Sustainable fabrication of graphene oxide/manganese oxide composites for removing phenolic compounds by adsorption-oxidation process

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To develop effective strategies for removing phenolic compounds, in-situ graphene oxide/manganese oxide (GO/MnOX, X = 2, 3/4) composites were fabricated via a sustainable method by synchronously utilizing manganese ions and acidic liquid waste during synthesis of GO. Comparatively, traditionally ex-situ GO/MnO2 composites were synthesized to verify the difference between in-situ and ex-situ synthesis. Based on the schematic and mass flow analysis, in-situ synthesis exhibited better atom economy and less waste emission than ex-situ synthesis. Then, the results of batch experiments exhibited that GO/MnOX composites possessed higher removal efficiency and wider pH range for p-cresol (p-CR) and p-tert-butylphenol (p-TBP) than GO/MnO2 composites. The maximum removal capacities of GO/MnO2 composites were 107.68 mg/g for p-CR and 135.41 mg/g for p-TBP. And GO/MnO2 composites could retain high removal efficiency for p-TBP (>90%) after five recycles. For in-situ GO/MnOX composites, GO sheets not only promoted the adsorption of phenolic compounds and by-products, but also enhanced the oxidation capacity of MnOX via an electron transfer interaction. Especially, the detection of ring cleavage products indicated further oxidation for p-TBP. Possessing an eco-friendly fabrication strategy and augmented adsorption-oxidation capability, in-situ GO/MnOX composites are expected to be applied in the removal of phenolic compounds.

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1. Introduction

Phenolic compounds have given rise to emerging concerns regarding human health and ecosystems due to their widespread use in the pharmaceutical, petroleum and petrochemical, pesticide, plastic, and paper industries (Danquah et al., 2018). Consisting of a hydroxyl group bonded directly to a benzene ring, phenolic compounds possess a stable conjugated system, leading to biological accumulation and poor biodegradability (Ou et al., 2018). Thus, an urgent need exists to develop an efficient method for removing phenolic compounds (Villar da Gama et al., 2018; Zhong et al., 2018).

Various methods, including chemical oxidation (Jiang et al., 2015), adsorption (Villar da Gama et al., 2018), and membrane separation (Zagklis and Paraskeva, 2015), have been reported to remove phenolic compounds. Among them, oxidation constitutes an effective and attractive method due to the potential to disrupt the structural stability of pollutants (Wang et al., 2015). Manganese oxides, ubiquitous in natural soil and synthetic materials, are traditional and cost-effective adsorbents and oxidants in wastewater treatment. Especially, manganese oxides are able to oxidize various aromatic Lewis bases, such as phenolic and aniline compounds (Grebel et al., 2016; Wang et al., 2018b). Previous studies demonstrated that phenolic compounds are susceptible to oxidation by manganese dioxide (MnO2) through sequential one electron-transfer reactions, forming a series of intermediate products (Abdullah et al., 2017; Remucal and Ginder-Vogel, 2014). However, the intermediate products, such as phenolic multimer and benzoquinones, would be released back into the aqueous solution. Meanwhile, during the oxidation of phenolic compounds, reductive
dissolution of manganese oxides would occur (Grebel et al., 2016), leading to the release of manganese ions. The above by-products are undesirable in practical wastewater treatment processes. Thus, effective adsorption of the above by-products during or after the oxidation process is essential for avoiding secondary pollution.

In recent years, graphene oxide-based composites have attracted extensive attention as potential adsorbents based on the structural functionality and surface properties (Yan et al., 2014). Compared with traditional materials, the composite materials possess multifunction of different components, such as adsorption and oxidation properties (Awual, 2014, 2016, 2017). In addition, the synergistic effect of components in composites enhances the application prospect (Awual et al., 2015b, 2018). Especially, the reserved sp²-hybridized carbon configurations in graphene oxide (GO) sheets possess strong adsorption ability to aromatic compounds with π-π interactions (Jin et al., 2015). The oxygenated groups from GO sheets in aqueous solution can rapidly adsorb metal cation by electrostatic attraction. These excellent properties meet the precise need of effective adsorption for both phenolic compounds and by-products (aromatic intermediate products and Mn²⁺) during oxidation by manganese oxides. Thus, it is a significant and meaningful aim to develop graphene oxide/manganese oxide composites with efficient adsorption and oxidation capacity for removing phenolic compounds.

Up to date, various types of graphene oxide/manganese oxide composites have been reported and mainly applied as electrodes because of their remarkable electrochemical properties (Buke et al., 2018; Chen et al., 2010; Wan et al., 2018; Wang et al., 2018a; Ye et al., 2018). These excellent properties may also provide a new insight into the interaction with environmental pollutants (Deng et al., 2015; Xu et al., 2015b). However, the extant literature that relates to the removal of phenolic compounds directly by graphene oxide/manganese oxide composites remains limited. In particular, conventional preparation methods of graphene oxide/manganese oxide composites consume great amounts of chemicals and energy, and produce a large volume of highly acidic wastewater containing manganese ions (Duan et al., 2016; Jiangying et al., 2013; Qu et al., 2014; Rathour and Bhattacharya, 2018). Therefore, it is also significant to develop an eco-friendly method for preparing graphene oxide/manganese oxide composites.

Herein, this work presented a sustainable strategy to prepare in-situ graphene oxide/manganese oxide (GO/MnOₓ, X = 2, 3/4) composites. Based on the fabrication hypothesis and objective, manganese ions in acidic wastewater were served as Mn(II) source to synthesize MnOₓ, which directly anchored onto GO sheets to obtain GO/MnOₓ composites in the particularly acid condition. Thus, the proposed strategy provided an effective solution to recycle acidic wastewater and fabricate in-situ GO/MnOₓ composites. Further, traditionally ex-situ graphene oxide/manganese oxide (GO/MnO₂) composites were synthesized to contrastively elucidate the removal difference for p-cresol (p-CR) and p-tert-butylphenol (p-TBP). Based on characterization and batch experiments, the unique synthesis process provided GO/MnOₓ composites with excellent physicochemical properties and enhanced adsorption-oxidation capacity for phenolic pollutants in comparison with GO/MnO₂ composites. Possessing the superiority of sustainable fabrication, convenient addition, and excellent adsorption-oxidation properties, GO/MnOₓ composites have great potential to be employed into practical environmental remediation.

2. Experimental

2.1. Chemicals and materials

Graphite powder (granularity ≤ 30 μm), KMnO₄, H₂SO₄ (98%), MnSO₄·H₂O, NaOH, ascorbic acid, and HCl were purchased from the Sinopharm Chemical Reagent Co., Ltd., with high chemical purity. p-cresol (p-CR) and p-tert-butylphenol (p-TBP) were purchased from the Shanghai Macklin Biochemical Co., Ltd., of analytical grade. Their physicochemical properties, such as molecular structure, molecular weight (MW), aqueous solubility (Cs), and octanol-water partition coefficient (KOW) are listed in Table S1 in the Supporting Information. Deionized (DI) water was produced using an ultra-pure water purification system, with a resistivity of 18.2 MΩ cm⁻¹. All chemicals and materials were used without further purification.

2.2. In-situ fabrication of GO/MnOₓ composites

Pristine graphene oxide (GO) and MnOₓ were first synthesized as precursors (Hummers and Offeman, 1958; Zhang et al., 2018a). Detail of synthesis process was provided in the Supporting Information. As shown in Fig. 1a, in-situ GO/MnOₓ composites were fabricated as follows. Typically, during synthesis of GO, the graphite oxide/MnSO₄ suspension was exfoliated by ultrasonication for 15 min. 250 mL of KMnO₄ solution (0.05 M) was then directly dropped into this suspension with stirring at 85 °C for 1 h. Then, the brown mixture was aged at 60 °C for 6 h. GO/MnOₓ dispersion was then obtained by washing thoroughly with DI water. The final product, GO/MnOₓ powder, was obtained by a freeze-drying process.

2.3. Ex-situ preparation of GO/MnO₂ composites

In order to compare with in-situ GO/MnOₓ composites, ex-situ GO/MnO₂ composites were prepared as shown in Fig. 1b. Typically, GO powder was dispersed in 250 mL DI water by ultrasonication at 250 W for 5 min with a sonifier. A certain content of MnSO₄·H₂O solution was mixed with GO dispersion with stirring at 85 °C for 1 h. Then, 250 mL of KMnO₄ solution (0.05 M) was directly dropped into the suspension with stirring at 85 °C for another 1 h. The following procedures to obtain GO/MnO₂ composites were the same as the above methods. To ensure an accurate comparative study, the theoretical content of GO and manganese oxide in GO/MnOₓ and GO/MnO₂ composites was equal by controlling the dosage of GO powder, MnSO₄·H₂O, and KMnO₄.

2.4. Characterization

The morphology of samples was characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010, Japan), transmission electron microscope (TEM, JEM-1011, Japan; HRTEM, JEM-2100, Japan). Energy-dispersive X-ray spectroscopy (EDX, Hitachi SU8010, Japan) was utilized to investigate the composition of GO/MnOₓ and GO/MnO₂ composites. Surface area & porosity analyzer (ASAP, 2020 HD88, Micromeritics, U.S.A.) was used to analyze pore structure of samples. X-ray diffraction (XRD) spectra were measured to examine the structural properties of samples on a diffractometer (Rigaku D-Max 2200, Japan). Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a FT-IR spectrophotometer (JASCO, FT/IR-6300, Japan). To examine the elementary transformation of samples, X-ray photoelectron spectroscopy (XPS) analysis was carried out with an X-ray photoelectron spectrometer (Thermo ESCALAB 250XI, U.S.A.). Moreover, the zeta potential was determined by a zeta-potential analyzer (Zeta-PALS, Brookhaven, U.S.A.).

2.5. Batch experiment

Typical batch experiments were performed by dispersing samples (1.0 g/L) in solution of p-CR and p-TBP (50 mg/L) under
optimum condition (pH = 5, temperature = 25 °C). The samples (GO, MnO₂, GO/MnOₓ, GO/MnO₂) were selected to investigate the difference of removal efficiency for p-CR and p-TBP. In addition, to analyze the influence and optimize condition of pH for adsorption and oxidation pollutants, the initial solution pH (1–12) was adjusted by NaOH and HCl aqueous solution. Kinetic experiments at different temperatures (15 °C, 25 °C, and 35 °C) were also carried out to achieve optimum parameters with GO/MnOₓ and GO/MnO₂ composites for removal of p-CR and p-TBP. Ascorbic acid (0.01 M) was used to quench reaction under optimum condition.

2.6. Regeneration experiment

To investigate the reusability of GO/MnOₓ and GO/MnO₂ composites, NaOH aqueous solution (0.1 M) was used as an eluent. The regenerated composites were then washed with DI water, and collected by centrifugal separation for the next cycle. The regeneration experiment was conducted under optimum parameters for five cycles.

2.7. Analytical methods

After the removal process, the supernatants of the mixture were separated by centrifugation (8000 rpm). The concentration of p-CR and p-TBP was measured using a UV/vis spectrometer (TU-1810 PC, China) and calculated by absorbance at 277 nm and 275 nm. The supernatants were filtrated by 0.22 µm membrane to measure total organic carbon (TOC) with an analyzer (TOC-V CPN, Shimadzu, Japan). Then, the organic contaminants from supernatants were analyzed by high performance liquid chromatography tandem-mass spectrometry (HPLC/MS-MS) with an Agilent 6460 system. The HPLC column used was an Agilent Zorbax SB-C18 column with the dimensions 2.1 mm × 50 mm and 1.8 µm pore size. Details of the HPLC/MS-MS method parameters are provided in the Supporting Information. Furthermore, the concentration of Mn²⁺ from supernatants during synthesis of samples and removal of pollutants was determined by formaldehyde oxime spectrophotometry (Kalembkiewicz et al., 2008). Specifically, the brown complex, generated from Mn and formaldehyde oxime under an alkaline condition, was measured using a UV/vis spectrometer (TU-1810 PC, China) at 450 nm.

The percentage of removal efficiency (R) for p-CR and p-TBP was calculated by the following equation (1):

\[
R = \left( \frac{c_o - c_e}{c_o} \right) \times 100\% \tag{1}
\]

The percentage of TOC removal efficiency (R_TOC) for p-CR and p-TBP was calculated by the following equation (2):

\[
R_{TOC} = \left( \frac{c_o \_TOC - c_e \_TOC}{c_o \_TOC} \right) \times 100\% \tag{2}
\]

3. Results and discussion

3.1. Comparative strategy of fabricating graphene oxide/manganese oxide composites

As shown in Fig. 1a and b, compared with ex-situ fabrication of GO/MnO₂ composites (Fig. 1b), a sustainable strategy of synchronously utilizing manganese ions and highly acidic wastewater was proposed to synthesize GO/MnOₓ composites (Fig. 1a). During in-situ synthesis of GO/MnOₓ composites (Fig. 1a), pristine GO/MnSO₄ suspension was produced using graphite, KMnO₄, and H₂SO₄ as ingredients. Then, the Mn²⁺ was transformed into MnOₓ by adding additional KMnO₄ to obtain GO/MnOₓ composites. In addition, the mass flow analysis during synthesis of composites is shown in Fig. 1, indicating that in-situ synthesis exhibited better atom economy and less waste emission than ex-situ synthesis. Considering the
prospective production on a larger scale, GO/MnOX composites could be conveniently obtained via adding KMnO₄ into conventional synthesis process of GO. Especially, with increasing production demand of GO material, the in-situ synthesis provide a sustainable strategy for disposing acidic wastewater under the perspective of cleaner production. Specifically, the acidic wastewater containing abundant K⁺, SO₄²⁻, and H⁺ could achieve sustainable utilization by concentration with evaporation or dialysis methods. In addition, desalinization treatment could be adopted to retain ion strength. The in-situ GO/MnOX composites could be continually produced by adding graphite and KMnO₄, avoiding consuming a vast amount of H₂SO₄ and discharging a mass of highly acidic wastewater in prospective application.

3.2. Characterization

The morphologies and heterostructure of samples are characterized by FE-SEM, TEM, and HRTEM (Fig. 2, Figure S1). GO exhibits a typical laminar structure, and presents some folding and wrinkles (Figure S1a). As shown in Figure S1b, tightly packed MnO₂ sheets could be assigned to layered δ-MnO₂, which is in accordance with conventional preparation methods (Ren et al., 2011). It should be noted that the morphologies of manganese oxides in GO/MnOX (Fig. 2a and c) and GO/MnO₂ (Fig. 2b and d) composites are distinctly different. Compared with mesoporous composites (Abbas et al., 2018; Awual et al. 2015a, 2017) and GO/MnO₂, the HRTEM images of MnOₓ in GO/MnOX (Fig. 2e and f) show different crystal lattice in different regions. The isolated MnOₓ in GO/MnOX (Fig. 2e) presents ribbon-like structure with uniform crystal lattice. For MnOₓ stacked in GO/MnOX (Fig. 2f), anisotropic lattice fringes are observed, indicating the presence of mixed phase. In contrast, layered δ-MnO₂ is observed on the GO sheets for GO/MnO₂ composites (Fig. 2b and d). Moreover, EDX analysis of GO/MnOX and GO/MnO₂ composites (Figure S1c) reveals a nearly equivalent mass percentage of C, O, and Mn.

The N₂ adsorption-desorption isotherms, surface area, and pore distribution of samples are characterized as shown in Fig. 3. The N₂ isotherms of GO/MnOX (Fig. 3a) and GO/MnO₂ (Fig. 3b) composites exhibit type IV isotherm with an H3-type hysteresis loop according to IUPAC nomenclature, indicating presence of slit-shaped pores. GO/MnOX composites possess larger surface area (259.65 m²/g) and pore volume (0.44 cm³/g) than GO/MnO₂ composites (S BET = 92.08 m²/g, V p = 0.11 cm³/g). In addition, the sharp peak is observed in pore distribution of GO/MnOX composites due to uniform pore structure. Thus, the excellent pore structure and surface features provide GO/MnOX composites with better adsorption and removal performance than GO/MnO₂ composites.

To further illustrate crystal feature and structural differences of

![Fig. 2. FE-SEM images, TEM images, and HRTEM images of GO/MnOX (a, c, e, f) and GO/MnO₂ (b, d).](image-url)
the spectra of GO exhibit bands at 3422, 1718, 1621, and 1052 cm\(^{-1}\) corresponding to the stretching vibration of \(\text{O-H, C-O, C-C, and C-OH}\), respectively (Xu et al., 2015b; Zhang et al., 2018b). The vibrational bands at 1224 and 838 cm\(^{-1}\), which are attributed to the antisymmetric and symmetric stretching vibrations of C-O-C (Zhang et al., 2018a), disappear in the spectra of GO/MnOX composites. Meanwhile, a strong band at 1130 cm\(^{-1}\) for GO/MnO\(_2\) composites is assigned to the formation of covalent bonds (Mn-O-C) (Xu et al., 2015b). The bands at about 1400–1500 cm\(^{-1}\) are ascribed to the in-plane bending vibration of the C=O-H, which is attributed to the retention of C-O-H after combination of GO and manganese oxides. For GO/MnO\(_2\) composites, the strength of bands for oxygen-containing functional groups on GO sheets decreases with the combination of MnO\(_2\). Compared with GO/MnO\(_2\) composites, the weaker Mn-O-C bonds are also observed on GO/MnO\(_2\) composites. Moreover, the band of MnO\(_2\) at 544 cm\(^{-1}\) corresponding to the Mn-O bending vibration is red-shifted in the spectra of GO/MnOX composites (526 cm\(^{-1}\)) and GO/MnO\(_2\) composites (523 cm\(^{-1}\)). The change of Mn-O bending vibration was related to the structural composition of manganese oxides (Rathour and Bhattacharya, 2018; Yang et al., 2005). And \(\alpha\)-MnO\(_2\), \(\beta\)-MnO\(_2\), and Mn\(_3\)O\(_4\) possessed different Mn-O bending vibration in FT-IR spectra. In addition, the formation of covalent bonds (Mn-O-C) in GO/MnO\(_2\) and GO/MnOX composites would influence the Mn-O bending vibration.

To further investigate the chemical component and features of samples, XPS spectra are recorded in Figure S4 and Fig. 4. As shown in Figure S4, the wide scan XPS spectra of samples exhibit raw peaks of characteristic elements (C, O, and Mn). In the high-resolution XPS Mn 3s spectra (Fig. 4a) of MnO\(_2\), GO/MnO\(_2\), and GO/MnOX composites, the energy separation between the two split peaks reflects the mean manganese valence (Lei et al., 2012; Toupin et al., 2004). Compared with the energy separation value \(\Delta B.\)E. of MnO\(_2\) (\(\Delta B.\)E. = 4.70 eV) and GO-MnO\(_2\) (\(\Delta B.\)E. = 4.95 eV), the higher \(\Delta B.\)E. of GO/MnO\(_2\) (\(\Delta B.\)E. = 6.10 eV) implies a lower manganese valence (Mn(IV) \(\rightarrow\) Mn(III) \(\rightarrow\) Mn(II)), which is ascribed to the fact that more electrons exist in the 3d orbit. The Mn 2p spectra (Fig. 4b) of MnO\(_2\) and GO-MnO\(_2\) retain the same trend, confirming that Mn(IV) is dominant in both of them. In contrast, the chemical shift of Mn 2p\(_{3/2}\) on GO/MnOX composites indicates obvious transformation of chemical environment for Mn atom, which is in accordance with the result of Mn 3s spectra. Furthermore, the raw peaks of Mn 2p\(_{3/2}\) are deconvoluted into the fitting peaks at 643.00 eV (Mn(IV)) and 64.17 eV (Mn(II)), indicating coexistence of Mn(IV) and Mn(II) in GO/MnOX (\(X = 2, 3/4\) ) composites. The relevant dates are recorded in Table S2. As shown in Fig. 4c, the deconvolution of the O 1s peak of MnO\(_2\) resolves to two fitting peaks at 531.20 eV and 530.00 eV, which are attributed to the Mn-OH and Mn-O-Mn. It should be noted that the O 1s spectra of GO/MnO\(_2\) and GO/MnOX composites obviously change due to the involvement of GO sheets. According to the fitting peaks (Fig. 4c) and relevant date (Table S2) of samples, the Mn-O-C in GO/MnO\(_2\) becomes the dominant component (41.11%) with a sharp decline of Mn-O-Mn, indicating the mass generation of covalent bonds when in-situ bonding with GO sheets. However, a relatively small proportion of Mn-O-C (7.39%) exists in GO-MnO\(_2\) composites, suggesting that physical interaction may play a dominant role in the combination of GO and MnO\(_2\) for the ex-situ method. In addition, for GO/MnO\(_2\) and GO/MnOX composites, the content of C=C-C=C in C 1s spectra (Fig. 4d), representing the content of sp\(^2\)-hybridized domains, is higher than pristine GO. Meanwhile, the relative content of C=C, C-O, and O=C-O decreases after combination. The results indicate that partly oxygen-containing functional groups are broken and reduced after introducing Mn atoms.

Based on the above characterization, the formation mechanism and structural properties of GO/MnOX and GO/MnO\(_2\) composites...
are further clarified. During the *in-situ* synthesis process of GO/MnOX composites, the oxygen-containing functional groups (largely C-O-C and partly C=O) of GO sheets combine the Mn atoms by covalent Mn-O-C. Meanwhile, the mass of Mn$_3$O$_4$ crystals is anchored onto the GO sheets via heterogeneous nucleation. Under the strong acid condition with K$^+$ and SO$_4^{2-}$/C$_0^-$, partly α-MnO$_2$ nanowires generate and tightly grow on the GO sheets. Comparatively, during the *ex-situ* synthesis process of GO/MnO$_2$ composites, layered δ-MnO$_2$ is stacked on the GO sheets via weak covalent bonds and physical interaction. In comparison with GO-MnO$_2$ composites, the abundant Mn-O-C bonds (Toupin et al., 2004) in GO/MnOX could provide an efficient channel for electron transfer from GO to MnOX, thereby enhancing valence variation of Mn and the oxidation capacity for pollutants.

### 3.3. Adsorption and oxidation of p-CR and p-TBP

The adsorption and oxidation characteristics of GO/MnOX and GO/MnO$_2$ composites for the removal of p-CR and p-TBP are investigated by batch experiment. As shown in Fig. 5a, the removal efficiency and TOC removal efficiency of GO, MnO$_2$, GO/MnOX, and GO/MnO$_2$ composites for p-CR and p-TBP are determined. GO presents the lowest removal efficiency for both p-CR and p-TBP. Although residual sp$^2$-hybridized domains possess π–π interaction with pollutants, the electrostatic repulsion between abundant oxygen functional groups on GO sheets and phenolic hydroxyl groups of pollutants impedes further adsorption of pollutants. In addition, pollutants-adsorbed GO sheets are dispersion-stable and difficult to separate from aqueous solution due to their strong hydrophobicity with small size, leading to an unsatisfactory removal effect. Pristine MnO$_2$ also exhibits good oxidation removal efficiency for pollutants. However, it should be noted that the relatively low TOC removal efficiency of MnO$_2$ is probably due to the release of oxidation product (phenolic multimer and benzoquinones). After *in-situ* combining GO sheets and MnO$_2$, the GO/MnOX composites exhibit the best removal efficiency and TOC removal efficiency for both p-CR and p-TBP. However, the *ex-situ* GO/MnO$_2$ composites possess low removal capacity. The removal mechanism of GO/MnOX and GO/MnO$_2$ composites would be further elucidated with the following experiment investigation.

In addition, all samples present better removal efficiency and TOC removal efficiency for p-TBP than p-CR. This is because p-TBP, with low Cs and high KOW (Table S1), possesses strong hydrophobic interaction with samples, and thus easily achieves adsorption separation from aqueous solution. Moreover, due to the existence of tertiary butyl as a strong electron-donating group, p-TBP is more likely to be oxidized than p-CR by manganese oxide in samples.

The initial pH is a key factor of influencing adsorption and oxidation capacity of samples. As shown in Figure S5, the removal efficiency for pollutants and variation tendency of dissolved Mn with different initial pH are determined to test removal properties and chemical stability of samples. For both GO/MnOX and GO/MnO$_2$ composites, the removal efficiency of p-CR (Figure S5a) and p-TBP (Figure S5b) exhibits high values at pH < 6, and gradually decreases with increasing initial pH. Under the acid condition, manganese oxides in samples possess stronger oxidation potential than under...
the alkaline condition (Zhang et al., 2009), thereby achieving higher oxidation removal capacity for pollutants. Moreover, according to Figure S6, the absolute value of zeta potentials for all samples in the acid condition is lower compared with the alkaline condition due to the protonation effect. Thus, partly reduced GO sheets both in GO/MnOX and GO/MnO₂ composites could ensure the effective adsorption of p-CR and p-TBP in the acid condition due to the weakened electrostatic repulsion and strong π-π interaction. Thus, the changes of oxidation ability of samples and interaction (electrostatic and π-π interaction) with pollutants cause the trend in pH analysis. Compared with GO/MnO₂ composites, GO/MnOX composites still exhibit high removal efficiency in the alkaline condition. Considering the removal efficiency and practical wastewater, pH 5.0 was chosen as the optimum pH in experiments.

In addition, it should be noted that the content of dissolved Mn for GO/MnOX composites is obviously lower than GO/MnO₂ composites at pH < 5. The Mn(II) cations could be reserved and involved into the re-oxidation process in GO/MnOX (Duan et al., 2016), leading to stronger affinity for Mn(II) than GO/MnO₂. Especially for GO/MnO₂ composites, the strong acid condition during the synthetic process and Mn-O-C bonds ensure good structural stability at low pH. Thus, compared with GO/MnO₂ composites, GO/MnOX composites possess high removal efficiency and low content of dissolved Mn in a wider pH range for both p-CR and p-TBP.

The quenching experiment was carried out as shown in Fig. 5b and Figure S6b. The removal efficiency obviously declined with the increased ascorbic acid, indicating that oxidation process of p-CR and p-TBP by GO/MnOX composites was suppressed with interrupted electron transfer process. In addition, the removal efficiency of GO/MnO₂ composites (Figure S6b) presented similar trend with addition of ascorbic acid. It should be noted that GO/MnO₂ and GO/MnOX composites still possessing a certain amount of removal capacities, which is ascribed to the adsorption of p-CR and p-TBP onto GO sheets in composites.

To further optimize experimental parameters and examine the difference of removal process between p-CR and p-TBP by GO/MnOX and GO/MnO₂ composites, the effect of contact time and temperature is determined by batch experiment. As shown in Figure S7, for both GO/MnOX and GO/MnO₂ composites, the removal of p-CR reaches equilibrium (approximately 8 h for GO/MnOX and 18 h for GO/MnO₂) faster than p-TBP (approximately 24 h for GO/MnOX and 48 h for GO/MnO₂), respectively. Compared with GO/MnO₂ composites, GO/MnOX composites exhibit more rapid equilibrium and higher removal efficiency for both p-CR and p-TBP, ensuring more effective application. In addition, with temperature rising, the removal efficiency for both p-CR and p-TBP by samples gradually decreases, indicating the exothermic nature of the removal process. To achieve well removal efficiency for p-CR and p-TBP, the contact time and temperature were set as 48 h and 25 °C. In addition, Langmuir and Freundlich isotherms are analyzed with removal capacities of GO/MnOX and GO/MnO₂ composites. As shown in Fig. 5c, d, and Table S3, the results show that Langmuir isotherm possesses better fitting with higher value of R² than Freundlich isotherm, indicating that the adsorption of p-CR and p-TBP on composites tend to monolayer adsorption process. GO/MnOX composites exhibit higher maximum removal capacities for p-CR (107.68 mg/g) and p-TBP (135.41 mg/g) than GO/MnO₂ composites (98.64 mg/g for p-CR).
and 121.86 mg/g for p-TBP).

The regeneration capabilities of GO/MnOx and GO/MnO2 composites are further evaluated for practical application. As shown in Figure S8, the removal efficiency of samples for pollutants gradually decreases with increasing recycle number. The main reason for this is that the oxidation capacity of GO/MnOx and GO/MnO2 composites for pollutants gradually weakens due to the reduction of Mn(IV) after recycling. Meanwhile, the content of dissolved Mn gradually decreases. For both GO/MnOx and GO/MnO2 composites, the content of dissolved Mn for p-TBP is higher than p-CR due to stronger oxidation. It is also noteworthy that GO/MnOx composites could retain high removal efficiency for p-TBP (>90%) after five recycles, which is ascribed to strong adsorption and remaining oxidation capacity. In addition, GO/MnOx composites possess higher removal efficiency after recycling and better regeneration than GO/MnO2 composites, indicating the potential as a cost-effective material.

To further investigate the transformation of p-CR and p-TBP after adsorption and oxidation process for GO/MnOx and GO/MnO2 composites, the products are detected by HPLC/MS-MS. The mass spectra at different retention times for p-CR and p-TBP are recorded in Figure S9 (GO/MnOx) and Figure S10 (GO/MnO2). The mass fragments of transformation products for p-CR and p-TBP at different retention times are also listed in Table S4 (GO/MnOx) and Table S5 (GO/MnO2). Accordingly, the tentative pathways of p-CR and p-TBP, comparing GO/MnOx and GO/MnO2 composites, are shown in Fig. 6.

As shown in Fig. 6, Figure S9 and Table S4 (GO/MnOx), for p-CR,
the parent ion m/z 241 at retention time 3.361 min may be assigned to the dimers (P1) of oxidation products via dimerization (Lu and Gan, 2013). Correspondingly, the possible structure of daughter ions reveals that the methyl in p-CR may be oxidized to form carbonyl (D1), hydroxyl (D2), and carboxyl (D3) via the oxygen addition process (Li et al., 2015). At retention time 13.264 min, the trimers (P2) of oxidation products for p-CR may be achieved, which is in accordance with the analysis of its daughter ions (D4 and D5).

Regarding p-TBP, it should be noted that the parent ion m/z 197 at retention time 9.592 min may be ascribed to the ring cleavage products (P4) of p-TBP, indicating that further oxidation occurs compared with p-CR.

Comparatively, as shown in Fig. 6, Figure S10 and Table S5, the oxidation products of p-CR and p-TBP by GO/MnO2 composites are mainly assigned to the dimers (P15 for p-CR, and P35 for p-TBP), trimers (P45 for p-TBP), and tetramer (P25 for p-CR and P55 for p-TBP). The result indicates that GO/MnOX composites possess higher oxidation capacity than GO/MnO2 composites via more varied oxidative pathways, such as oxygen addition and ring-opening reactions.

3.4. Relationship between structure and adsorption-oxidation mechanism

Based on the above analysis of characterization, batch experiment, and transformation pathways, the relationship between different structure and adsorption-oxidation properties for the removal of pollutants by GO/MnOx and GO/MnO2 composites is further clarified.

Compared with ex-situ GO/MnO2 composites, in-situ GO/MnOx composites possess stronger removal properties with a synergistic effect between adsorption and oxidation due to their unique structure features.

Specifically, the adsorption of pollutants on partly reduced GO sheets promotes the removal process and oxidation capacity of GO/MnOx composites by enhancing mass transfer and electron transfer process. For GO/MnOx composites, the partly reduced GO sheets exhibit an enhanced π–π interaction with pollutants, thereby accelerating diffusion of pollutants into the boundary layer. Similarly, the oxidation products and Mn(II) can be effectively diffused away from MnOx and adsorbed onto GO sheets, promoting the oxidation process. Moreover, abundant π electrons on partly reduced GO sheets can be transferred into MnOx as an electron source through Mn–C bonds during interaction with pollutants and promote one electron-transfer reactions. In addition, during oxidation of pollutants by MnOx (X = 2, 3, mixture of π–MnO2 and Mn3O4), Mn(IV) species is reduced to Mn(II) with generating intermediate Mn(III). Especially, the oxygen functional groups on GO sheets can re-oxidize Mn(II) as the oxidants to form Mn(III), and then participate in the oxidation of pollutants.

The oxidation of pollutants by MnOx contributes to the positive shift of adsorption equilibrium and augments the adsorption capacity of GO sheets by strengthening the charge-transfer interaction for GO/MnOx composites. After adsorption on GO sheets in GO/MnOx composites, pollutants (p-CR and p-TBP) are transferred into the MnOx surface and oxidized, changing the adsorption equilibrium. Thus, more pollutants are adsorbed and oxidized. In addition, during the oxidation of pollutants through sequential one electron-transfer reactions, the charge density on GO sheets is changed and produces many regions of electron deficiency. This is conducive to strengthening charge-charge interaction with electron-rich pollutants, thus enhancing adsorption capacity. However, for GO/MnO2 composites, the weakened bonds between GO and MnO2 are difficult to promote interactions with pollutants and achieve this synergistic effect between adsorption and oxidation. Thus, GO/MnO2 composites possess lower removal efficiency and less oxidized products for pollutants than GO/MnOX composites.

Both GO/MnOx and GO/MnO2 composites exhibit higher removal efficiency for p-TBP than p-CR. Based on the above analysis of contrastive batch experiment, in comparison with p-CR, p-TBP exhibits stronger adsorption (hydrophobic interaction and π–π interaction) with samples. Tertiary butyl in p-TBP as a strong electron-donating group is also more likely to be oxidized by manganese oxides. Especially for GO/MnOx composites, the transformation products of p-TBP contain not only dimer and trimer of oxidation products, but also ring cleavage products. The further oxidation for p-TBP contributes to the mineralization of p-TBP.

3.5. Application expectation and environmental implications

Considering the application in actual phenolic pollution treatment, GO/MnOx composites could be employed as powdered treatment agent, which is similar to commercial powdered activated carbon. Based on the batch experiments, GO/MnOx composites exhibited well removal efficiency for wide concentration range of aromatic pollutants. Thus, in reactor units of sewage treatment plants, GO/MnOx powder could be applied in pretreatment unit to removal refractory aromatic pollutants. Also, during the advanced treatment after traditional biological treatment, GO/MnOx powder possessed excellent removal efficiency for low-level aromatic pollutants. Moreover, for urgently polluted water due to leakage of phenolic pollutants, it is convenient to utilize GO/MnOx powder and adjust the dosage along with the concentration of pollutants. In addition, mild reaction process in the system has the advantage of low requirements for devices and is easy to realize. In consideration of environmental implications, manganese oxides exhibited well feasibility as traditional oxidants in wastewater treatment. Although the introduction of GO-based materials into water environment remain research stage due to potential toxicological effects for organism, the effective separation and regeneration in batch experiments could promote progress in prospective application.

4. Conclusions

In summary, graphene oxide/manganese oxide (GO/MnOx, GO/MnO2) composites, synthesized via in-situ and ex-situ methods, possess different structural features and removal properties for p-CR and p-TBP. Compared with ex-situ GO/MnO2 composites, in-situ GO/MnOx composites possess higher removal efficiency and TOC removal efficiency, lower content of dissolved manganese ions, and wider pH range for p-CR and p-TBP. The partly reduced GO sheets and MnOx (X = 2, 3, 4), combined with Mn–O–C covalent bonds in GO/MnOx composites, produce a synergistic effect of adsorption and oxidation during the removal process. Meanwhile, GO/MnOx composites exhibit stronger oxidation capacity for pollutants than GO/MnO2 composites. Especially, cleavage of aromatic rings for p-TBP occurs during the further oxidation process by GO/MnOx composites, indicating the potential of mineralization for pollutants. Thus, by comparing structural features with different fabrication strategies and clarifying removal mechanisms, the work is anticipated to promote practical application of graphene oxide/manganese oxide composites in removing phenolic compounds.

Declarations of interest

None.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.01.055.

References

Xu, H., Qu, Z., Zhao, S., Mei, J., Quan, F., Yan, N., 2015a. Different crystal-forms of one-dimensional MnO2 nanomaterials for the catalytic oxidation and adsorption of elemental mercury. J. Hazard Mater. 299, 86–93.