pH-Dependent Structure–Activity Relationship of Polyaniline-Intercalated FeOCl for Heterogeneous Fenton Reactions

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ABSTRACT: In this study, we prepared polyaniline-intercalated iron oxychloride (FeOCl-PANI) by aqueous intercalation method to use it as a Fenton-like catalyst that was then assessed in terms of behavior of intercalation, structural evolution, Fenton-like activity, and catalytic mechanism. Gel-permeation chromatography demonstrated that the molecular weight (polymerization extent) of polyaniline fragment gradually increased with the increase of intercalation time. Interestingly, the polyaniline-intercalated materials with varying intercalation times exhibited distinctly different Fenton-like activity trends under acidic (pH 4) and neutral (pH 7) conditions. Specifically, Fenton-like degradation is favored with a shorter intercalation time under acidic conditions, while it is preferred with a longer intercalation time under neutral pH values. We propose that an additional pH-dependent charging of FeOCl-PANI with different polymerization extents of the intercalated polyaniline promotes a switch in the contaminant degradation pathway, leading to opposite trends in observable activity at different pH values. As a class of typical layered metal chalcogenohalides (MeAX, A = O, S, Se, X = Cl, Br, I), FeOCl-PANI is expected to provide new insights into the development of other similar materials. This work could be useful to further understand the H$_2$O$_2$ heterogeneous activation behavior, which is of significance to the application of iron-based heterogeneous Fenton oxidation.

1. INTRODUCTION

The generation of reactive oxygen species (ROS) by reacting ferrous iron (Fe$^{2+}$) and hydrogen peroxide (H$_2$O$_2$), namely Fenton’s reaction, has been widely employed as an effective route of degrading organic pollutants in water treatment and soil remediation.1 Heterogeneous Fenton systems that activate H$_2$O$_2$ on the surface of iron-based solid catalysts have recently attracted extensive attention owing to their high efficiency and low cost.$^{2−6}$ Similar to the classical Fenton (Haber–Weiss) mechanism, H$_2$O$_2$ activation on solid iron-based catalysts is achieved via the catalytic Fe(II)/Fe(III) cycle$^7$ and the heterogeneous nature of such surface reactions can potentially enable Fenton chemistry near neutral conditions. In the catalytic cycle, Fe(III) reduction on air-stable heterogeneous Fenton catalysts is considered the rate-determining step, and the thermodynamically unfavorable Fe(III) reduction under near-neutral pH conditions causes a significantly reduced ROS generation rate.$^8$ In such a context, developing novel iron-based materials with a controlled electronic structure and facile active site generation is highly desired for promoting heterogeneous Fenton activity under environmentally relevant and more practical near-neutral pH conditions.

Among all iron-based heterogeneous Fenton catalysts, iron oxychloride (FeOCl) is one of the most promising candidates, exhibiting 2–4 orders of magnitude higher hydroxyl radical generation rates than traditional iron-based materials.$^{9−11}$ Fabricated FeOCl-based nanocatalysts were recently demonstrated to be efficient for photo-Fenton,$^{12−14}$ water splitting,$^{15}$

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heavy metal adsorption,16−18 or the catalytic hydroxylation of benzene.19 In addition, an interesting and unique property of FeOCl is its layered crystal structure, in which the FeOCl sheets are stacked via weak van der Waals interactions allowing for the intercalation of various guest molecules, such as amines and organometallic cations.10−22 For example, the intercalation of amines induces a charge transfer between the lone electron pair on the nitrogen atom and the conduction band in FeOCl, causing the in situ reduction of Fe(III) in the FeOCl matrix and the oxidative polymerization of amines.23−25 The tunable charge transfer between the intercalated guests and the FeOCl matrix offers the exciting opportunity to alter the surface electronic states of FeOCl catalysts as well as to improve heterogeneous Fenton activity for sustainable applications.25,24,26 In the meantime, the intercalation will transfer the bulk crystal of FeOCl into two-dimensional nanolayered materials, increase the specific surface area, and create new catalytic environment to facilitate the reaction.

In this work, polyaniline-intercalated FeOCl (FeOCl-PANI) was prepared by in situ polymerization of aniline in the interlayer region and used as a Fenton-like catalyst to degrade bisphenol A (BPA) and other organic pollutants under acidic and neutral pH. Intercalation of polyaniline significantly enhanced the Fenton-like activity at both acidic and neutral pH conditions, compared to the FeOCl parent material. FeOCl−PANI with varying intercalation times exhibited distinct Fenton-like activity trends in a pH-dependent manner. It is postulated that the effect of in situ aniline polymerization on the structural and chemical properties of the FeOCl leads to the differences in Fenton-like activity between acidic and neutral pH values. These results of this study will further provide insights into designing more efficient catalysts for promoting the potential applications of iron-based solid materials in Fenton oxidation.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of FeOCl and FeOCl−PANI. Herein, we report the synthesis of polyaniline-intercalated FeOCl (FeOCl−PANI) by in situ polymerization of aniline in the interlayer region and the application of FeOCl−PANI for organic pollutant degradation in near-neutral pH conditions. The FeOCl was prepared using the chemical vapor transport method, which can be upscaled much more readily.27 During intercalation with aniline, the solids gradually turned into dark brown and black microcrystals within 4 h. Ex situ X-ray diffraction (XRD) analysis (Figure 1a) was performed to investigate the structural evolution during the intercalation process. Pristine FeOCl showed reflections at 2θ values consistent with the standard XRD pattern of pure FeOCl (JCPDS no. 73−2229), while intercalated FeOCl showed peaks shifted toward smaller angles, indicating successful intercalation. Calculated unit cell parameters (Table S3) demonstrate that intercalation of aniline into FeOCl resulted in a lattice expansion of 5.69 Å (from 7.92 to 13.61 Å), consistent with reported values.21,22,28 The heterogeneous Fenton application of FeOCl was limited by its small surface area (<10 m²/g). However, the pristine van der Waals (vdW) layer (7.92 Å) was almost fully occupied by the Cl atoms (with vdW radius of 1.75 Å), and the free transportation space (~4.42 Å) is limited for most apolar molecules. After intercalation, the distance between Cl···Cl vdW layer and the free space could increase simultaneously. More interestingly, the samples obtained after different durations of intercalation exhibited almost identical XRD peak positions, but, gradually, broadened peaks with increasing intercalation times were obtained (Table S4). These results imply that the change of the crystalline structure of FeOCl matrix is completed within 4 h, whereas, the structural evolution within the layers continues to take place over the course of our experiments (12 days). Because we consistently observed FeOCl plate-like structures in all samples with scanning electron microscopy (SEM) (Figures 1b,c and S1), we propose that the structural evolution takes place within the particles and sheets rather than at the macroscopic scale.

The chemical nature of the polyaniline-intercalated FeOCl was further investigated using a range of complementary spectroscopic techniques. In the Fourier-transform infrared (FTIR) spectrum, pristine FeOCl had two major peaks at 490 and 1630 cm⁻¹ (Figure 2a), which are attributed to Fe−O and Fe−Cl vibrations, respectively.29 The presence of characteristic PANI peaks at 650−1600 cm⁻¹ (cyan-colored region in Figure 2a) further corroborates the intercalation and in situ polymerization of aniline within the FeOCl layers, in which the vibration peaks at 1490, 745, and 687 cm⁻¹ are assigned to the protonated aniline monomer (AnH⁺).24 The polymerization of aniline was induced by the electron transfer from FeOCl matrix to aniline in the intercalation process, as evidenced by the larger molecular weight of PANI after longer intercalation times (Table S5). Surprisingly, the peak indicative of Fe−Cl vibrations (1630 cm⁻¹) diminished and almost disappeared during the intercalation process, indicating the weakening or breaking of Fe−Cl bonds in FeOCl upon intercalation. This observation is further supported by the attenuated and positively shifted Fe−Cl bond distances at ~2.3−2.4 Å in the extended X-ray absorption fine spectra (EXAFS, Figure 2b). The presence of observable Fe−Cl bond distances after a relatively short intercalation time (4 h and 3 days) suggests that the Fe−Cl bond breaking process is a kinetically slow process, which may be attributed to the interaction between the spatially confined aniline in the interlayer region and Fe(III) centers of the Fe−Cl entities. The loss of Cl from Fe centers could potentially create an open coordination site for catalysis, which will be discussed later. The XPS study was carried out to explore the change of the element’s chemical environment during the intercalation process. The survey XPS spectra (Figure S2) show that Fe, O, and Cl signals are present in pristine FeOCl and FeOCl−PANI samples, while the N signal only exists in the FeOCl−PANI sample. The Cl 2p binding energy of PANI-intercalated FeOCl is increased by ~0.4 eV (Figure 2c), which may be due
to the increase of Cl valence caused by the cleavage of Fe−Cl bond. The high-resolution curve-fitted Fe 2p3/2 spectra show that an additional shoulder peak at a lower binding energy appears after intercalation, corresponding to a reduced Fe(II) species (Figure 2d). We further discovered that the Fe(II)/Fe(III) ratio gradually increased with increasing intercalation times (Table S6), which could be contributed by Fe(III) reduction under oxidative aniline polymerization. This result is consistent with the increase of molecular weight of PANI confirmed by gel-permeation chromatography (GPC). According to the aforementioned data, we proposed that the aniline intercalation into FeOCl is a fast process, while the in situ oxidative aniline polymerization is slow and may take several days to complete.

More information about charge transfer that was suggested to occur during the intercalation process could be revealed by Mössbauer spectroscopy, which shows that Fe in both FeOCl and FeOCl-PANI is mostly present as the oxidized Fe(III) species, with no detectable Fe(II) in the spectra of pristine FeOCl (Figure 3, Table S7). The Fe(II) content detected with Mössbauer spectroscopy is highly similar in all FeOCl-PANI samples and ranges between 9.2 and 11.9% of the total Fe with no clear trend with the intercalation time (Table S7). The presence of Fe(II)-like species was identified by the emergence of an additional Fe(III) component in the Mössbauer spectra of FeOCl-PANI, with parameters consistent with those of akageneite.24,30 Interestingly, in Mössbauer spectra acquired at 50 K, we observed broadening of one of the Fe(III) doublets with increasing intercalation time and, after 7 and 12 days of intercalation, even partial magnetic ordering of one or more of the Fe(III) components. The observed trends are indicative of increasing long-range (magnetic) ordering of differently coordinated Fe species within the FeOCl sheets. We suspect that this observation can be rationalized by the increased PANI polymer size within the FeOCl interlayers, which could increase the connectivity of Fe(III) centers that have been separated by the formation of presumably randomly distributed Fe(II) species during the polymerization process and/or by redistribution of Fe(II) and Fe(III) in the FeOCl sheets over time via bulk electron conduction. The emerging interlayer structure is a unique property of FeOCl with this intercalation modification strategy. The structural evolution is demonstrated as Scheme 1.

### 2.2. Catalytic Activity

We first distinguished the effect of aniline from the aspects of physical mixing versus chemical
intercalation aniline on the catalytic activity of FeOCl in control reactors. In one control group, namely “aniline-dropping”, a certain amount of aniline was directly added to reactors containing pristine FeOCl, whose amount added was calculated based on the nitrogen element content of FeOCl-PANI sample (after 12 days of intercalation) obtained by elemental analysis. Thus, aniline did not affect BPA degradation by regulating the structure of FeOCl in this control group. In the other control group (“aniline-mixing”), again, the same amount of aniline was dropped onto pristine FeOCl and left for 5 min prior to starting the transformation experiment to mimic the initial intercalation process. As shown in Figure S3, the aniline-dropping control showed comparable activity to that of pristine FeOCl, implying that the addition of aniline alone cannot facilitate Fe dissolution or enhance Fe(III)/Fe(II) redox cycling on the surface of FeOCl to increase Fenton activity. In contrast, the aniline-mixing control group exhibited significantly higher reactivity, demonstrating that aniline affects the intrinsic activity of FeOCl by intercalation and/or structural alterations.

Subsequently, we analyzed the Fenton activity of our FeOCl-PANI materials in reactions buffered at pH 4. FeOCl-PANI subjected to 4 h of intercalation showed a much higher BPA degradation after 60 min compared to pristine FeOCl, and the observed reactivity gradually decreased for FeOCl-PANI with longer intercalation times. More interestingly, when the pH value of the buffer solution was changed to ~7, the FeOCl-PANI catalysts displayed the

Scheme 1. Structural Evolution During the Aniline Intercalation and in Situ Polymerization within FeOCl

Figure 4. Degradation and adsorption of BPA. Temporal profiles of BPA degradation at pH 4 (a) and pH 7 (b). Total removal and adsorption of BPA at pH 4 (c) and pH 7 (d). Experimental conditions: catalyst loading = 200 ppm, [H$_2$O$_2$] = 15 mM, [BPA] = 10 ppm, and reaction time: 1 h for acidic condition and 24 h for neutral condition.
reverse trend: the observed reactivity increased with increasing intercalation time. The FeOCl-PANI sample with 12 days intercalation time could reach an unprecedented $\sim 53\%$ BPA degradation in neutral circumstances, which is much higher than that of the pristine FeOCl ($\sim 20\%$), demonstrating the high potential of heterogeneous Fenton reactivity on intercalated FeOCl systems (Figure 4a,b). The time evolution of BPA degradation followed pseudo-first-order kinetics (Figure S4), whose calculated reaction rates are listed in Table 1. Compared with the pristine FeOCl, the reaction rate of PANI-intercalated FeOCl increased by $\sim 12$ times (4 h intercalated sample) and $\sim 3$ times (12 days intercalated sample) at pH 4 and pH 7, respectively. The distinct reactivity trends observed at the two pH values suggest a crucial role of the FeOCl-PANI structure for the resulting Fenton reactivity. We suspect that the strong pH-dependence might be connected to changes in the structure of the polyaniline-intercalated FeOCl, which could strongly affect the adsorption behavior of BPA. To verify our hypothesis, we evaluated the adsorption capacities of FeOCl-PANI for BPA at different pH values in adsorption experiments without H$_2$O$_2$. The adsorption of BPA showed a similar trend of BPA degradation (Figure 4c,d), suggesting that the adsorption of BPA was a crucial step for its degradation in the subsequent heterogeneous Fenton reaction.

Table 1. Pseudo-First Reaction Rates for the Degradation of BPA Over Pristine and PANI-Intercalated FeOCl Systems

| pH  | reaction rate     | pristine  | 4 h   | 3 days | 7 days | 12 days |
|-----|------------------|-----------|-------|--------|--------|---------|
|     | $k_{app^1}$/h$^{-1}$ | 0.11 ± 0.01 | 1.31 ± 0.07 | 0.89 ± 0.06 | 0.31 ± 0.02 | 0.19 ± 0.02 |
|     | $k_{app}$/k$_{pristine}$ | 11.90 | 8.08 | 2.81 | 1.73 |
| pH = 7 | $k_{app}$/100 h$^{-1}$ | 1.04 ± 0.06 | 0.76 ± 0.05 | 1.18 ± 0.09 | 2.18 ± 0.18 | 3.31 ± 0.14 |
|     | k$_{app}$/k$_{pristine}$ | 0.73 | 1.13 | 2.08 | 3.17 |

To exclude the possibility of specific BPA adsorption in our FeOCl-PANI system, three other organics, nitrobenzene (NB), 2-chlorophenol (2-CP: orange), and 2-methoxyphenol (2-MeOP: blue) were chosen as model pollutants to further investigate the reactivity of this system. Due to the difference in the influence of the substituent on the π electron density of benzene ring, the reactivity of these compounds when oxidized by Fenton mechanism is as follows: 2-MeOP > 2-CP > NB. These compounds can represent different types of wastewater, and their basic physical and chemical properties are listed in Table S8. Similar pH-dependent adsorption and degradation were also found for these pollutants (Figure 5a,b), indicating that the catalytic activity of FeOCl-PANI with different intercalation times on pollutants is nonspecific. Although the adsorption and degradation behaviors of the three pollutants have the same trend as the change of intercalation time, there are significant differences among them. Under any reaction condition, 2-MeOP showed the highest degradation rate among the three pollutants, while NB was always the lowest. The difference in the degradation ability between 2-MeOP and NB is due to differences in their intrinsic reactivity because the methoxyl and phenolic hydroxyl groups are electron-donating groups that contribute to the activation of the benzene ring. In contrast, electron-withdrawing nitro group has an inhibitory effect on the activation of the benzene ring.

Figure 5. Degradation and adsorption of other pollutants. Total removal and adsorption of nitrobenzene (NB: red), 2-chlorophenol (2-CP: orange), and 2-methoxyphenol (2-MeOP: blue) at pH 4 (a) and pH 7 (b). The experimental conditions are the same as that of BPA degradation.

Figure 6. (a) Five cycles of degradation of BPA at pH 4 and pH 7, in which the best activity catalysts under the two pH values (FeOCl-PANI 4 h at pH 4 and FeOCl-PANI 12 days at pH 7) were selected to test, respectively; FTIR spectra (b) and SEM image (c) of reused pristine and intercalated FeOCl after reaction at pH 7.
ability of 2-CP at different pH values is quite different. At acidic condition, it can degrade as easily as 2-MeOP. But its degradation ability is close to that of NB under neutral condition, showing a strong reaction inertness. This characteristic degradation ability of 2-CP may be related to its adsorption behavior in the interlayers between FeOCl-PANI, in which it can generate H-bonds with PANI. The pH may change the stability of H-bonding network in the interlayers, which has a great influence on the degradation activity of 2-CP. We will elaborate in the reaction mechanism section.

2.3. Structural Stability of Catalyst. Detailed characterization results have confirmed that aniline is polymerized to form PANI in the intercalated preparation of FeOCl-PANI, in which PANI is stabilized between the FeOCl interlayers by Cl−N bonding interaction. However, considering aniline is an organic chemical that is harmful to the environment and human health, it is necessary to clarify the structural stability of FeOCl-PANI under the reaction conditions. As for all sample solutions, aniline peak was not found in the high-performance liquid chromatography (HPLC) diagrams, indicating that the PANI in the FeOCl interlayers did not depolymerize and release into the solution during the reaction. The stability and reusability were further evaluated. As shown in Figure 6a, no significant differences are found for BPA degradation activity after at least five cycles. The characteristic PANI peaks and FeOCl skeleton vibration peaks of used catalyst showed no obvious change in the FTIR spectra (Figure 6b), which further suggests that no (poly)aniline release results from the deintercalation process under the reaction conditions. The high structural stability was also evidenced by similar morphology under SEM observation (Figures 6c and S5). In addition, we tested the leaching of Fe during the reaction. Our measured aqueous Fe concentrations in all samples after the reaction were less than 7.4 ppm at pH 4 (7.1% dissolution of FeOCl) and less than 0.22 ppm at pH 7 (0.21% dissolution of FeOCl) (Table S9), which was also the proof of high stability. In both conditions, activity contribution from homogeneous Fenton is negligible and could not explain the observed pH-dependent reactivity trends. All these results point to the conclusion that FeOCl-PANI is a class of heterogeneous Fenton catalysts with high structural stability.

2.4. ROS and Active Sites Investigation. Since the catalytic activity of the heterogeneous Fenton reaction stems from the generation of ROS by activating H2O2 on the catalyst surface, we further investigated the difference in ROS generation between pristine FeOCl and FeOCl-PANI using electronic paramagnetic resonance (EPR) spectroscopy. DMPO (5,5-dimethyl-1-pyrroline N-oxide) was utilized to capture free radicals and the signature peaks of the DMPO·OH adduct with an intensity ratio of 1:2:2:1 were observed at both pH 4 and pH 7 (Figure 7a,b, respectively), suggesting the existence of hydroxyl radicals (·OH) at both pH values.32 In addition, other small peaks were observed at pH 7, and the similar peaks were also found at pH 4 when we amplified the EPR signal within a narrow intensity range (Figure S6), which may be due to the presence of impurities in the DMPO or their oxidation to other paramagnetic species.33,34 Moreover, after the PANI intercalation, the FeOCl showed a slightly enhanced adduct signal, which was not sufficient to explain the significant increase in pollutant degradation activity. We could not observe much difference between the FeOCl-PANI samples intercalated for different durations, suggesting that ROS generation might not be the critical parameter that is affected by the structural evolution in the interlayer spaces and responsible for the distinct catalytic activity trends observed.

Figure 7. EPR spectra of the DMPO·OH adduct formed in the presence of pristine and intercalated FeOCl at different pH values: (a) pH 4 and (b) pH 7.

Figure 8. Effect of phosphate on the BPA degradation at pH 4 (a) and pH 7 (b), in which the best activity catalysts under the two pH values (FeOCl-PANI 4 h at pH 4 and FeOCl-PANI 12 days at pH 7) were selected to test, respectively.
which has stronger affinity to the surface coordinatively unsaturated metal sites than H$_2$O$_2$ or water, was used to regulate the amount of surface active sites of FeOCI-PANI.\textsuperscript{35} As shown in Figure 8, the degradation of BPA was almost unaffected at pH 4 by the addition of 10 mM phosphate but was significantly inhibited at pH 7, indicating that the degradation process is controlled by intrinsic reactions on the catalyst surface at pH 7, while the process is switched to diffusion-controlled reaction at pH 4.

2.5. Effect of Interlayer Structure on Heterogeneous Fenton Activity of FeOCI-PANI.\textsuperscript{36,37} EPR studies have shown that the generation of ROS is not a decisive factor in the difference in FeOCI-PANI heterogeneous Fenton activity. Therefore, we believe that the interlayer structure evolution of FeOCI caused by aniline intercalation is the key in the enhancement of its activity. According to our observation that the intercalation is kinetically fast and polymerization is relatively slow, FeOCI-PANI with shorter intercalation time should mostly consist of AnH$^+$ and short PANI fragments in the interlayer region, which is confirmed by gel-permeation chromatography (GPC) (Table S5). Under pH 4 conditions when turnovers for the Fenton reaction are favored, the accessibility of organic pollutant molecules to the catalytic sites may be critical to its degradation, that is, the diffusion of pollutants to the active sites in the interlayer region is the rate-determining step. So, FeOCI intercalated for short durations has a comparatively dilute and exchangeable environment in the interlayer that can possibly facilitate the diffusion organic pollutant molecules into the vicinity of the catalytic sites, which is also evidenced by the higher adsorption capacity of these samples. Moreover, the poorly polymerized aniline has the extensive H-bonding network and can share H-bond with phenolic pollutants, where the phenolic hydroxyl radical may serve as the proton donor.\textsuperscript{38} The formation of H-bond enhances the electronegativity of the aromatic ring of phenolic pollutants, which is more conducive to the attack of HO$^·$.\textsuperscript{39}

At pH 7, in contrast, the Fenton reaction is less favored for turnovers and thus the H$_2$O$_2$ activation is expected to become the rate-determining step. The increase in pH enhances the deprotonation tendency of AnH$^+$ and PANI fragments and limits the formation of H-bonds, which adversely affects the diffusion and adsorption of pollutants into the interlayers. Thus, the neutral reaction behavior may be attributed to the reduction of Fe(III) and the weakening of Fe−Cl bonds, which create unique reaction spaces that strengthen the adsorption and degradation of pollutants. Phosphate experiments revealed that the coordinatively unsaturated Fe(II) sites induced by PANI intercalation are the Fenton active sites, in which the coordinatively unsaturated Fe(II) sites induced by aniline polymerization on the structural and chemical properties of the FeOCI matrix was further investigated. Synthesizing FeOCI-PANI with shorter intercalation time has a more detrimental effect on pollutant adsorption because of more AnH$^+$ in the interlayer region.

3. CONCLUSIONS

The structural evolution of the FeOCI catalyst upon aniline intercalation and in situ polymerization provides a versatile way of altering its heterogeneous Fenton reactivity for pollutant degradation. The intercalated structure not only showed an expansion of interlayer lattice but also exhibited surface changes in the chemical environment of the Fe/Cl species. The enhanced activity was tentatively attributed to the H-bonding network provided by the intercalated aniline and the generation of structural Fe(II) sites and akagene-like phase induced by aniline polymerization (Scheme 2). We used a facile way of intercalating FeOCI catalysts, which not only provides a new route of improving heterogeneous Fenton reaction but also enables high pollutant degradation rates at environmentally relevant circum-neutral pH values, opening up a broad range of potential future applications. Intercalation of polyaniline significantly enhanced the catalytic activity and organic pollutants degradation at neutral pH conditions, compared to the FeOCI parent material. The effect of in situ aniline polymerization on the structural and chemical properties of the FeOCI matrix was further investigated. Synthesizing our results, we propose a possible mechanism for ROS production on the surface of FeOCI-PANI, which may further provide insights into designing more efficient catalysts. The development of such highly active FeOCI-PANI catalysts may not only shine light on heterogeneous Fenton chemistry but also open up a new avenue of exploring layered materials in environmental applications using intercalation chemistry.

Scheme 2. Schematic Diagram of Reaction Mechanism for Pollutant Removal at Different pH Values

![Scheme 2](image-url)
4. MATERIALS AND METHODS

4.1. Material Synthesis and Characterization. FeOCl was synthesized using the chemical vapor transport method. Fe₂O₃ and anhydrous FeCl₃ powders with a molar ratio of 1:1.3 were first mixed in a glove box under N₂ atmosphere. The mixed powder was sealed in a glass container, which was then heated to 653 K at a ramping rate of 1 K/min and maintained at 653 K for 40 h in a muffe furnace. Once cooled to room temperature, the obtained purple product was rinsed with anhydrous acetone to remove excess FeCl₃ and dried overnight at 60 °C in a vacuum oven. FeOCl-PANI was prepared using the modified method reported by Wu et al. In a typical procedure, 60 mL of 5% aniline solution in acetonitrile was stirred with 0.50  g FeOCl in air at 25 °C. The intercalated products were washed and dried following the same procedures as the nonintercalated FeOCl.

Pristine FeOCl and its products intercalated for different time intervals were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure spectroscopy (EXAFS), and Mössbauer spectroscopy. The polymerization degree of PANI was determined by gel-permeation chromatography (GPC), and ROS generation was investigated by electronic paramagnetic resonance (EPR) spectroscopy. The detailed information about the characterization can be found in the Supporting Information (SI).

4.2. Catalytic Activity Measurements. The catalytic activities of unintercalated and intercalated FeOCl were evaluated by the degradation of bisphenol A (BPA), nitrobenzene (NB), 2-chlorophenol (2-CP), and 2-methoxyphenol (2-MeOP) under both acidic and neutral pH. All experiments were performed in 100 mL reactors (50 mL reaction solution containing 0.2 g/L catalyst and 15 mM H₂O₂) with constant stirring at 600 rpm at 25 °C. Acetate (20 mM) and 20 mM piperazine-N,N'-bis(ethanesulfonic acid) (PIPES) aqueous buffer solutions were used for reactions at pH 4.0 ± 0.2 and 7.0 ± 0.2, respectively, which was demonstrated to be the most suitable buffer matrix before. The suspension was stirred for 30 min to reach the adsorption equilibrium and the reaction was initiated by adding a desired dosage of H₂O₂. Finally, 0.5 mL of methanol was added into the reaction solution to quench the reaction, and the samples were filtered immediately through a 0.22 μm PTFE filter film for analysis.

The concentration of BPA and other probe pollutants was determined by high-performance liquid chromatography (HPLC, Waters 2795). The leaching concentrations of Fe were determined using inductively coupled plasma optical-emission spectroscopy (ICP-MS, Agilent 725ES). More details about the analyses can be found in the SI. At least three replicates for each experiment were carried out, and the average values with standard deviations are presented for each set of data.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03008.

Characterization, activity measurement, figures of XPS in full-spectrum scan, SEM of spent catalysts, tables of XRD, XPS, Mössbauer, and GPC results (PDF)

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Notes
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