Iron Based Catalysts Used in Water Treatment Assisted by Ultrasound: A Mini Review

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The characteristics and performances of catalyst are the key in catalytic ultrasonic treatment of wastewater, and iron based catalysts are known for low cost, high accessibility and safety. This paper reviewed the current research status of iron-based catalysts in water treatment assisted by ultrasound. Zero valent iron, Fe₃O₄ and iron compositied with other metals were analyzed, their behaviors in catalytic sonochemistry were summarized, and the potential catalytic mechanisms were discussed in details. Finally, the future development in this field was proposed.

Keywords: ultrasound, iron, sonocatalyst, organic pollutants, mechanisms

INTRODUCTION

Each year, many kinds of refractory organic pollutants are charged into water (Richardson and Kimura, 2017). These pollutants are hard to be removed by conventional treatment methods, and development of advanced treatment technology is necessary. Ultrasound has attracted great attentions for its safety, easy operation, high degradation efficiency, and free of secondary pollutants (Pokhrel et al., 2016). But removal efficiencies of organic pollutants by ultrasound are sometimes low and the energy consumption is high. Combination with catalyst to form catalytic sono-reactions can improve the efficiency of organic pollutants removal and reduce the energy consumption (Chatel et al., 2016). Many catalysts have been applied in the ultrasonic degradation of pollutants (Descorme, 2017). More and more papers are published in this field from 2010 to 2017 according to search results of the Web of Science (Figure 1).

Among all types of catalysts, iron-based catalysts are of the highest potential due to their low cost, high safety and wide-distribution. Zero valent iron (ZVI), Fe₂(SO₄)₃, FeSO₄, FeCl₃, and FeOOH have long been used in water and wastewater treatment. Sonication alone achieved 22% diclofenac degradation while combination of FeCeOx improved the efficiency to 81% (Chong et al., 2017). Fe⁹/TiO₂ nano-particle catalytic sonication achieved 100% removal of reactive black 5 in 20 min (Bhaumik et al., 2017).

This paper aims to provide an overview of this developing field of iron-based catalysts in water treatment assisted by ultrasound. The properties, performances, and combination with other metals of iron-based sonocatalysts were discussed. Reaction mechanisms of sonocatalytic degradation of organic pollutants were reviewed. Future development was proposed.
Iron element is famous for Fenton’s reagent (Fe²⁺+H₂O₂), a classic advanced oxidation technology. However, hazards associated with the transport, handling and storage of bulk quantities of H₂O₂ have made the process unsafe and economically challenging. The combination of ultrasound and iron-based catalysts can achieve high degradation efficiency of organic pollutants without H₂O₂ (Chandran et al., 2014). Iron based sonocatalysts, ZVI, Fe₃O₄ and iron composites with other metals (lutetium and silver), have been examined. The catalytic activity of Fe⁰ is also based on the surface chemistry reactions of Fe⁰ to initiate the reactions in water, as shown in Equations (6–8). Application of Fe⁰ as catalyst has a few advantages: enhance mass transfer to the surface of the catalyst, continuous damage of the catalyst surface to create more defects, and cleaning of the catalyst surface (Güyer and Ince, 2011).

\[ \text{H}_2\text{O(g)} + \text{ultrasound} \rightarrow \cdot\text{OH(aq)} + \cdot\text{H(aq)} \quad (1) \]
\[ \cdot\text{OH(aq)} + \cdot\text{OH(aq)} \rightarrow \text{H}_2\text{O}_2(aq) \quad (2) \]
\[ \text{Fe}^{2+}(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{Fe}^{3+}(aq) + \cdot\text{OH(aq)} + \text{OH}^-(aq) \quad (3) \]
\[ \text{Fe}^{2+}(aq) + \cdot\text{OH(aq)} \rightarrow \text{Fe}^{3+}(aq) + \text{OH}^-(aq) \quad (4) \]
\[ \text{Fe}^{3+}(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{Fe}^{2+}(aq) + \cdot\text{OOH(aq)} + \text{H}^+(aq) \quad (5) \]
\[ \text{Fe}^0(s) + \text{ultrasound} \rightarrow \text{Fe}^{2+}(aq) + 2e^- \quad (6) \]
\[ \text{Fe}^0(s) + 2\text{Fe}^{3+}(aq) \rightarrow 3\text{Fe}^{2+}(aq) \quad (7) \]
\[ \text{Fe}^0(s) + \text{H}_2\text{O}_2(aq) \rightarrow \text{Fe}^{2+}(aq) + \cdot\text{OH(aq)} + \text{OH}^-(aq) \quad (8) \]

Table 1 summarizes the typical iron-based sonocatalysts. The dechlorination of Fe⁰ for complicated chlorinated compounds is often incomplete and with low efficiency. Luo et al. (2010) found that the Ag/Fe catalyst was quite effective for the degradation of chlorinated organics, and silver also provide some disinfection effect.

When nonmagnetic catalysts (e.g., TiO₂) are employed, their recovery is a troublesome issue. Super-paramagnetic Fe₃O₄ facilitates fast recovery/re-dispersion of the catalyst by simply switching on/off an external magnet (Richardson and Kimura, 2017), which is the most effective and simplest method to enhance the recovery and reuse of catalysts (Kang et al., 2015). Taghizadeh and Seifi-Aghjekohal (2015) found that the sonocatalytic activity of Fe₃O₄ was the best among Fe₃O₄, Rutile-TiO₂, ZnO, and Anatase-TiO₂ nanoparticles. The proposed reason was that Fe₃O₄ enhanced the ·OH radical generation by the electron transfer between iron ions and H₂O molecules.

The activity of ZVI and Fe₃O₄ is promoted in acidic solution. However, the reuse property is poor due to severe iron leaching in acidic condition. Besides, acidic pH limits the practical application of sonocatalysts. Therefore, iron composites catalysts have been proposed. Zhou et al. (2015) found that the pH value had a small effect on the sonocatalytic degradation of RhB by LuFeO₃, and the LuFeO₃ particles exhibited a good structural stability with no structural change before and after sonication. Alwash et al. (2013) found that Fe/Ti-NaY kept its high activity...
in the decolorization of amaranth after three times of reuse; X-ray diffraction proved that the catalyst was stable after reuse and maintained its crystallinity. Another method to improve the stability of catalyst is doping the active component on supports like graphene and zeolite (Rakmae et al., 2016). Even at neutral and alkaline medium, a good decolorization and degradation efficiency could still be achieved in the present of Fe-doped zeolite Y under ultrasound. Fe (III)/Y demonstrated good catalytic efficiency, low Fe leaching, and good reusability (Jamalluddin and Abdullah, 2014).

Iron has been used to modify TiO$_2$ and formed new sonocatalysts. TiO$_2$ nano-tubes possess a relatively wide energy band gap (3.2 or 3.0 eV in Anatas or Rutile phase) and fast recombination rate of charge carriers (Richardson and Kimura, 2017). One possible solution to this problem is introducing suitable transition metals such as Fe, Cr, or Co into TiO$_2$ to form a new sonocatalyst with narrower band gap and longer lifetime of charge carriers (Pang and Abdullah, 2013).

**TABLE 1 | Ultrasonic catalytic degradation of organic pollutants by iron sonocatalysts.**

| Sonocatalyst                      | Organic pollutant               | Removal efficiency (%) | References               |
|-----------------------------------|---------------------------------|------------------------|--------------------------|
| 1 Reactive ZVI                    | Diclofenac                      | $k = 0.0786 \text{ min}^{-1}$ | Güyer and Ince, 2011     |
| 2 Fe$^0$                          | Phenol                          | 90 (TOC)               | Segura et al., 2012      |
| 3 ZVI aggregate                   | C.I. Direct Red 23              | 95                     | Weng and Tsai, 2016      |
| 4 Rectonite-supported nanoscale ZVI | Methyl orange and metronidazole | 93 and 97              | Yuan et al., 2016        |
| 5 Chitosan-stabilized nanoscale ZVI | Acid fuchsin                   | 99                     | Jin et al., 2016         |
| 6 Fe$_2$O$_4$ nanoparticles       | 2-hydroxyethyl cellulose        | $k = 3.9 \times 10^{10} \text{ mol}^{-1} \text{ L}^{-1} \cdot \text{min}^{-1}$ | Taghizadeh and Sefie-Aghjekohal, 2015 |
| 7 Nanosized Fe$_2$O$_4$-loaded coffee waste hydrochar | Acid red 17                     | 100                    | Khataee et al., 2017     |
| 8 Fe$_3$O$_4$/Polyaniline         | Methyl orange                   | 100                    | Wang et al., 2015        |
| 9 Fe$_3$O$_4$-SiO$_2$-TiO$_2$     | Ibuprofen                       | 70                     | Kang et al., 2015        |
| 10 α-Fe$_2$O$_3$ nanoparticles    | Eosin Y                         | 72.5                   | Gobouri, 2016            |
| 11 Fe$_2$O$_3$/SBA-15             | Phenolic aqueous                | 100                    | Bremner et al., 2009     |
| 12 LuFe$_3$O$_4$                  | Acid orange 7                   | 89                     | Zhou et al., 2015        |
| 13 Fe/Ti-NaY                      | Amaranth                        | 75                     | Alwash et al., 2013      |
| 14 Fe-doped zeolite Y             | Acid red B                      | 100                    | Jamalluddin and Abdullah, 2014 |
| 15 FeCeO$_x$                      | Diclofenac                      | 83                     | Chong et al., 2017       |
| 16 Fe-TiO$_2$ nanotubes           | 17α-ethynylestradiol            | 100                    | Frontistis and Mantzavinos, 2012 |
| 17 Fe$_{3+}$ doped TiO$_2$ nanotubes | Rhodamine                     | 99                     | Pang and Abdullah, 2012  |
| 18 Fe-tufenerene/TiO$_2$           | Acid red 17                     | 79.9                   | Pang and Abdullah, 2013  |
| 19 Fe-based catalysts             | Ibuprofen                       | 92                     | Meng and Oh, 2011        |
| 20 Fe$_{2+}$                      | Reactive blue 181               | 93.5                   | Zylan and Ince, 2015     |
| 21 Modified montmorillonite       | Acid red 17                     | 82                     | Basturk and Karatas, 2014 |
| 22 Iron-silver bimetallic nanoparticle | Tetrabromobisphenol A         | 100                    | Luo et al., 2010         |

**Cavitation Effects**

The most import sonocatalytic mechanism lays in the cavitation of water during ultrasonic irradiation (Wang et al., 2015). The cavitation involves the processes of formation (nucleation), rapid growth (expansion), and violent collapse (implosion) of cavitation bubbles. Such a violate collapse of cavitation bubbles cause local high temperature and pressure (up to 5,000 K and 1,000 atm) and the emission of light (sono-luminescence), and generate free radicals including ·OH, ·OOH, and O$_2^·$ (Pokhrel et al., 2016). The free radicals can react with target contaminants.

Mechanical effect is a main advantage of ultrasound irradiation (Alwash et al., 2013). Ultrasound can promote the mass transfer, which leads the contact of pollutants with free radical or the catalyst more sufficiently. In addition, the micro jet can collapse the catalyst into smaller particles, which offer a higher surface area, thus enhances the surface reaction.
The Enhancement of Cavitation Effects by Catalyst
Catalyst particles in water can act as nucleus for cavitation bubbles (Zhao et al., 2014). Once the catalyst particles sizes are in the same order of magnitude with the size of the cavitation bubbles, catalyst particles can form extra nucleus of cavitation bubbles. Extra nucleus generates more cavitation bubbles, causes stronger cavitation effects, leading to higher degradation efficiency.

Adsorption of Catalysts
Organic pollutants can be adsorbed on the surface of catalysts due to electrostatic attraction and sonication (Thangavel et al., 2015). The adsorbed pollutants then react with the sono-generated free radicals from/around the catalyst. Moreover, the concentration of free radicals is high on the surface of catalysts and the adherence of organic pollutants upon the catalyst can shorten the path for radicals/cavities to decompose the pollutants. Then the degradation rate of organic pollutants is improved.

Redox Reaction between Sonocatalyst and Organic Pollutants
Organic pollutants can react with the surface of sonocatalyst. The free radicals produced by ultrasound improve the redox reaction between sonocatalyst and organic pollutants, which accelerates the removal of organic pollutant. Free radicals react with polyvalent metal sonocatalyst such as iron-based composites, which may produce some new valence state sonocatalyst to accelerate the reaction (Chong et al., 2017).

The Cleaning Effects of Ultrasound for Catalyst
The cleaning effect of ultrasound for catalysts refers to the phenomenon that ultrasound waves in the ultrasonic system continuously remove the intermediates or by-products from the surface of catalysts to reactive the surface (Alwash et al., 2013). The cleaning effects of ultrasound are based on the cavitation effects. Ultrasound generates many bubbles in water and they collapse fast, then the catalysts are cleaned by the shock wave. Such an ultrasonic regeneration of the sonocatalyst is of great advantage via removing the contaminants and decomposition of toxic organic pollutants (Wang et al., 2015).

CONCLUSIONS AND PERSPECTIVES
In this mini-review, the typical iron-based sonocatalysts are summarized. Their sonocatalytic activity is different for different organic pollutants. The special property for iron-based sonocatalysts is magnetism, which is beneficial to separate catalysts from water. The mechanisms of sonocatalytic degradation of organic pollutants involve both ultrasound irradiation and sonocatalyst. In the future, more works will be done on this developing field and following issues might be of great values:

1. Produce better sonocatalysts
   Obviously the sonocatalytic efficiency depends on the type of catalyst. Development of novel catalyst with higher efficiency has always been the hot topic, and better understanding of the sonocatalytic mechanisms is also necessary to promote the application of the sonocatalytic technology.

2. Pay more attention to the safety and cost efficiency
   Most researchers only investigate the activity of sonocatalyst, but pay little attention on the economy and safety of sonocatalyst. If the materials for preparing sonocatalyst are rare or expensive and the preparation method is complex, these sonocatalysts are difficult to be applied. The stability and reusability of sonocatalyst also need be considered, which are relative to the service life of sonocatalyst.

3. Enhance the selectivity of sonocatalysts
   In some situations, trace toxic substances and high concentration of non-poisonous pollutants co-exist in water, the sonocatalyst must have good selectivity, but little
invention is available on this subject, which needs be addressed.

**AUTHOR CONTRIBUTIONS**

NZ collected and read papers and contributed partially to the Introduction and mainly to Table 1; GX collected and read papers and contributed to paper writing; XL contributed greatly to the writing of Potential Mechanisms of Sonocatalytic Degradation of Organic Pollutants section; JZ contributed to the paper design and refine; PZ contributed to paper design and data analysis; GZ was in charge of the whole writing.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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