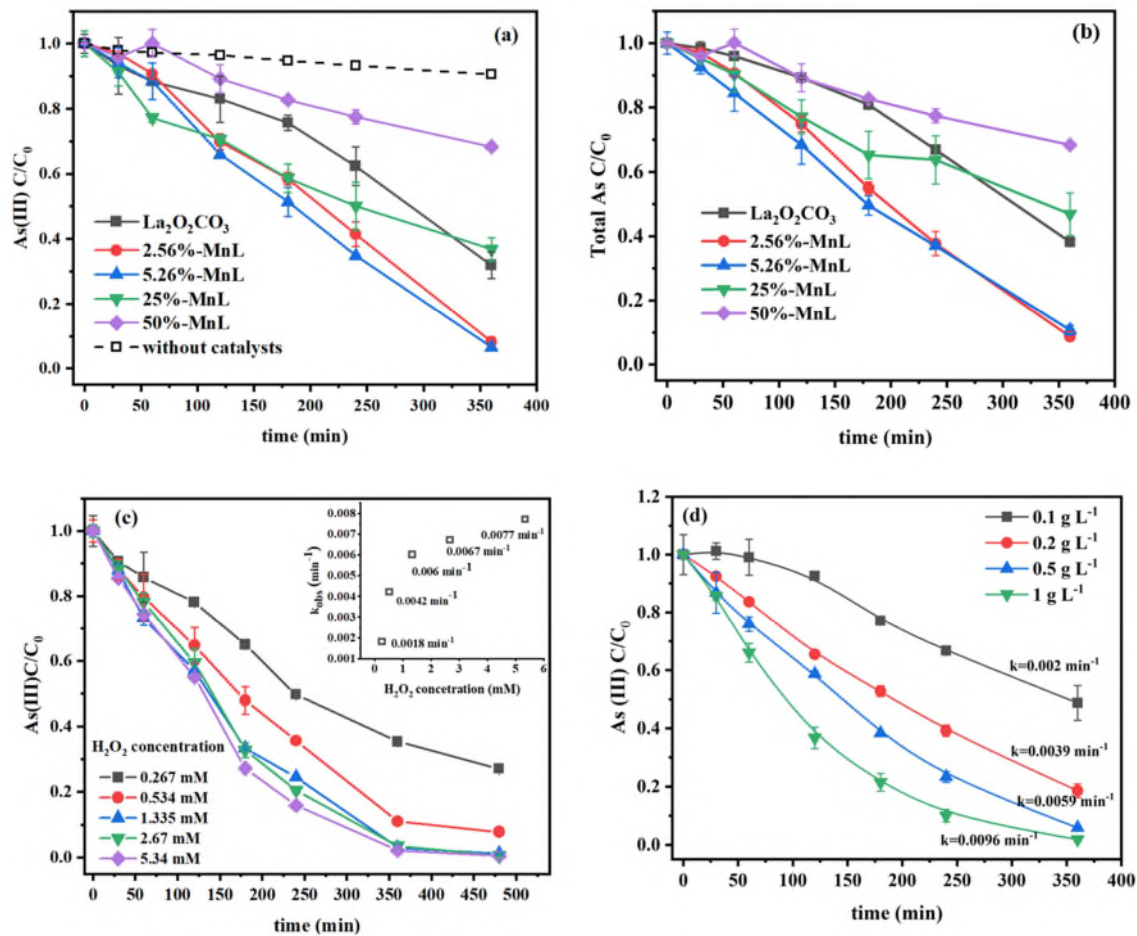


Fig. 2. (a) The kinetics of As(III) oxidation/removal and (b) total As removal from H_2O_2 oxidation systems with various Mn-doped $\text{La}_2\text{O}_2\text{CO}_3$ (MnL) catalysts under neutral conditions, and (c) the influences of initial H_2O_2 concentration and (d) MnL dosage, on As(III) removal.

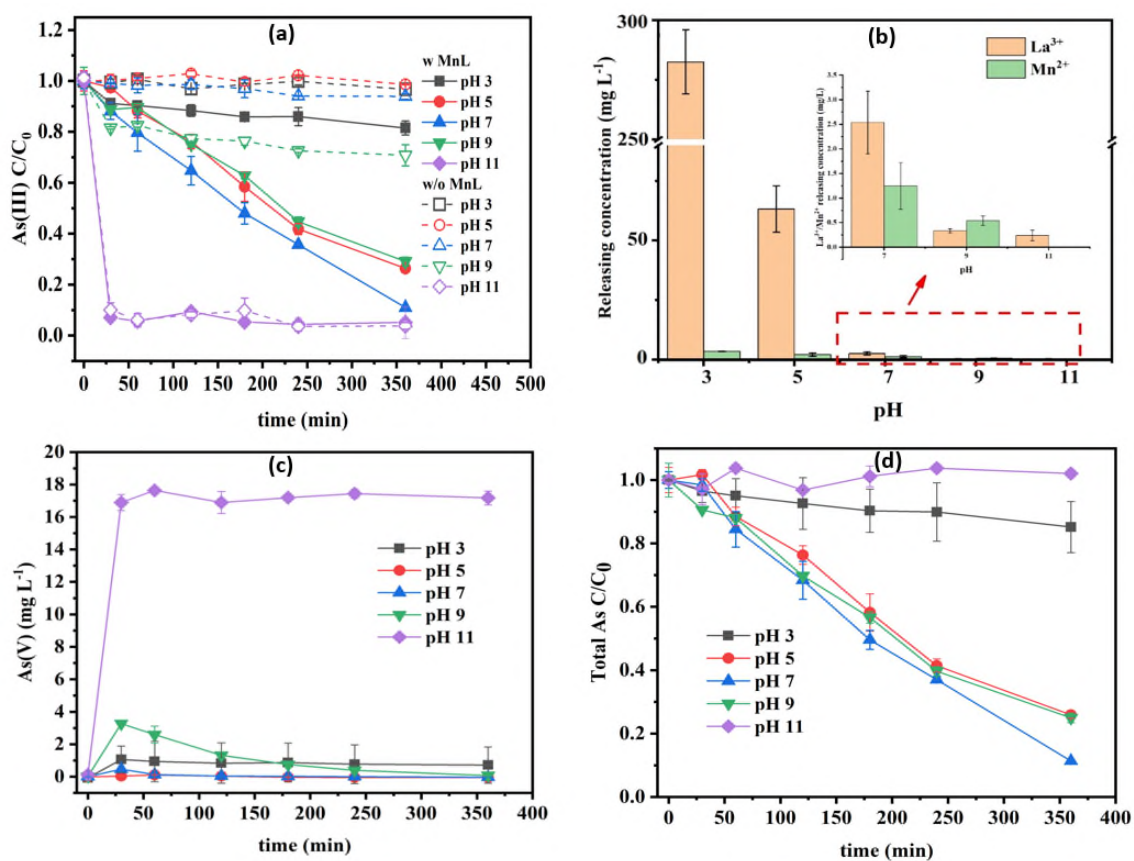


Fig. 3. (a) As(III) oxidation in the MnL/H₂O₂ and H₂O₂-only treatment systems under various pH conditions. (b) Amounts of La and Mn released under various pH conditions in the MnL/H₂O₂ - coupled system. (c) As(V) generation and (d) total As removal, in the MnL/H₂O₂ -coupled treatment system, under various pH conditions.

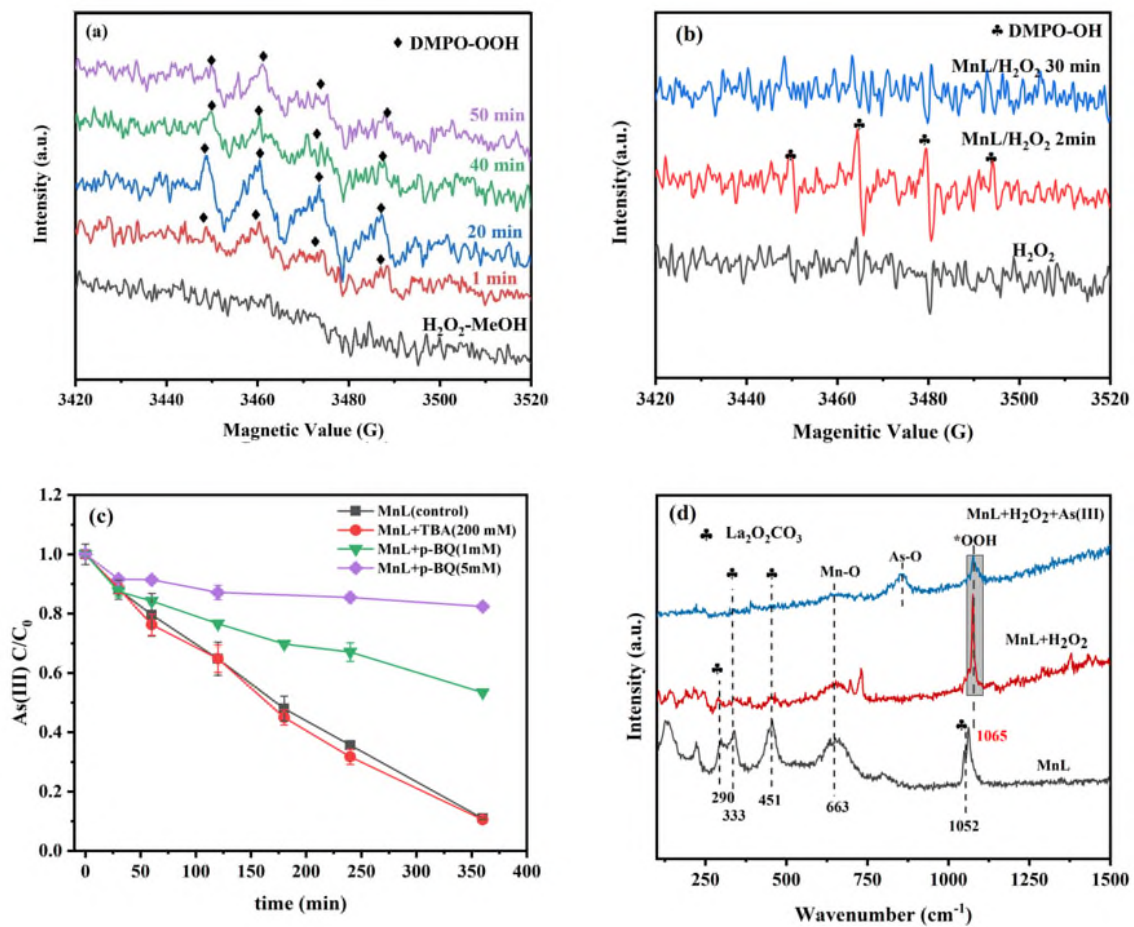


Fig. 4. (a) ESR spectra of DMPO-OOH and (b) DMPO-OH formed in the MnL/H₂O₂-coupled system. (c) Effect of quenching agents on As(III) oxidation by MnL/H₂O₂-coupled treatment. (d) Raman spectra of MnL in the presence or absence of H₂O₂ and in the presence of As(III).

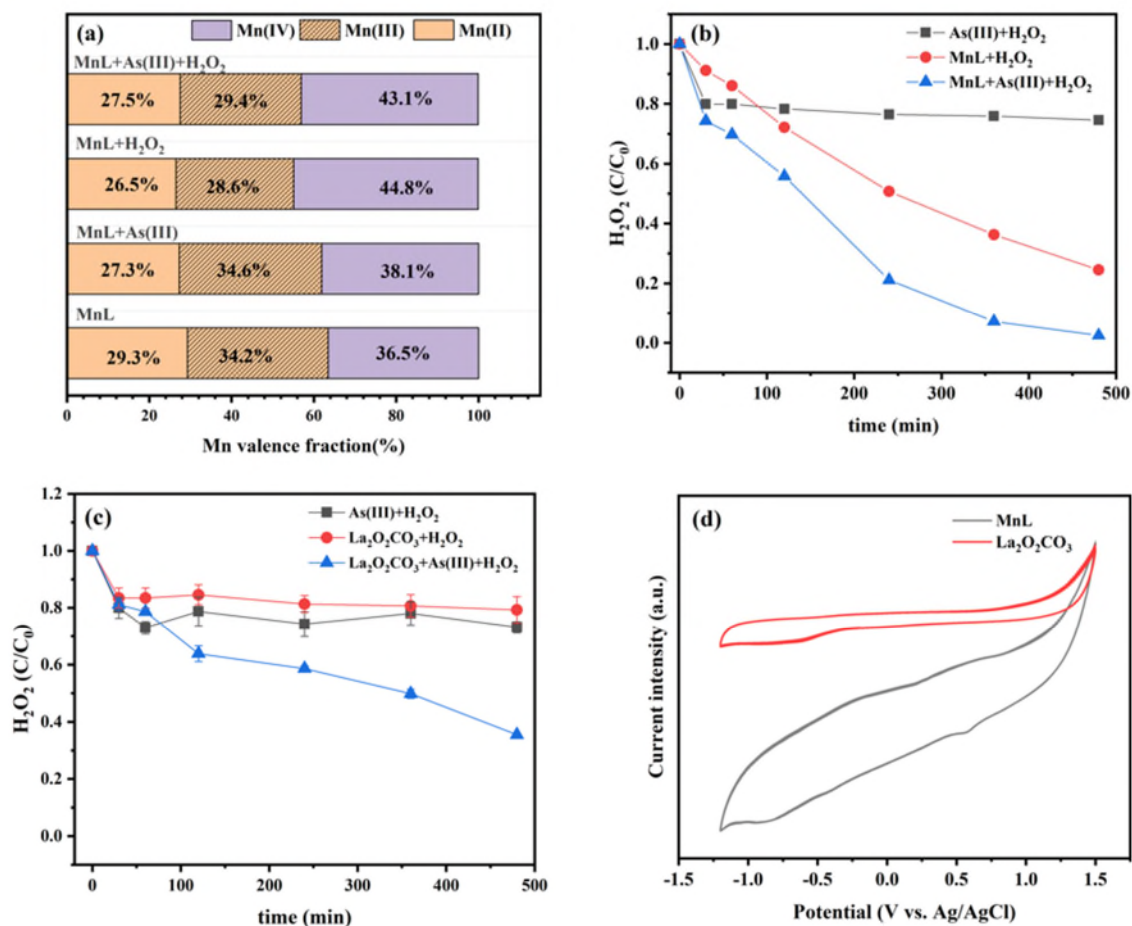


Fig. 5. (a) Fractions of Mn species under different treatment conditions, (b) evolution of H₂O₂ by MnL activation with and without As(III) addition, (c) evolution of H₂O₂ by pure La₂O₂CO₃ activation with and without As(III) addition and (d) cyclic voltammetry plots of MnL and pure La₂O₂CO₃ in 0.267 mM H₂O₂ and 50 mg L⁻¹ As(III).

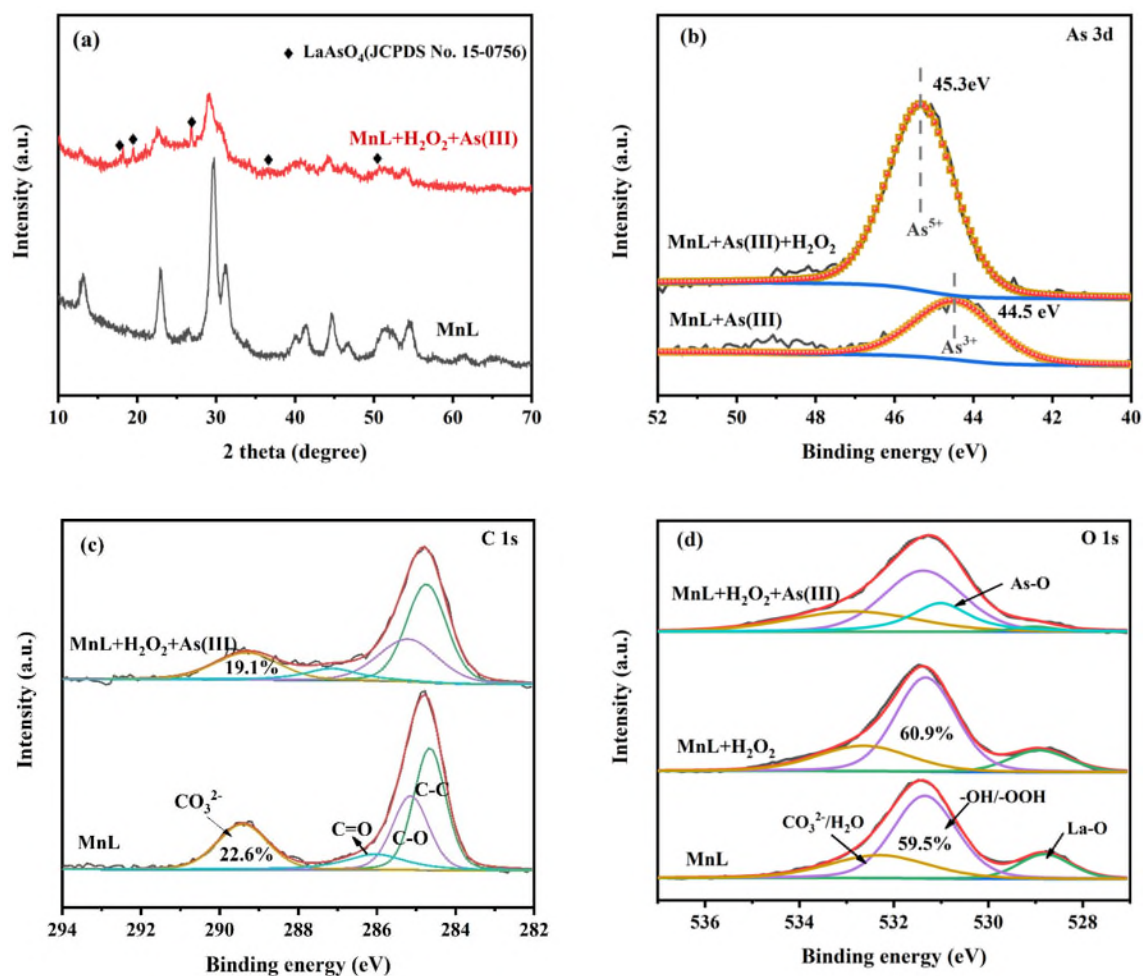


Fig. 6. (a) XRD spectra of MnL, (b) XPS spectra of As3d, (c) C1s and (d) O1s of MnL, before and after As(III) oxidation.

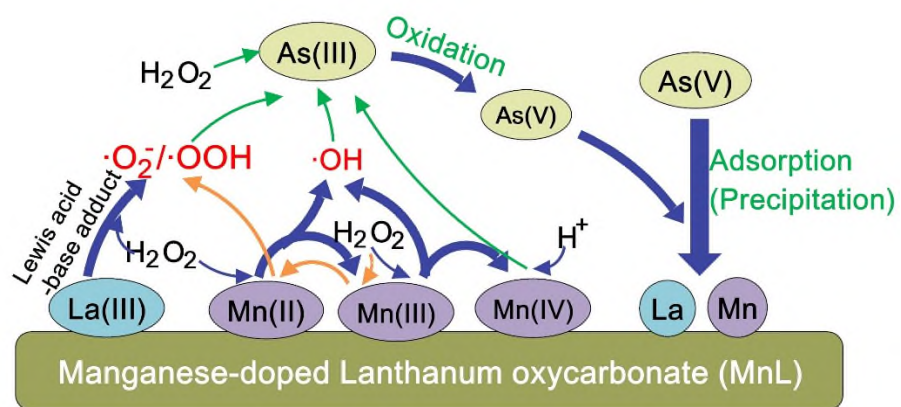


Fig.7. The removal processes of As in MnL/H₂O₂ -coupled system.

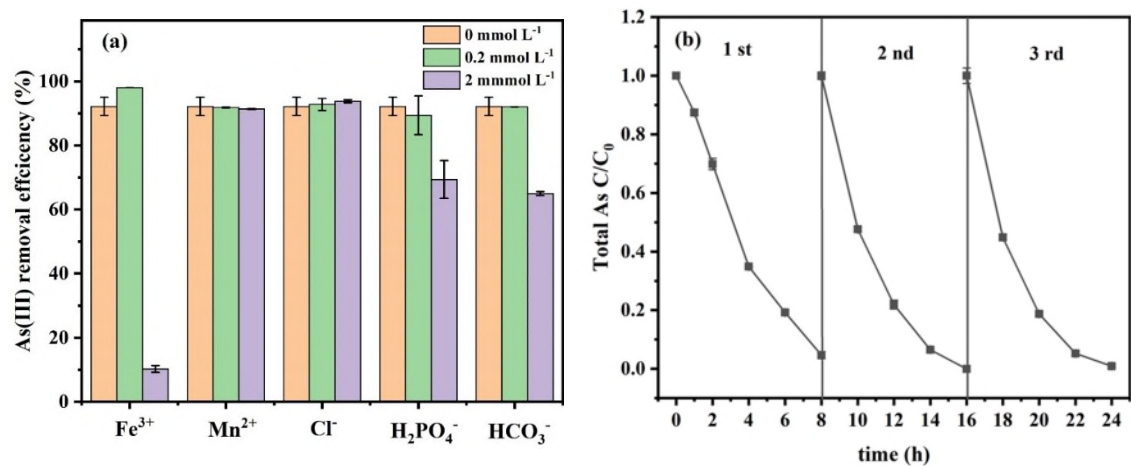


Fig. 8. (a) The effect of coexisting ions on As(III) removal in MnL/H₂O₂ system. (b) The removal efficiency of As(III) over sequential MnL regeneration cycles.

Supporting Information

The SI has 5 pages, which includes 1 table and 6 figures.

Table S1.

The contents of La and Mn in the procreated manganese-doped Lanthanum oxycarbonate (MnL) materials.

Content (g/g adsorbent)	La ₂ O ₂ CO ₃	2.56%-MnL	5.26%-MnL	25%-MnL	50%-MnL
La	0.751	0.74	0.729	0.626	0.479
Mn	--	0.0078	0.016	0.091	0.197

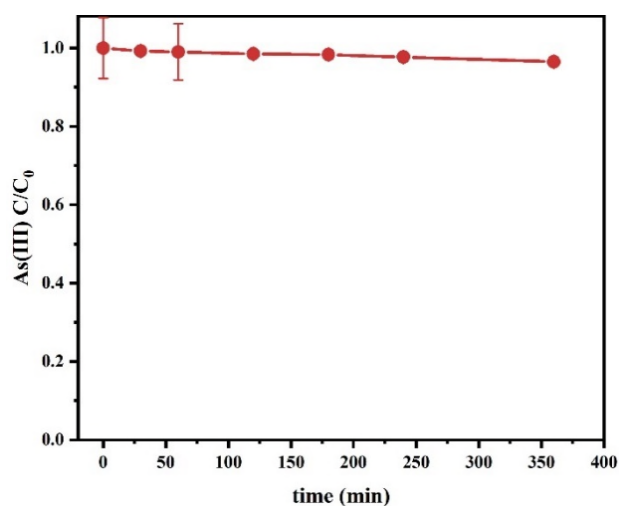


Fig. S1. The adsorption capabilities of As(III) by 5.26%-MnL along the experiment. As(III) initial concentration: 20 mg L⁻¹, pH=7, 5.26%-MnL dosage=0.2 g L⁻¹.

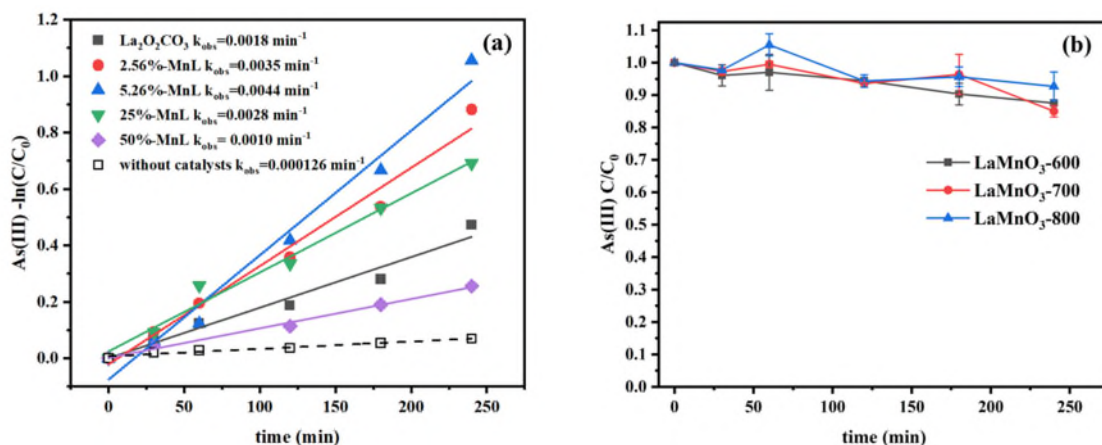


Fig. S3. (a) Pseudo-first order plots for As(III) oxidation in the MnL/H₂O₂ system, and (b) the oxidation efficiency of As(III) in LaMnO₃/H₂O₂ -coupled system with the LaMnO₃ synthesized at 600 °C, 700 °C, and 800 °C.

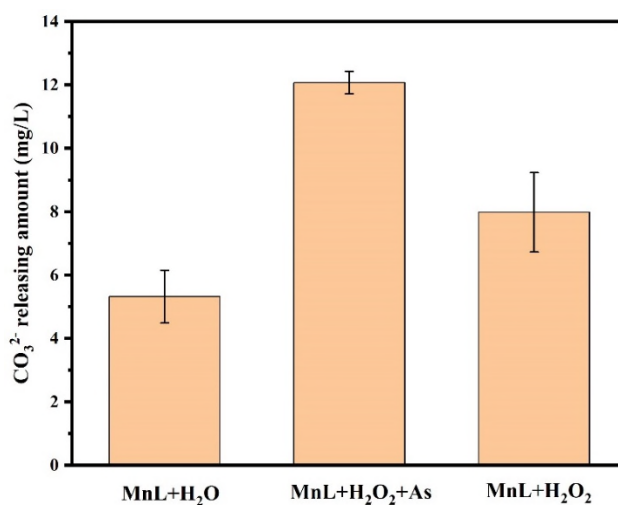


Fig. S3. The releasing amount of CO₃²⁻ from 5.26%-MnL in pure water, H₂O₂ and arsenic oxidation systems.

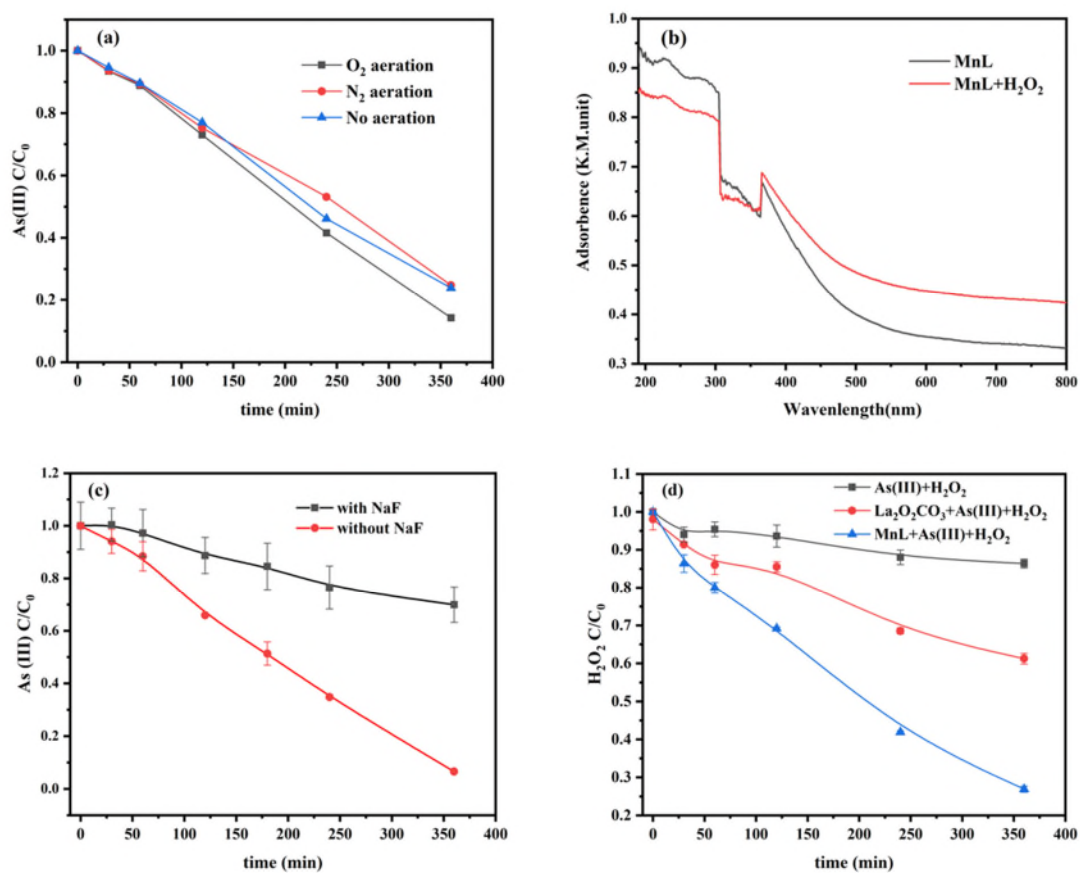


Fig. S4. (a) The effect of dissolved oxygen on As(III) oxidation in MnL/ H_2O_2 system, (b) diffuse-reflectance UV-visible spectra (DR-UVS) of MnL in the presence and absence of H_2O_2 , (c) the effect of NaF on As(III) oxidation in MnL/ H_2O_2 system, and (d) the evolution of H_2O_2 during As(III) removal by MnL or $La_2O_2CO_3/H_2O_2$.

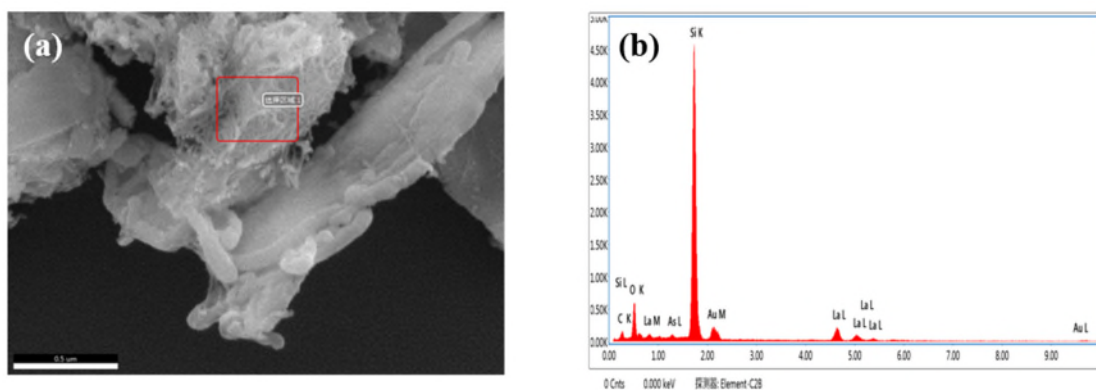


Fig. S5. (a) ESEM image and (b) EDS spectrum of MnL after As(III) oxidation.

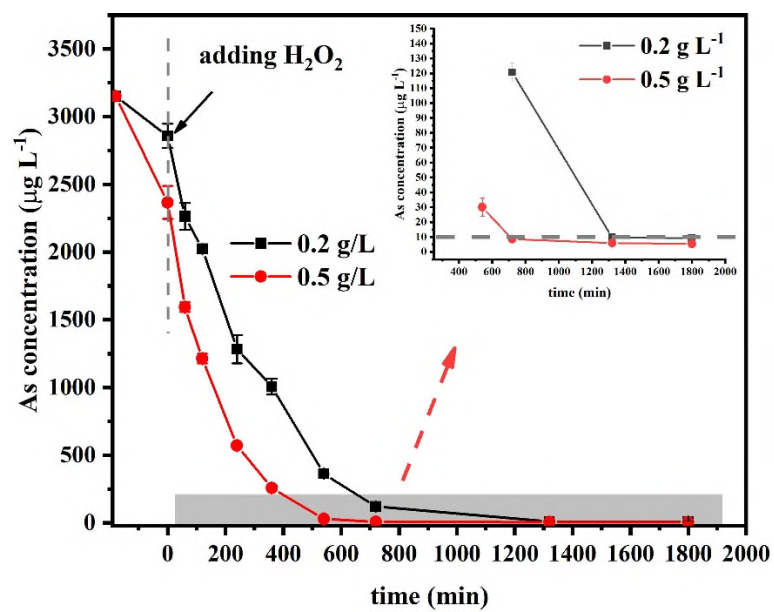


Fig. S6. Remnant As(III) in the MnL/ H_2O_2 system with initial As(III) concentration of 3.15 mg L^{-1} .



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Efficient arsenic removal by a bifunctional heterogeneous catalyst through simultaneous hydrogen peroxide (H₂O₂) catalytic oxidation and adsorption

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