

EFFECT OF Fe^{2+} ON CATALYTIC OXIDATION IN A FLUIDIZED BED REACTOR

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ABSTRACT

The aim of this study was to investigate the effect of Fe^{2+} on the catalytic oxidation in the fluidized-bed reactor (FBR) applying supported $\gamma\text{-FeOOH}$ as the carrier. Processes without Fe^{2+} addition and with Fe^{2+} addition (FBR-Fenton method) were performed on the oxidation of benzoic acid (BA) by H_2O_2 . When Fe^{2+} was not added in the FBR, the high COD removal at low pH was caused by homogeneous catalysis of Fe^{2+} formed via reductive dissolution of $\gamma\text{-FeOOH}$. In the FBR-Fenton process, both mineralization of organics and crystallization of Fe(III) were simultaneously well performed under adequate condition. The reaction mechanism, including the reductive dissolution and crystallization of $\gamma\text{-FeOOH}$ as well as the oxidation of BA, was proposed based on the experimental results. ©1999 Elsevier Science Ltd. All rights reserved

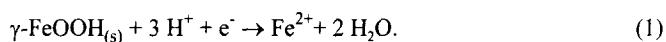
Key words: catalyst, crystallization, fluidized-bed, hydrogen peroxide, iron oxide, oxidation

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1 INTRODUCTION

Hydroxyl radical (OH•) is very reactive, underlying the chemistry of advanced oxidation processes (AOPs) for degrading organic compounds in water. Among various AOPs, Fenton's (H₂O₂/Fe²⁺) reaction has been known to successfully treat aromatic compounds (1-3). The drawback of Fenton's reaction is the production of substantial amount of Fe(OH)₃ precipitate. To solve this problem, the application of iron oxides as catalysts in oxidizing organic contaminants has been studied extensively (4-7). Goethite, hematite, semicrystalline, and ferrihydrite have been used as catalysts to treat organic contaminants (4-6). In our previous work, we developed a novel supported iron oxyhydroxide (γ-FeOOH) granular catalyst and proved that it can be an effective catalyst of H₂O₂ in oxidizing benzoic acid (BA) and 2,4,6-trichlorophenol in a batch reactor (7). It was found that at pH 3.2, dissolved Fe increased with time in oxidizing BA. The formation of dissolved Fe was via the reductive dissolution (7-9) of γ-FeOOH as below:



However, the exact effect of Fe²⁺ on the catalytic oxidation is not clear due to the dynamic behavior of Fe²⁺ in the batch reactor.

In this study, we attempted to investigate the effect of Fe²⁺ on the catalytic oxidation at steady state using a continuous circulating fluidized-bed reactor (FBR). Benzoic acid was selected as the target compound because of its no-volatility. It was treated by H₂O₂ with and without Fe²⁺ addition. The process with Fe²⁺ addition is named FBR-Fenton method, in which Fe²⁺ is the homogeneous catalyst and γ-FeOOH is the heterogeneous catalyst of H₂O₂ to oxidize organic contaminants. The removal efficiencies of BA and COD (or TOC) were adopted as indices of oxidation and mineralization. The supported γ-FeOOH acts as both the catalyst of H₂O₂ and the carrier of FBR. The Fe (III) hydrolysis product of Fenton's reaction can crystallize and grow on the surface of this carrier to reduce the precipitation of Fe(OH)₃. The full-scale application of the pellet reactor, a crystallizer of the FBR, in the removal of hardness, heavy metals, fluoride, and phosphate has been demonstrated by the DHV company (10). However, little has been studied on the removal of iron with the crystallizer of the FBR (11). In this study, therefore, the effectiveness of crystallization in the FBR-Fenton system was investigated by determining the removal of Fe (III). The performances in mineralization and crystallization were compared between this FBR-Fenton method and conventional Fenton's reaction.

2 EXPERIMENTAL

2.1 Preparation of supported γ-FeOOH

The supported γ-FeOOH was developed in the following manner (12). The brick grains were packed in a 6.1

liter FBR (6.8 cm- ϕ \times 170 cm-H) as carriers. H₂O₂ (Union Chemical) and FeSO₄ (Merck) in molar ratio of 1:2 were fed continuously into the bottom of reactor. The crystal was allowed to grow on the surface of brick grains for one week before starting to operate. The pH of solution in the reactor was maintained at 3.5 to prevent Fe(OH)₃ precipitation. The major component coated on the surface of brick grains was identified as γ -FeOOH with a Mössbauer spectrometer (Austin S-600). The properties of this iron oxide are listed in Table 1.

2.2 Catalytic oxidation of BA by FBR system without Fe²⁺ addition

The experiment was conducted at room temperature (24 \pm 4°C). The schematic apparatus is shown as Figure 1. A FBR (3 cm- ϕ \times 200 cm-H) was packed with 4 mm and 2 mm of glass beads on the bottom separately, and topped with 590 g of supported γ -FeOOH grains. By controlling the internal circulation, the upflow superficial velocity was maintained at 40 m/h with 50% bed expansion. Both BA and H₂O₂ were introduced into the bottom of FBR. The flow rate of the feed was determined by the desired residence time (τ). The applied H₂O₂ dosage was 50% of the theoretical dosage to achieve 100% mineralization (13). The pH of the reactor was controlled by adding H₂SO₄ or NaOH during the operation. The effluent was collected with two vials after 5 τ 's when steady state of the reaction was reached (14). The sample in one vial was filtered for the analyses of H₂O₂, COD, and BA; the other sample was mixed with concentrated H₂SO₄ to determine the total iron concentration.

Table 1. Properties of supported γ -FeOOH

Parameters	Value
Total iron content (g/kg)	135
Total surface concentration of iron ^a (g/kg)	95
Bulk density (g/cm ³)	1.11
Average particle size (mm)	0.564
Specific surface area (m ² /g)	48.3

^atotal surface concentration of iron = total iron content – iron content of support

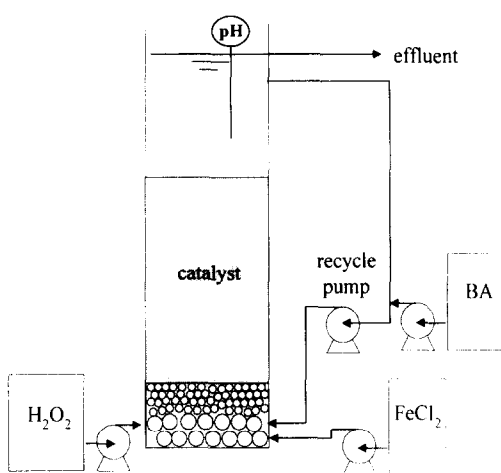


Figure 1. The schematic diagram of FBR. FeCl₂ was fed in the case of FBR-Fenton process.

2.3 Catalytic oxidation of BA by FBR system with Fe²⁺ addition (FBR-Fenton process)

The experimental apparatus and method are similar to that in the last section except that a smaller FBR

(2 cm- ϕ \times 100 cm-H) and 80 g of supported γ -FeOOH grains were applied. Ferrous chloride was introduced into the bottom of the FBR along with BA and H₂O₂. Two control experiments were conducted. In the control experiment A, the FBR was operated without the supported γ -FeOOH grains to simulate the conventional Fenton's system. The control experiment B, in which BA was not fed into the reactor, was to investigate the effect of its presence upon the crystallization of Fe(III). The filtered sample was analyzed for H₂O₂ immediately. The remained sample was adjusted to pH > 10 with NaOH to strip H₂O₂, before COD (or TOC) and BA were determined.

2.4 Analytical methods

Benzoic acid and H₂O₂ were analyzed using HPLC with a reverse phase Merck LiChrospher C-18 column (25 cm-L \times 4 mm-ID); the mobile phase contained 40% methanol (Fisher) and 60% deionized water with tetra-n-butylammonium phosphate PICA reagent (paired ion chromatography reagent for acid, TCI). The COD was analyzed according to the Methods suggested by APHA (15). Total organic carbon (TOC) was determined using a TOC analyzer (Dohrmann DC-190). Total iron concentration was determined by an atomic absorbance spectrophotometer (Varian Spectra AA-30).

3 RESULTS AND DISCUSSION

3.1 Catalytic oxidation of BA by FBR system without Fe²⁺ addition

In this experiment, supported γ -FeOOH served as the heterogeneous catalyst in the FBR. The changes in removal efficiencies of BA, COD and mCOD are displayed in Figure 2, where mCOD (modified COD) is obtained by subtracting the COD value contributed by residual H₂O₂ (i.e., 1 mg/l H₂O₂=0.47 mg/l COD) from the total COD. The results indicate that the removal efficiency of BA remained around 96% at pH < 5.3 and decreased to 80% gradually as pH increased to 7.0. The removal efficiency of mCOD had no significant change (59-63%) at pH < 4.4, and decreased to 19% at pH 7.0. Since the H₂O₂ dosage applied here can attain 50% mineralization at most, the maximum removal efficiency should be 50% theoretically, as described in section 2.2. Therefore, there must be another reason for the removal efficiency of mCOD to exceed 50%. We suggest that this enhancement in the mineralization of BA at low pH was caused by the organic radical, as the organic radical can be released during reductive dissolution of γ -FeOOH (8).

To investigate the variation in removal efficiencies with pH, the dissolved Fe concentrations (C_{Fe}) at various pH values were determined, as shown in Figure 3. It was observed that C_{Fe} was below 4 mg/l within pH 4.4~7.0 but increased dramatically at pH < 4.0, which can be attributed to the reductive dissolution of γ -FeOOH (7- 9). This suggests that the homogeneous catalysis by Fe²⁺ may play an important role at the acidic condition. The control experiment (4 mg/l of Fe²⁺ instead of γ -FeOOH was added) showed that Fe²⁺ had no catalytic capability to oxidize BA within pH 4.4~7.0 under this condition. From the above results,

we deduce that the oxidation of BA within pH 4.4~7.0 was attributed to the heterogeneous catalysis alone. Below pH 4.4, however, the homogeneous catalysis shows increasing importance with decreasing pH. Therefore, the large variation in removal efficiencies with pH was observed. The residual H_2O_2 concentration (C_H) was also analyzed, with result shown in Figure 3. It was discovered that C_H decreased suddenly at pH < 4.0 and at pH > 6.0. The decrease of C_H at pH < 4.0 was due to the reaction between H_2O_2 and dissolved Fe^{2+} . In contrast, the decrease of C_H at pH > 6.0 was attributed to the higher reactivity between H_2O_2 and supported γ -FeOOH at higher pH (16). At high pH, the high consumption of H_2O_2 but low removal efficiency of mCOD corresponds to a low utilization efficiency of H_2O_2 for mineralization (E_H) which is defined as below:

$$E_H (\%) = \frac{\text{actual COD removal}}{\text{theoretical COD removal by consumed } H_2O_2} \times 100\%$$

$$= \frac{COD_i - COD}{(C_{H_i} - C_H) \times 0.47} \times 100\% \quad (2)$$

where C_{H_i} denotes the inlet H_2O_2 concentration, and COD_i and COD are the inlet and outlet COD concentrations, respectively. The term of 0.47 in Equation (2) is based on the disproportionation of H_2O_2 by catalyst to give 0.5 mole O_2 per mole H_2O_2 (14). When E_H is low, few radicals react with BA and its oxidation intermediates, instead they undergo inefficient scavenging reaction (6, 7). Therefore, it was concluded that the scavenging behavior of $OH\cdot$ occurs at high pH.

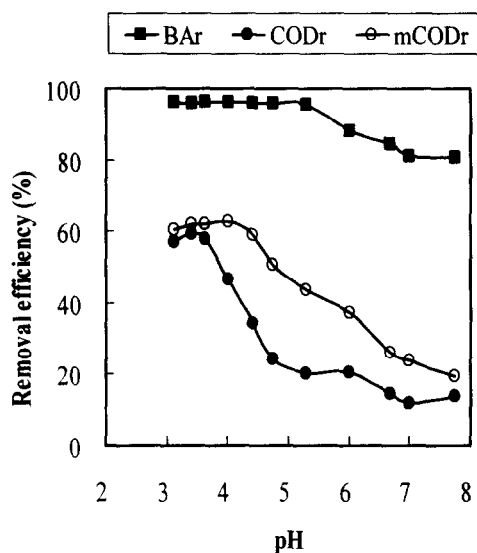


Figure 2. Effects of pH on removal efficiencies of BA, mCOD and COD in oxidation of BA by FBR system without adding Fe^{2+} . $C_{BAi}=190\text{--}227$ mg/l, $C_{Hi}=377\text{--}414$ mg/l, $\tau = 50$ min, $m = 590$ g/l.

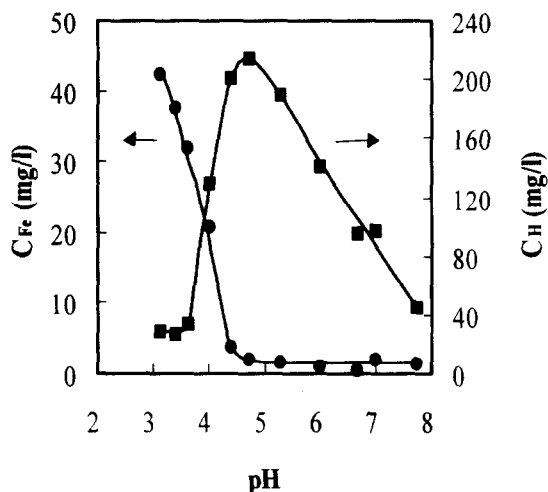


Figure 3. Effects of pH on C_{Fe} and C_H in oxidation of BA by FBR system without adding Fe^{2+} . The experimental conditions are the same as in Figure 2.

3.2 Catalytic oxidation of BA by FBR system with Fe^{2+} addition (FBR-Fenton process)

The result of last section suggests that dissolved Fe plays an important role upon the oxidation and mineralization of BA. Within pH 3.0–4.0, the high C_{Fe} enhances the mineralization. After neutralization, however, Fe(II) precipitates as $Fe(OH)_3$, which requires additional separation and disposal. Since the rate of reductive dissolution is proportional to the surface area of oxide (8), we lower the surface area by decreasing the concentration of supported γ -FeOOH from 590 mg/l to 133 mg/l in the FBR to reduce the dissolved Fe concentration. Moreover, refer to the preparation of supported γ -FeOOH as described in section 2.1, the iron oxide can crystallize onto the surface of brick grain by introducing H_2O_2 and $FeSO_4$ (i.e., Fenton's reagent) in the FBR. Hence, we add Fe^{2+} in this FBR system to study the effect of Fe^{2+} on the catalytic oxidation and to clarify if the mineralization of BA and crystallization of Fe(III) can occur simultaneously.

When both Fe^{2+} and supported γ -FeOOH were introduced in the FBR to treat BA, the supported γ -FeOOH acts as the heterogeneous catalyst of H_2O_2 as well as the seeding carrier for crystallization. Because pH 3–4 is the most efficient condition of Fenton's reaction (2), we first conducted the experiments near this pH range (i.e. 2.85–3.74). This FBR-Fenton method was compared with the conventional Fenton's method (control experiment A) in the effectiveness of mineralization and crystallization. The effects of inlet Fe^{2+} concentration (C_{Fei}) on the removal efficiencies of BA, TOC, and Fe (III) are depicted in Figure 4, where TOC(C) denotes the removal efficiency of TOC in the control experiment A. In the FBR-Fenton process, the removal efficiency of BA was 66% in the blank test ($C_{Fei}=0$, pH=3.5), and it remained around 95% as C_{Fei} of 28–180 mg/l was added. We also discovered that the removal efficiency of TOC slightly increased with C_{Fei} and attained to a plateau when C_{Fei} exceeded 100 mg/l. It is also noted that all the removal efficiencies of TOC in the conventional Fenton's process were less than that in the FBR-Fenton process.

In Figure 4, only the removal efficiency of Fe (III) within pH 3.40–3.55 were selected and plotted by assuming that the effect of pH variation on the removal of Fe(III) can be neglected in this pH range. The blank test shows that 3.9 mg/l Fe(III) formed in the FBR. It was found that the removal efficiency of Fe (III) increased with C_{Fei} to a maximum (i.e. 90.2%) at 100 mg/l of C_{Fei} , then gradually decreased with C_{Fei} . At $C_{Fei} < 50$ mg/l, the low removal efficiency of Fe (III) was because that the reductive dissolution of γ -FeOOH released a certain amount of Fe^{2+} which increased the measurement of total iron. At $C_{Fei} > 100$ mg/l, the low removal efficiency of Fe (III) was due to the larger surface loading of crystallization (11). It was found that significant removal of BA (i.e. 95%), TOC (i.e. 49–59%) and Fe(III) (i.e. 70–90%) was attained within pH 3.4–3.7 and C_{Fei} of 28–130 mg/l. Since the maximum theoretic removal efficiency of

TOC is 50%, as described before, the mineralization of contaminant and the crystallization of Fe(III) can be conducted simultaneously at these experimental conditions. This novel FBR-Fenton process not only enhances the effectiveness of mineralization but also reduces the amount of Fe(III) sludge. It is evident that the FBR-Fenton process improves the performance of Fenton's process.

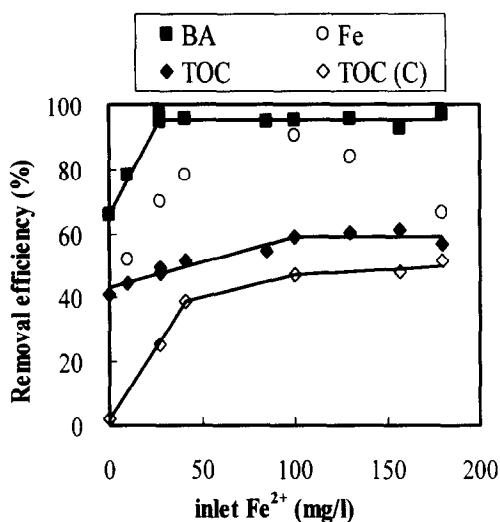


Figure 4. Effects of inlet Fe^{2+} (C_{Fei}) on removal efficiencies of BA, TOC, and Fe (III) with FBR-Fenton method. $C_{BAi} = 100$ mg/l, $C_{Hi} = 200$ mg/l, $\tau = 52$ min, $m = 133$ g/l, $pH = 2.85 \sim 3.74$.

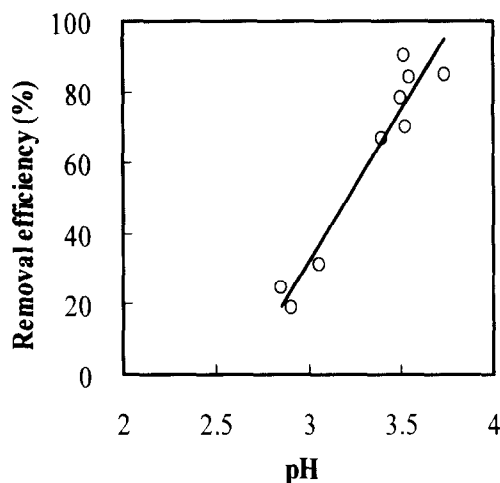


Figure 5. Effect of pH on the removal efficiency of Fe (III) with FBR-Fenton method. $C_{Fei} = 28 \sim 180$ mg/l. The other experimental conditions are the same as in Figure 4.

To understand the pH effect on Fe(III) removal, we combined most of the data ($C_{Fei} = 28 \sim 180$ mg/l) concerning Fe (III) removal, as shown in Figure 5, and discovered that the removal efficiency of Fe(III) is highly pH-dependent regardless of the range of C_{Fei} . To clarify the pH effect on BA oxidation and Fe(III) removal, the experiments were performed under larger pH range (i.e. 2.8~5.5) while C_{Fei} was kept constant. The experimental results are depicted in Figure 6, in which the control experiment B (i.e., in the absence of BA) was also conducted. This figure shows that both the removal efficiencies of Fe (III) increased within pH 2.8~4.5 but decreased above pH 4.5 because of the formation of $Fe(OH)_3$ precipitate, which is similar to the result of iron removal from acid mine drainage (11). The low removal efficiency of Fe (III) at low pH was due to the high Fe (III) solubility (17) and high reductive dissolution of γ - $FeOOH$ (8). As shown in Figure 6, the removal efficiency of Fe (III) was higher in the absence of BA than in the presence

of BA within pH 2.8–4.5. It is attributed to more reductive dissolution when the solution contains organic compounds (8).

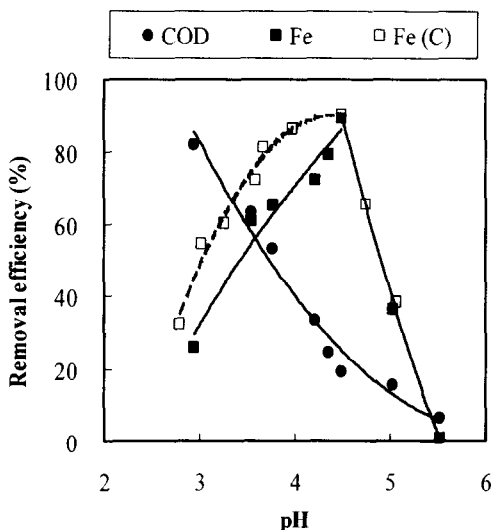


Figure 6. Effect of pH on the removal efficiencies of COD and Fe (III) with FBR-Fenton method (constant $C_{Fe(II)}$). $C_{BAI} = 100$ mg/l, $C_{H_2O_2} = 200$ mg/l, $C_{Fe(III)} = 50$ mg/l, $\tau = 52$ min, $m = 133$ g/l. Fe(C) denotes the removal efficiency of Fe (III) in the absence of BA.

Based on the above results and discussion, the reaction mechanism in the FBR-Fenton process is proposed in Figure 7. This mechanism has three parts: (A) reductive dissolution of γ -FeOOH, including the precursor complex formation (reaction a), electron transfer (reaction b), and release of organic radical and aqueous Fe^{2+} (reaction c) (8); (B) synthesis of γ -FeOOH, including Fenton's reaction (reaction d) and crystallization (reaction e) (14, 17); (C) degradation of BA, including further oxidation by organic radical (reaction f) and $OH\cdot$ (reaction g), where $OH\cdot$ is produced via the heterogeneous catalysis (reaction h) (16) and homogeneous catalysis (reaction d).

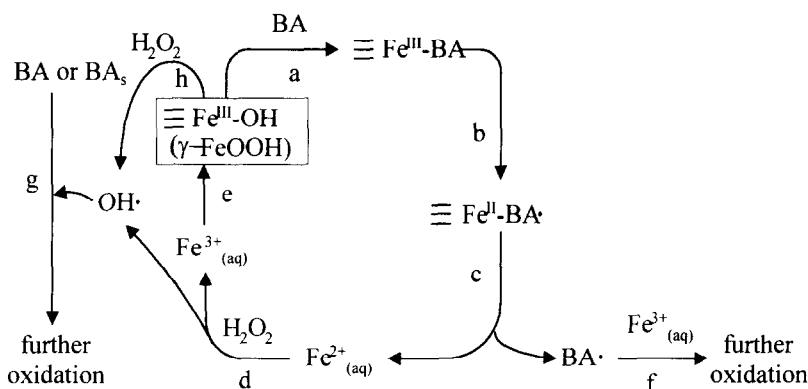


Figure 7. The reaction mechanism in the FBR-Fenton process: (A) **reductive dissolution**: reactions a, b, and c; (B) **synthesis of Fe(III) hydroxide**: reactions d and e; (C) **oxidation of BA**: reactions f, g, and h. BA, (5) denotes the surface complex of BA and γ -FeOOH.

4 CONCLUSIONS

From the above study, we made the following conclusions:

- (1) When BA is treated by the FBR system without Fe^{2+} addition, the dissolved Fe and the removal efficiency of COD at low pH are higher than those at medium pH, which indicates that the oxidation of BA at pH 4.4~7.0 is attributed to the heterogeneous catalysis alone. However, the high removal of BA and COD at pH < 4.0 is due to the homogeneous catalysis by Fe^{2+} formed via the reductive dissolution of $\gamma\text{-FeOOH}$.
- (2) When BA is treated by the FBR system with Fe^{2+} addition (FBR-Fenton method), it is found that the efficiencies of both BA mineralization and Fe(III) crystallization relate to pH and inlet Fe^{2+} concentration (C_{Fei}). The low removal efficiency of Fe(III) at high C_{Fei} is subjected to the surface loading of crystallization, and at high pH, it is limited by the solubility of Fe(III). The FBR-Fenton method is proven superior to the conventional Fenton's reaction in the effectiveness of crystallization and mineralization
- (3) The reaction mechanism in the FBR-Fenton method consists of the reductive dissolution and synthesis of $\gamma\text{-FeOOH}$ as well as the oxidation of the organic compound.

5 ACKNOWLEDGMENTS

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